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APPLICATION OF SOLID PHASE EXTRACTION AND GAS CHROMATOGRAPHY - MICROWAVE PLASMA ATOMIC EMISSION SPECTROMETRY IN THE DETERMINATION OF METHYLCYCLOPENTADIENYL MANGANESE TRICARBONYL (MMT) IN AIR

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Application of solid phase extraction and gas chromatography - microwave plasma atomic emission spectrometry in the determination of Methylcyclopentadienyl manganese tricarbonyl (MMT) in air

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Abstract

There are not too many methods available for the determination of MMT in environmental samples. The methods not only require high sensitivity, but must also have specificity required for environmental analysis. Available method involved the use of liquid extraction of MMT in air and in solid followed by gas chromatography-plasma atomic emission spectroscopy (GC-AED) determination. The present method described the use of solid extraction for the collection of MMT from air prior to the GC-AED determination. The method has a better recovery for MMT in air than the liquid extraction techniques, and is more convenient to use in the field and for large volume sampling.

Keywords

Methylcyclopentadienylmanganese tricarbonyl (MMT); air; gas chromatography; microwave plasma atomic emission detection

Résumé

Les méthodes de détermination du MMT dans les échantillons prélevés dans l'environnement ne sont pas nombreuses. En plus de devoir être hautement sensibles, ces méthodes doivent aussi avoir la spécificité requise pour les analyses environnementales. Les méthodes existantes utilisent l'extraction liquide du MMT présent dans l'air ou dans des solides, suivi d'une détermination par chromatographie gazeuse et spectrométrie d'émission atomique (CG-SEA). La présente méthode décrit l'utilisation de l'extraction solide pour la récupération du MMT présent dans l'air avant la détermination par CG-SEA. Cette méthode assure une meilleure récupération du MMT présent dans l'air que les techniques d'extraction liquide, et elle est plus pratique sur le terrain et pour le traitement de gros échantillons.

Mots clés

MMT, air, CG, SEA

Management Perspective

Methylcyclopentadienylmanganese tricarbonyl (MMT) has been used in Canada since 1976 (Environment Canada 1987) as anti-knocking agent to replace alkyllead in unleaded gasoline. The combustion of MMT leads to the formation of manganese oxides, especially manganese tetraoxide Mn_3O_4. It is evident that Mn from MMT source is an important constituent of the urban air pollution and that it is related to traffic density on a local scale.

There have been controversial opinions for a number of years between the automakers and the MMT producers. The major objection raised by the automakers to this compound was that MMT caused harm to automotive catalytic converters and sensor systems, whereas MMT producers denied such effects. Medical research suggested that Mn produced by the degradation of MMT could cause Parkinsonism-like symptoms. A ban was proposed in 1995 by the Minister of Environment in Canada. After lengthy parliamentary discussion, MMT was finally allowed to be used in gasoline formulation until adverse effects being proven. Similar controversy on MMT has been going on in USA, MMT ban in USA was introduced in 1978, but recently the EPA has granted the major producer Ethyl Corporation the emissions waiver which means that MMT causes no significant increase in emissions. It is evidenced that MMT is working its way back to the US market place.

Available method developed in this laboratory involved the use of liquid extraction of MMT in air and in solid by iso-octane. The present study describes a method using a solid extraction technique which is simple and convenient for field use and large volume sampling. The recovery of MMT from air by the present method is also superior to the previous solvent extraction technique.

Sommaire à l'intention de la direction

Le méthylcyclopentadiényl manganèse tricarbonyle (MMT) est utilisé au Canada depuis 1976 (Environment Canada, 1987) comme agent antidétonant pour remplacer les alkyles de plomb dans l'essence sans plomb. La combustion du MMT entraîne la formation d'oxydes de manganèse, particulièrement de tétraoxyde de manganèse (Mn_3O_4). Il est évident que le Mn issu du MMT est une composante importante de la pollution atmosphérique urbaine et qu'il est relié à la densité du trafic à l'échelle locale.

Il y a eu durant un certain nombre d'années des controverses entre les constructeurs d'automobiles et les producteurs de MMT. La principale objection soulevée par les constructeurs d'automobiles concernant le MMT était que ce composé endommageait les convertisseurs catalytiques et les systèmes de senseurs, alors que les producteurs de MMT niaient ces effets. Des recherches médicales ont laissé entendre que le Mn produit par la dégradation du MMT pouvait faire apparaître des symptômes de parkinsonisme. Le ministre de l'Environnement du Canada a proposé l'interdiction de ce produit en 1995. Après de longues discussions au Parlement, on a finalement permis l'utilisation du MMT dans les formulations d'essence jusqu'à ce que ses effets néfastes éventuels soient démontrés. Une controverse similaire a eu cours aux États-Unis, le MMT ayant été interdit dans ce pays en 1978, mais, récemment, l'EPA a levé ses restrictions en matière d'émissions pour l'important producteur Ethyl Corporation, ce qui signifie que le MMT n'entraîne pas d'accroissement significatif des émissions. Il appert que le MMT fait un retour sur le marché américain.

La méthode disponible élaborée dans ce laboratoire utilise l'extraction liquide du MMT présent dans l'air et les solides au moyen de l'iso-octane. La présente étude décrit une méthode utilisant une technique d'extraction solide simple et pratique sur le terrain et pour le traitement de gros échantillons. Cette méthode assure aussi une meilleure récupération du MMT présent dans l'air que la technique antérieure d'extraction au solvant.

INTRODUCTION

Methylcyclopentadienylmanganese tricarbonyl (MMT) has been used in Canada since 1976 (Environment Canada 1987) as anti-knocking agent to replace alkyllead in unleaded gasoline. The combustion of MMT leads to the formation of manganese oxides, especially manganese tetraoxide Mn_3O_4 (Ter Haar et al. 1975). It is evident that Mn from MMT source is an important constituent of the urban air pollution and that it is related to traffic density on a local scale (Loranger et al. 1994).

There have been controversial opinions for a number of years between the automakers and the MMT producers. The major objection raised by the automakers to this compound was that MMT caused harm to automotive catalytic converters and sensor systems, whereas MMT producers denied such effects (C&EN, April 24, July 24, 1995). Medical research suggested that Mn produced by the degradation of MMT could cause Parkinsonism-like symptoms (Donaldson 1982; Barbeau 1984). A ban was proposed in 1995 by the Minister of Environment in Canada. After lengthy parliamentary discussion, MMT was finally allowed to be used in gasoline formulation until adverse effects being proven. Similar controversy on MMT has been going on in USA, MMT ban in USA was introduced in 1978, but recently the EPA has granted the major producer Ethyl Corporation the emissions waiver which means that MMT causes no significant increase in emissions (E&EN, July 24,1995). It is evidenced that MMT is working its way back to the US market place.

MMT degraded readily in air under sun light (Ter Haar et al. 1975; Garrison et al. 1995)

with half life of less than 1 minute. However, its environmental fate has not been fully studied. In our recent investigations of MMT occurrence in rainwater and storm runoff collected along highways, MMT was found in most of the samples (Yang and Chau, 1999). It is not understood why a readily photodegraded compound can exist in rain and runoff water. Continuous monitoring of MMT residues in environmental samples and studies of its pathways are essential in understanding its fate.

Available specific method for MMT determination involved the use of liquid extraction of MMT in air and in solid samples by iso-octane followed by gas chromatography-plasma atomic emission determination (Chau et al. 1997). The use of solid extraction described in the present study not only improves the recovery for MMT in air but also provides a much simpler and convenient method for field sampling and for larger volume sampling.

Experimental

Apparatus

The air sampling apparatus consisted of a valveless ceramic piston pump Model QD 2C5C (FMI LAB Pump, Oyster Bay, N.Y. 11771). The pump rate, hence the air flow, was controlled (deviation ±1%), by a Mass-Flo Controller, Model 1159B-00200SV, with a Power supply unit, MKS Type 246 (MKS Instruments, Canada, Ltd., 30 Concourse Gate, Nepean, Ontario, K2E 7V7). All these units were conveniently housed in a wooden box for portability in field sampling. The air sample was pumped through two traps in series to prevent possible sample leakage. The sampling tubes are Pyrex tubes 1.3 cm dia.x8 cm long with a B-10 ground glass cone at one end and a socket at

the other for connection in series. Fig. 1 shows the setup of the sampling assembly. The Gas chromatography-plasma atomic emission detection (GC-AED) system (Hewlett Packard, PA) and operation parameters for the determination of MMT have been described in a previous study (Chau et al. 1997).

Reagents

The absorbent, Tenax GC (60-80 mesh), and other absorbents were obtained from Chromatographic Specialties, Inc. (Brockville, Ontario). The absorbent (ca. 5 cm absorbent bed) was packed in glass absorbent tubes with glass wool plugs at both ends. The sampling traps were wrapped in aluminum foil or black paper to prevent from light exposure. All glass sampling traps used in the study were silanized. Methylcyclopentadienylmanganese tricarbonyl (MMT) was obtained from Aldrich (Milwaukee, WI, USA). Standard solution (1000 μg/ml as Mn) of MMT was prepared in iso-octane (J.T. Baker, USA) and stored in amber glass bottles. The air intake of the solvent dispensers in the laboratory was protected from contamination by a micro absorption tube containing Tenax. Distilled water was further purified by a Milli-Q system (Millipore, Bedford, MA, USA).

Procedure for air sampling

Two sets of assembly were used at a chosen sampling location to provide duplicate readings. Air was pumped through the traps at 200 ml/min for 2 hr. After sampling, the traps were stored in ice-cooler for shipment to laboratory for immediate analysis

according to the procedure described for recovery test. If analysis is not performed on the same day, sample traps can be stored in freezer in the dark for several days without loss of analyte.

Results and discussion

Recovery of MMT by absorbents

The recovery of MMT by various absorbents was evaluated by pumping air at the rate of 200 ml/min for 2 hour over a MMT standard solution (100 pg of MMT (as Mn) in iso-octane) injected to the glass wool plug at the sample entry point of the first trap. The absorbent to be evaluated was packed (ca. 5 cm absorbent bed) in the two traps with glass wool plugs at both ends. When sampling was completed, each of the traps was eluted with two 6-ml portions of hexane. The recovery assessment was performed exactly in the manner as for real sample analysis. After reduction of the combined eluate to 1 ml under nitrogen flow, 1μl of the each fraction was injected to the GC-AED system for analysis. The volume reduction of the eluate was necessary for environmental samples because of their low MMT concentrations. The recovery was assessed by comparing the GC-AED signal to that of a standard prepared by adding the same amount of MMT to 1 ml of hexane.

In similar manner, the recovery of several other absorbents was assessed and summarized in Table 1. Among the five absorbents evaluated, Tenax, Florisil and C18 recovered the MMT satisfactorily in the first trap. Tenax was arbitrarily chosen for use. The used traps can be regenerated after use by eluting with ca. 15 ml of hexane or iso-

octane and dried by blowing air through them followed by further drying in oven.

In an earlier study, the use of an impringer containing iso-octane could only recover some 74% of MMT from air (Chau et al. 1997), whereas the use of absorbent in the present study can quantitatively recover it. It is also more convenient to use absorbent traps in the field and for large volume air sampling.

The laboratory air was occasionally monitored by sampling for 2 hr. (24 L) through the traps for MMT contamination. No MMT residues were found. MMT was found strongly absorbed on walls of glass containers. The absorbed MMT can be de-contaminated by rinsing twice with ca. 20 ml hexane or iso-octane and once with acetone and drying in oven. This procedure is recommended for cleaning glassware previously used in MMT work.

Effect of flow rate on recovery of MMT

The effect of air flow rates on the recovery of MMT by the Tenax trap was investigated by varying the air flow from 100 ml/min to 500 ml/min for recovering 100 pg of spiked MMT in the same manner as in experiments described for recovery. It was observed that an air flow rate of 200 ml/min was optimal and convenient for air sampling. A 2 hr sampling time will collect 24 L of air which will give sufficient analyte for MMT determination. Faster air flow rates may cause sample leakage in the traps leading to low recovery.

Breakthrough volume

The breakthrough volume of the absorbent traps was investigated by varying the run time, hence the volume of air passing through the traps in trapping an air sample contained in a 2-L separatory funnel. The MMT-spiked air samples were prepared as described in a previous study (Chau et al. 1997) by injecting MMT vapour using a gas syringe into the air in a 2L separatory funnel. The air sample was evacuated by suction through the two sampling traps in series for different period of time. The two traps in series can detect any "washout" effect of MMT from the first trap and also the capacity of the assembly to hold the analyte under various sample volumes. It was found that there was no MMT in all of the second traps, indicating that prolonged running of the pump up to 8 hr (96 L of air) did not displace the trapped MMT to the second trap. A pumping time of 30 min (equivalent to 6 L of air) was basically sufficient to recover the MMT spiked to 2L of an air sample (Table 2).

Storage of MMT samples

It has been shown that MMT solution was stable when stored in amber glass bottle and kept in freezer for a period of up to eleven days (Chau et al. 1997). The effect of storage of trapped samples was investigated by trapping MMT-spiked air samples in the sample tubes and storing them in freezer over a period of time. The MMT-spiked air samples were prepared as described in a previous study (Chau et al. 1997). The traps containing MMT were wrapped in aluminium foils and stored in freezer for two weeks. It

was found that the trapped MMT did not leak out nor was decomposed during this period. It was reported that MMT was fairly stable in aquifer materials and sediments at various Eh levels. Half-lives ranged from 0.2 to 1.5 years in aquifer materials at 25°C (Garrison et al. 1995). In any case, light protection is necessary as MMT decomposes under ambient light conditions with half life of about 3-4 days (Chau et al. 1997). It has been shown that MMT photolyzes rapidly in distilled water medium, its half-life under midday sunlight in water is approximately 1 min. (Garrison et al. 1995).

Bottles containing MMT chemical or solutions should always be stored in double containers and inside a plastic bag placed inside a fume cupboard. Care should also be exercised not to place the solvent close to the MMT solutions to avoid contamination (Chau et al. 1997). The air intake of the solvent dispenser should also be protected by a micro Tenax trap. In spite of all these precautions, the solvent should still be checked from time to time for MMT contamination.

Two air samples were taken simultaneously at one locations near Ethyl Corporation, where MMT was produced, to illustrate the application of the method. Results showed that MMT was present at 0.33 and 0.35 pg Mn/L respectively. Previous study showed that MMT was present in air in many underground car parks and also in air and in soils near the production plants (Chau et al. 1997). Its presence in runoff samples in highway locations and city sewage samples has been reported and discussed in a recent study (Fan and Chau 1999). However, It has not been found in any lake water samples. Systematic air sampling will be carried out to study the distribution patterns and persistence of MMT as a result of its use in gasoline.

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Table 1. Effect of absorbents on recovery of MMT from air

Absorbent	Recovery (%)
Tenax	89.0 ± 3.3
Florisil	90.0 ± 1.7
C18	93.9 ± 2.3
XAD-2	78.0 ± 4.1
Silica gel	22.3 ± 2.1

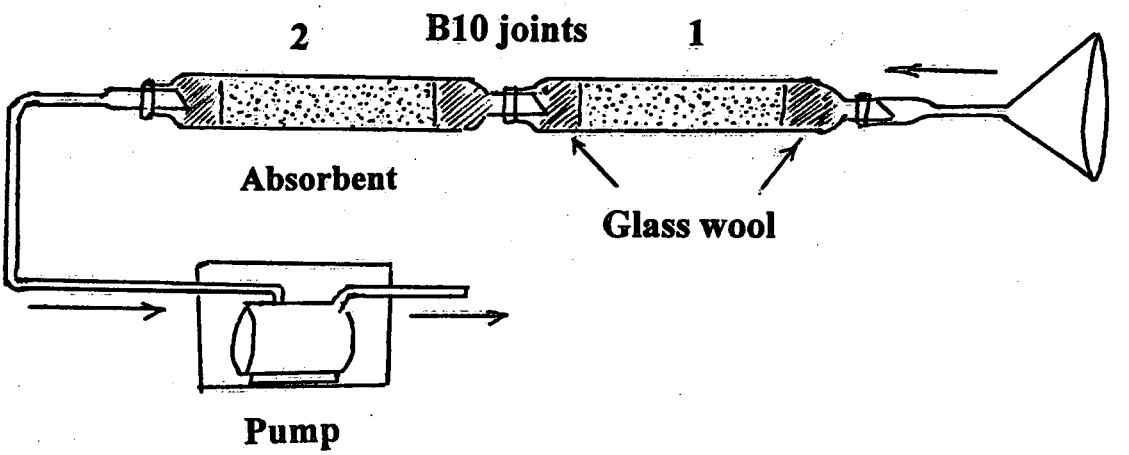
n = 3; a standard solution containing 100 pg MMT(as Mn) was spiked to the glass wool plug at the sample entry point of trap 1.

Table 2. Effect of pumping time on recovery of MMT from air

Pumping time Volume of air*	20 min (4L)	30 min (6L)	3 hr (36L)	5 hr (60L)	8 hr (96L)
Recovery (%)	19±7	105±0	93±5	100±1	05±3

Average of 2 runs; *volume of air through the traps; flow rate 200 ml/min.

Figure 1. Sampling Assembly



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