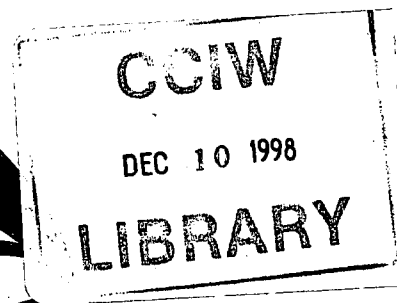


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RECHERCHE SUR LES EAUX**

**APPLICATION OF SOLID PHASE
MICROEXTRACTION (SPME) IN THE
DETERMINATION OF GASOLINE ADDITIVES
METHYLCYCLOPENTADIENYL MANGANESE
TRICARBONYL (MMT) AND METHYL TERT-
BUTYL ETHER (MTBE) IN AQUEOUS SAMPLES**

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NWRI Contribution No. 98-053

**Application of Solid Phase Microextraction (SPME) in the Determination of
Gasoline Additives Methylcyclopentadienyl Manganese Tricarbonyl (MMT) and
Methyl *tert*-butyl Ether (MTBE)
in Aqueous Samples**

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NWRI Contribution No. 98-053

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Management Perspective

Both methylcyclopentadienyl manganese tricarbonyl (MMT), and methyl *tert*-butyl ether (MTBE) have been used as substitutes for alkylleads as antiknock agents, and octane improvers in unleaded gasoline. MMT has been used in Canada since 1976, and recently approved for use in the United States. MMT is highly toxic to some animals through inhalation, ingestion and skin adsorption. MTBE is a common additive in unleaded gasoline used in the United States and other countries. MTBE is persistent in the environment, and has been detected in air, surface water, and ground water. Recently, health concerns have been raised on the occurrence of MTBE in the environment, especially in ground water.

Solid phase microextraction (SPME) was successfully applied to extract MMT and MTBE in aqueous samples. The procedure is simple, efficient, and solvent free. Concentrations of MMT and MTBE in water can be determined simultaneously with the combination of SPME and gas chromatography-plasma atomic emission spectrometry (GC-AED) dual-channel operation (manganese 259 nm and carbon 248 nm). The detection limits are 0.3 pg l^{-1} as Mn for MMT and $10 \text{ } \mu\text{g l}^{-1}$ for MTBE in water. Lower detection limits ($0.1 \text{ } \mu\text{g l}^{-1}$) can be obtained for MTBE by using the carbon 193 nm line and lower make-up flow rate (20 mL min^{-1}) in GC-AED determinations. In this study, the precision for replicate analysis ($n=4$) of a MMT solution (10 pg l^{-1} as Mn) was 7.1% relative standard deviation (RSD), and 8.8% and 3.9% for a MTBE solution ($100 \text{ } \mu\text{g l}^{-1}$) measured at carbon 284 and 193 nm respectively. Different kinds of aqueous samples were collected and analyzed for MMT and MTBE with the SPME technique. The liquid-liquid extraction (LLE) method was also used for MMT determination in highway runoff and lake water samples. Both results were comparable. This is the first determination of MMT in highway runoff and sewage samples in Canada.

Sommaire à l'intention de la direction

On a utilisé le méthylcyclopentadiénylmanganèse tricarbonyle (MMT) et l'éther méthyl-*tert*-butylique (MTBE) pour remplacer les dérivés d'alkylplomb comme agents antidétonants et comme agents améliorant l'indice d'octane dans l'essence sans plomb. Le MMT est utilisé au Canada depuis 1976, et son utilisation aux États-Unis a été approuvée récemment. Il s'agit d'un produit dont l'inhalation, l'ingestion et l'absorption cutanée sont très toxiques chez certains animaux. Le MTBE est un additif commun de l'essence sans plomb aux États-Unis et dans d'autres pays; il persiste dans l'environnement et on a détecté sa présence dans l'air, dans les eaux de surface et dans l'eau souterraine. Récemment, on s'est inquiété de la présence de MTBE dans l'environnement, et particulièrement dans l'eau souterraine.

On a utilisé avec succès la microextraction en phase solide (MEPS) pour l'extraction du MMT et du MTBE d'échantillons d'eau. Ce protocole est simple, efficace et n'utilise aucun solvant. On peut doser simultanément le MMT et le MTBE dans l'eau en combinant la MEPS et la chromatographie gazeuse-spectrométrie d'émission atomique du plasma (CG-SEAP) avec deux canaux réglés respectivement à 259 nm (manganèse) et à 248 nm (carbone). Les limites de détection sont de $0,3 \text{ pg}\cdot\text{l}^{-1}$ pour le MMT à l'état de Mn et de $10 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ pour le MTBE dans l'eau. On peut atteindre la limite inférieure de détection ($0,1 \text{ }\mu\text{g}\cdot\text{l}^{-1}$) pour le MTBE en utilisant la raie de 193 nm pour le carbone et le débit inférieur d'apport de $20 \text{ mL}\cdot\text{min}^{-1}$ lors des dosages CG-SEAP. Dans cette étude, la précision des analyses d'échantillons multiples ($n=4$) d'une solution de MMT ($10 \text{ pg}\cdot\text{l}^{-1}$ en Mn) était de 7,1 % (écart-type relatif, ETR) et, pour une solution de MTBE ($100 \text{ }\mu\text{g}\cdot\text{l}^{-1}$) dosée avec les raies de 284 et de 193 nm pour le carbone, de 8,8 et 3,9 %, respectivement. On a recueilli divers types d'échantillons d'eau dont on a dosé le MMT et le MTBE par MEPS. On a également utilisé la méthode d'extraction liquide-liquide (ELL) pour doser le MMT dans des échantillons d'eau de ruissellement des routes et d'eau de lacs, avec des résultats comparables. Il s'agissait du premier dosage du MMT dans les échantillons d'eaux de ruissellement des routes et d'eaux d'égout au Canada.

Abstract

Solid phase microextraction (SPME) was successfully applied to the determination of gasoline additives, methylcyclopentadienyl manganese tricarbonyl (MMT) and methyl *tert*-butyl ether (MTBE), in aqueous samples. The procedure is simple, efficient and solvent free. Concentrations of MMT and MTBE in water can be determined simultaneously with the combination of SPME and gas chromatography-plasma atomic emission spectrometry (GC-AED) dual-channel operation (manganese 259 nm and carbon 248 nm). The detection limits are 0.3 $\mu\text{g l}^{-1}$ as Mn for MMT and 10 $\mu\text{g l}^{-1}$ for MTBE in water. Lower detection limit (0.1 $\mu\text{g l}^{-1}$) can be obtained for MTBE by using the carbon 193 nm line and lower make-up flow rate (20ml min^{-1}) in GC-AED determination. In this study, the precision for replicate analysis ($n=4$) of a MMT solution (10 $\mu\text{g l}^{-1}$ as Mn) was 7.1% relative standard deviation (RSD), and 8.8% and 3.9% for a MTBE solution (100 $\mu\text{g l}^{-1}$) measured at carbon 248 and 193 nm respectively. Different kinds of aqueous samples were collected and analyzed for MMT and MTBE with SPME technique. Liquid-liquid extraction (LLE) method was also used for MMT determination in highway runoffs and lake water samples. Both results were comparable.

Key words

Solid phase microextraction (SPME), methylcyclopentadienyl manganese tricarbonyl (MMT), methyl *tert*-butyl ether (MTBE), gas chromatography, atomic emission detection, aqueous.

Résumé

On a utilisé avec succès la microextraction en phase solide (MEPS) pour le dosage d'additifs de l'essence, le méthylcyclopentadiénylmanganèse tricarbonyle (MMT) et l'éther méthyl-*tert*-butylique (MTBE) dans des échantillons d'eau. Ce protocole est simple, efficace et n'utilise aucun solvant. On peut doser simultanément le MMT et le MTBE dans l'eau en combinant la MEPS et la chromatographie gazeuse-spectrométrie d'émission atomique du plasma (CG-SEAP) avec deux canaux réglés respectivement à 259 nm (manganèse) et à 248 nm (carbone). Les limites de détection sont de $0,3 \text{ pg}\cdot\text{l}^{-1}$ pour le MMT à l'état de Mn et de $10 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ pour le MTBE dans l'eau. On peut atteindre la limite inférieure de détection ($0,1 \text{ }\mu\text{g}\cdot\text{l}^{-1}$) pour le MTBE en utilisant la raie de 193 nm pour le carbone et le débit inférieur d'apport de $20 \text{ mL}\cdot\text{min}^{-1}$ lors des dosages CG-SEAP. Dans cette étude, la précision des analyses d'échantillons multiples ($n=4$) d'une solution de MMT ($10 \text{ pg}\cdot\text{l}^{-1}$ en Mn) était de 7,1 % (écart-type relatif, ETR) et, pour une solution de MTBE ($100 \text{ }\mu\text{g}\cdot\text{l}^{-1}$) dosée avec les raies de 284 et de 193 nm pour le carbone, de 8,8 et 3,9 %, respectivement. On a recueilli divers types d'échantillons d'eau dont on a dosé le MMT et le MTBE par MEPS. On a également utilisé la méthode d'extraction liquide-liquide (ELL) pour doser le MMT dans des échantillons d'eau de ruissellement des routes et d'eau de lacs, avec des résultats comparables.

Mots clés

Microextraction en phase solide (MEPS), MMT, MTBE, aqueux, environnement

Introduction

Both methylcyclopentadienyl manganese tricarbonyl (MMT), and methyl *tert*-butyl ether (MTBE) have been used as substitutes for alkyllead as antiknock agents, and octane improver in unleaded gasoline. MMT has been used in Canada since 1976, and recently approved for use in the United State [1]. The combustion of MMT leads to the emission of the oxides of manganese to atmosphere. MMT is highly toxic to experimental animals through inhalation, ingestion and skin absorption. High ambient manganese levels may cause toxic effects to the central nervous system, pulmonary toxicity and severe injury to the kidneys, liver and lungs [1,4]. MMT is fairly stable in the absence of light and has been found in air [2,5,7]. MTBE is a common additive in unleaded gasoline used in United States and other countries. Because large amounts of the MTBE are added to gasoline (13-15%) as octane enhancer, it will inevitably enter the environment in different ways[8]. MTBE is persistent in the environment, and has been detected in air, surface water, and underground water [9,12]. Recently, the health concerns have been raised on the occurrence of MTBE in the environment, especially in ground water.

Solid phase microextraction (SPME) is a simple, solvent-free, and efficient extraction technique. The polymer-coated fibers are used to extract the analytes, and directly inserted to the injection port of the chromatograph for analysis. SPME has been successfully used in different organic analysis [13, 16]. Organometal and metal ions in aqueous solution can be also analyzed in headspace by SPME after derivatization [17-19]. SPME has exceptional advantages in volatile and semi-volatile chemical analysis over static and purge-and-trap techniques or liquid-liquid extraction methods because of its simplicity and good reproducibility.

MTBE is a volatile organic compound, with vapor pressure of $3.27\text{-}3.35 \times 10^4$ Pa at 25°C , [12], and it can be extracted with headspace SPME technique. The GC-AED is an extremely sensitive technique for MMT determination, with the absolute limit of detection of 0.5 fg expressed as Mn [6]. The combination of SPME and GC-AED

provides a simple and efficient analytical method for the determination of gasoline additives, MMT and MTBE in aqueous samples

EXPERIMENTAL

Reagents. Methylcyclopentadienyl manganese tricarbonyl (MMT) and methyl *tert*-butyl ether (MTBE) were obtained from Aldrich, Milwaukee, WI, USA. Distilled water was further purified by a Milli-Q system (Millipore, Bedford, MA, USA). Standard solutions of MMT and MTBE were prepared in distilled water and stored in amber glass bottles at 4°C in the dark.

SPME device and extraction procedure

A SPME fiber holder for manual injection and fused silica fiber coated with a 100 µm poly(dimethylsiloxane), PDMS, were obtained from Supelco (Bellafonte, PA). Fibers were conditioned for 1 h at 300°C in a helium atmosphere in the injection port of the GC prior to use. Aqueous samples were placed in 40 ml vials with septum caps.

Sampling was performed by exposing the SPME fiber to the headspace without touching the liquid or directly dipping the fiber into the liquid for aqueous samples in the vials with magnetic stirring for a known period of time. The fiber was then retracted into the syringe and quickly transferred to the GC inlet liner in the injection port. The fiber was manually pushed out of the syringe at 250°C for 15 seconds to allow the extracted analytes to be thermally desorbed from the fiber before the GC temperature program was initiated.

GC-AED and GC-MSD parameters

The GC-AED system consisted of a gas chromatograph (HP Model 5890) equipped with HP SPME inlet liner, a HP helium microwave plasma atomic emission detector (Model 5921A), and a HP automatic sampler (Model 7673A).

The optimal operation parameters of the GC-AED for manganese have been previously studied [6], and are listed in Table 1 for reference. MTBE was analyzed at two different carbon emission lines, 193 and 248 nm. The flow rates of make-up gas were optimized for both carbon lines, while the other GC-AED conditions were same as those for manganese determination.

Some samples and standards were also analyzed with a HP 5890 Series II gas chromatograph interfaced to a HP 5971A mass-selective detector for analytes confirmation. Operating parameters for the GC-MSD system are also listed in Table 1.

Analysis of aqueous samples

Highway run-off and lake water samples were collected in 40 ml vials and 4 l bottles respectively, and transferred back to the laboratory immediately for analysis with headspace SPME and LLE techniques. The liquid-liquid extraction (LLE) of MMT from aqueous samples was also performed for comparison with the SPME method. Sample extraction was carried out by adding 2 x 50 ml hexane to 1 l of water sample. Three sewage samples were also obtained from Burlington Waste Water Treatment Plant for SPME extraction in the same manner.

Results and Discussion

Optimization of the SPME technique

Absorption-time profiles were studied by determining headspace and aqueous-phase equilibration times for MMT and MTBE with 100 μm PDMS fiber, and the results are shown in Figures 1 and 2. The headspace SPME was used throughout the study. The more volatile compound MTBE reached equilibrium faster than MMT in headspace due to its faster diffusion in the headspace. From the equilibrium curves in Figures 1 and 2, 15 min equilibrium time was found optimal for both MTBE and MMT in the headspace SPME operation.

Effects of temperature on extraction efficiency of the headspace SPME technique was studied by sampling MMT and MTBE standard mixtures for 15 min at different temperatures intervals from 25^oC to 75^oC. The effect of temperature on extraction efficiency for MTBE and MMT in headspace is shown in Figure 3. Increasing temperature did not significantly affect the extraction of MMT. The extraction of the more volatile MTBE decreases beyond 60^oC, which may possibly be caused by desorption of MTBE from the SPME fiber coating since high temperature increases the volatility of a volatile analyte. Similar effects have also been observed by other workers [19].

After the fiber was exposed to 250^oC for 15 seconds in the GC inlet liner, the thermal desorption of MBTE and MMT was completed. The complete desorption could be assured by re-injecting fiber into the GC-AED system for the determination of residual analytes.

GC-AED determination and GC-MS confirmation

Simultaneous multiple-elements analysis can be achieved by the GC-AED system. The atomic emission detector used in this study was equipped with a movable photodiode array (PDA) having a nominal wavelength range of 160-800 nm, with range limitation of

~40 nm/run. The manganese 259 nm line has been verified the most sensitive channel for the analysis of MMT [6]. Therefore, sacrifice of sensitivity of the determination of MTBE has to be compromised by using the carbon 248 nm line for simultaneous analysis of MMT and MTBE. Higher sensitivity for MBTE determination can be achieved with carbon 193 nm line. The flow rate of the helium make-up gas significantly affects the emission intensity of MBTE and MMT on these channels (Figure 4). The responses of MTBE on both carbon lines (193 and 248 nm) increase greatly with decreasing make-up gas flow rate, especially at carbon channel 193 nm. The make-up gas flow rate for Mn 259 nm has been optimized as 280 ml min⁻¹ [6]. Although the carbon 248 nm was not the most sensitive emission line for the determination of MBTE, it could be used to screen the compound when MMT was analyzed on Mn 259 nm. The GC-AED chromatograms of the simultaneous headspace SPME extraction of MMT and MTBE is shown in Figure 5. GC-MSD was applied to confirm these species in environmental samples. It is necessary to identify MTBE in environmental samples, because other gasoline components, such as 2-methylpentane and 3-methyl-pentane, have similar retention times which may cause confusion in identification.

Linearity, precision and detection limits

The headspace SPME was carried out in 40 ml vial containing 20 ml aqueous solution. The linear ranges and the detection limits were summarized in Table 2. The limit of detection, LOD, was determined as 3 times the standard deviation of the background noise measured on an aqueous sample after repeating extraction for four times. The LOD's for MMT are 0.3 pg l⁻¹ as Mn for headspace SPME and 0.5 pg l⁻¹ in liquid-liquid extraction. Although MMT is a less volatile compounds (6.3 Pa at 20⁰C) [5], it shows higher concentrations in the solid coating phase at equilibrium on extraction. When MMT and MTBE were determined simultaneously, the LOD of MTBE was 10 µg l⁻¹ at C 248 nm channel. The Limit of detection of MTBE can be lowered to 0.1 µg l⁻¹ at C 193 nm line with lower make-up flow rates (20 ml min⁻¹). In Table 2, the precision indicated

that good reproducibility of MMT and MTBE determinations were achieved with the combination of SPME technique and GC-AED determination.

Determination of environmental aqueous samples

Environmental samples including highway run-off, sewage samples, and lake water were collected, extracted by SPME, and analyzed by Gas Chromatography-Plasma Atomic Emission Dual-channel Detection for the determination of MMT and MTBE. The results were summarized in Table 3.

MMT was present in all highway run-off, and sewage samples, but not detected in lake water. The concentrations of MMT in highway run-offs were determined by using both SPME and liquid-liquid extraction methods. Both results were comparable (Table 3). MTBE could not be detected when the samples were analyzed for both MMT and MTBE simultaneously, but was found in the three highway run-off samples when analyzed separately at C 193 nm channel and at 20 ml min⁻¹ make-up gas flow rate. Unfortunately, the presence of MTBE could not be identified by the GC-MSD instrument due to the low concentration and interference. Therefore, the ambient concentrations of MTBE in environmental samples were not reported in this paper. MMT was found in sewage influent sample, and less concentration of MMT was also determined in the effluent samples. In spite of its short half-life in the presence of light, MMT was found in all highway runoff and sewage samples. Such phenomenon warrants further investigations.

Conclusions

The occurrence of gasoline additives, MMT and MTBE, in air, water, and ground water, has raised much environmental and healthy concern. An efficient method for MMT and MTBE analysis is essential for monitoring their presence in the environment. Headspace solid phase microextraction of MMT and MTBE has remarkable advantages over the traditional liquid-liquid extraction or purge-and-trap method because of its

simplicity, excellent reproducibility and solvent-free. The gas chromatography-atomic emission detection is a multi-element selective detection system. The combination of SPME fiber coated with PDMS and GC-AED dual-channel detection can provide an efficient technique for the simultaneous determination of MMT and screening of MTBE in aqueous samples. The low concentration of MTBE in water can be determined separately by using GC-AED under optimized conditions.

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Table 1. Operating conditions for GC-AED and GC-MSD**GC-AED****GC parameters**

Injection Port	Splitless
Injection Port temperature	250°C
Column	SPB-1, 30 m x 0.53 mm
Column head pressure	Helium, 100 k Pa (14.5 psi)
Temperature program	45°C for 0.5 min, then 30°C/min to 200°C

AED parameters

Transfer line	SPB-1
Transfer line temperature	270°C
Cavity temperature	270°C
Spectrometer purge gas	N ₂ at 2 l/min
Helium make-up gas (dual-channels)	280 ml/min for Mn 259 nm and carbon 248 nm
(single channel)	20 ml/min for carbon 193 nm

Hydrogen pressure	517 kPa (75 psi)
Oxygen pressure	172 kPa (25 psi)

GC-SIM-MSD

Splitless injection	Purge time 1.0 min, He carrier
Injector temperature	250°C
Column	DB5, 30 m x 0.25 mm
Carrier gas	He, constant flow mode, 10 psi at 50°C
Temperature program	45°C for 0.5 min, then 30°C/min to 200°C
Ionization potential	70 eV
Source temperature	190°C

Compounds	Ions monitored
MTBE	73, 57
MMT	55, 79, 134

Table 2. The summaries of linearity, detection limit and the precision for the determination of MMT and MTBE

	channel (nm)	makeup gas (ml min ⁻¹)	range (ng l ⁻¹) ^a	linearity (c.c) ^b	precision (rsd %) ^c	LOD* (ng l ⁻¹)
MMT	Mn 259	280	1 - 1x10 ⁻³	0.999	7.1	3x10 ⁻⁴
MTBE	C 248	280	1x10 ⁷ - 5x10 ⁴	1.000	8.8	1x10 ⁴
MTBE	C 193	20	1x10 ⁵ - 300	0.999	3.9	100

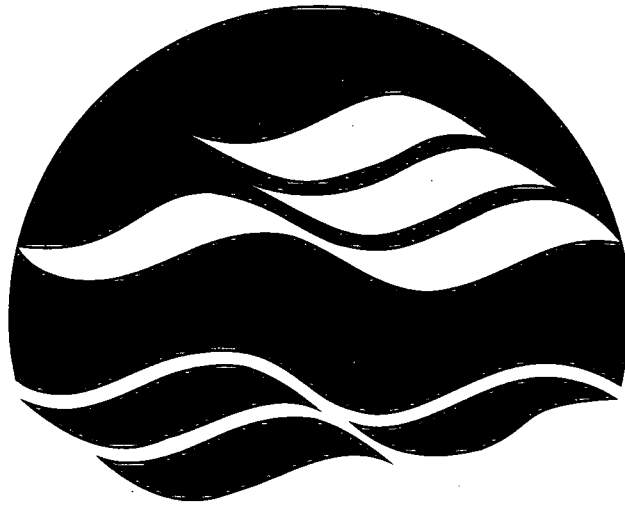
* - limit of detection (three times of the standard deviation of the noise); a - as ng Mn l⁻¹ for MMT; b - correlation coefficients; c - relative standard deviation.

Table 3. The concentration of MMT in environmental samples

Sample	MMT (pg Mn l ⁻¹)	
	SPME	liquid-liquid*
Highway runoff		
sample 1	2.0±0.2	2.4
sample 2	18.3±2.6	16.3
sample 3	1.0±0.1	2.8
sample 4	0.9±0.2	1.1
sample 5	1.7±0.1	2.8
sample 6	11.0±1.1	14.5
Sewage		
raw	50.0±5.1-	
primary	36.1±3.7	
final	12.0±1.3-	
Lake water		
sample A	nd	nd
sample B	nd	nd

n= 3; - no data; nd - not detected.

* - The recovery of MMT (at spike level of 10 pg MMT as Mn l⁻¹) with average LLE = 96±3.



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