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Determination of Methylcyclopentadienylmanganese Tricarbonyl (MMT) in Gasoline and Environmental Samples by Gas Chromatography with Helium Microwave Plasma Atomic Emission Detection

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A highly sensitive and specific method is described for the determination of methylcyclopentadienylmanganese tricarbonyl (MMT) in gasoline and environmental samples by gas chromatography–plasma atomic emission detection (GC–AED). The procedure is simple, rapid and free from interferences. The absolute limit of detection is 0.5 fg of MMT (0.5×10^{-15} g) expressed as Mn. The precision for replicate injections ($n = 5$) of an MMT solution (10 pg Mn) was 2.8% relative standard deviation (RSD). Applications of the method to analysis of gasoline (petrol), and preliminary results of the analyses of environmental samples such as air and roadside dirt, are given. © 1997 by John Wiley & Sons, Ltd.

Keywords: methylcyclopentadienylmanganese tricarbonyl (MMT); gas chromatography; helium microwave plasma atomic emission; air; soil

INTRODUCTION

Methylcyclopentadienylmanganese tricarbonyl (MMT) has been used as a partial substitute for alkyl-lead antiknocking agents in unleaded gasoline (petrol) to improve the octane rating. It is also used extensively as a boiler or gas turbine fuel additive to reduce deposits, smoke, particulates and sulphur trioxide formation. MMT is highly toxic and emission of manganese to the atmosphere may cause chronic manganese poisoning leading to Parkinsonism-like effects.[1] A sensitive and specific analytical method for continuous monitoring of its level in the environment is necessary.

Available analytical techniques for the determination of MMT are mainly gas chromatography with various detectors such as direct-current argon plasma emission,[2] helium microwave plasma emission,[3–5] hydrogen atmosphere flame ionization,[6] atomic absorption,[7] flame photometry,[8] electron capture[9] and alternating-current plasma emission.[10] All techniques can generally reach detection limits at the subnanogram to picogram level. Although MMT is known to decompose in air, and more quickly under light,[7] the presence of its residues in the atmosphere near gas (petrol) stations, in indoor car-parks and at places where it is handled will require highly sensitive and specific methods for its regular monitoring. The present study describes a simple, extremely sensitive and specific technique for the determination of MMT in gasoline and in environmental samples. The technique (GC–AED) is based on gas chromatography separation and helium microwave plasma emission detection of manganese at the femtogram level.

EXPERIMENTAL

Apparatus

The GC–AED system consisted of a gas chromatograph (HP Model 5890, Series II, Hewlett-Packard, PA, USA), equipped with a split-splitless injection port, an HP helium microwave plasma atomic emission detector (Model 5921A), and an HP automatic sampler

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Table 1 GC–AED operation parameters

GC parameters	
Injection port	Spitless
Injection port temp.	250 °C
Injection volume	1 μl
column	SPB-1, 30 m length × 0.53 mm
Column head pressure	Helium, 100 kPa (14.5 psi)
Temperature programme	80 °C (1 min); 20 °C min^{-1} to 200 °C
AED parameters	
Transfer line	SPB-1
Transfer line temp.	280 °C
Cavity temperature	280 °C
Solvent vent off-time	3 min
Spectrometer purge gas	Nitrogen at 2 1 min^{-1}
Helium make-up gas	280 ml min^{-1}
Manganese wavelength	259 nm
Hydrogen pressure	517 kPa (75 psi)
Oxygen pressure	172 kPa (25 psi)

(Model 7673A). The system was factory-interfaced and the operation was controlled by computer using the HP3592A ChemStation software. Operation software of the GC–AED system for manganese was supplied by Hewelett Packard and the parameters are given in Table 1.

Reagents

Methylcyclopentadienylmanganese tricarbonyl (MMT) and cyclopentadienylmanganese tricarbonyl (CMT) were obtained from Aldrich, Milwaukee, WI, USA. Solvents and common reagents were of analytical grade. Standard solutions of MMT and CMT (1000 μg ml^{-1} as manganese) were prepared in iso-octane for their stability.[2] Distilled water further purified by a Milli-Q (Millipore, Bedford, MA, USA) system was used throughout. The carrier gas for the GC–AED system was high-purity helium, (99.999%). Reagent gases for the AED were oxygen (99.999%) and hydrogen (99.999%), both supplied by Canox Ltd (Mississauga, Canada).

Optimization of operational parameters

The optimal operation parameters of the plasma emission detector for manganese have been studied on system fabricated in our laboratories[3–5] and on a commercial GC–AED system.[5] Since these are operational parameters, some variations may exist from instrument to instrument. The effect of make-up gas flow on sensitivity of manganese detection was investigated by repeated injections of 1 μl of an MMT standard solution (containing 10 pg Mn) into the GC–AED system at various helium make-up gas flow rates. The make-up gas flow was measured with a flow meter at the cavity vent outlet with the reagent gases and spectrometer window purge gas turned off. Results shown in Fig. 1 indicate that increase of make-up gas flow increased the sensitivity of manganese detection until a maximum was reached at 280 ml min^{-1}; then the sensitivity fell off rapidly. It is crucial that the instrument be operated at the optimal make-up gas flow rate. The optimum make-up gas flow rate was selected at 280 ml min^{-1} for subsequent work.

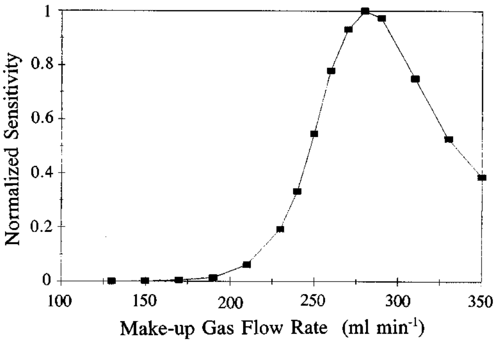

Figure 1 Effect of make-up gas flow rate on the sensitivity of MMT determination.

Effect of hydrogen pressure

The determination of manganese requires a mixture of oxygen and hydrogen as the reagent gas. The function of oxygen is to prevent carbon deposits forming on the discharge tube during

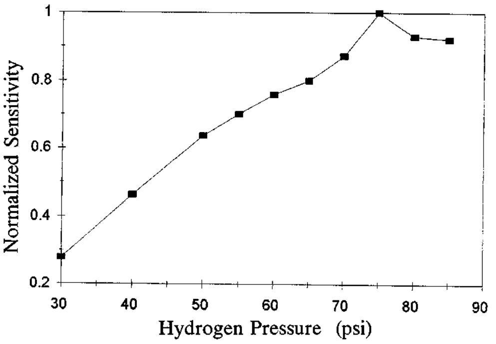

Figure 2 Effect of hydrogen pressure on the sensitivity of MMT determination.

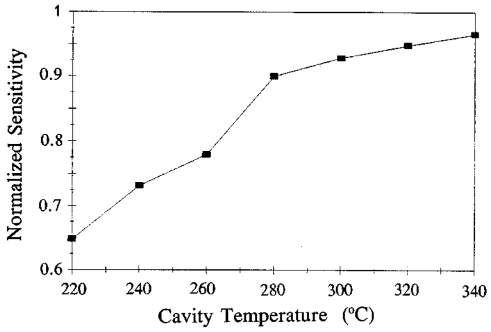

Figure 3 Effect of cavity temperature on the sensitivity of MMT determination.

the sample excitation process, and its pressure (172 kPa, or 25 psi) is recommended by the instrument manufacturer. The effect of hydrogen pressure on sensitivity for manganese detection was investigated by repeated injections of 1 μl of a MMT standard (containing 10 pg Mn) at different hydrogen pressures. It was observed that increase of hydrogen pressure increased the sensitivity for the Mn signal. A maximum was reached at 517 kPa (75 psi), after which it tailed off gradually. The hydrogen pressure of 517 kPa was chosen for subsequent operations (Fig. 2).

Effect of cavity temperature

The effect of cavity temperature on the sensitivity of manganese determination was investigated by repeated injections of 1 μl of an MMT standard solution (containing 10 pg Mn) to the GC–AED system at varying cavity temperatures. The temperature of the transfer line followed that of the cavity to avoid condensation of the analytes. Figure 3 indicates that the sensitivity increased rapidly with the cavity temperature from 220 to 280°C, after which the increase became gradual and was only about another 5% when the temperature was further increased to 340°C. The cavity temperature of 280°C was selected for use.

Table 2 Summary of absolute detection imits for manganese in MMT

Method	Abs DL	Reference
GC–MED	0.25 pg s^{-1}	3
GC–DCP	3 ng	2
GC–HAFID	17 fg	6
GC–MED	7.7 pg s^{-1}	4
GC–AED	0.1 pg	5
GC–ACP	62–69 pg s^{-1}	10
GC–AED	0.5 fg	This work

Abbreviations: Abs DL, absolute detection limit; MED, microwave emission detection; DCP, direct-current plasma emission detection; HAFID, hydrogen atmosphere flame ionization detection; AED, microwave plasma atomic emission detection; ACP, alternating-current plasma emission detection.

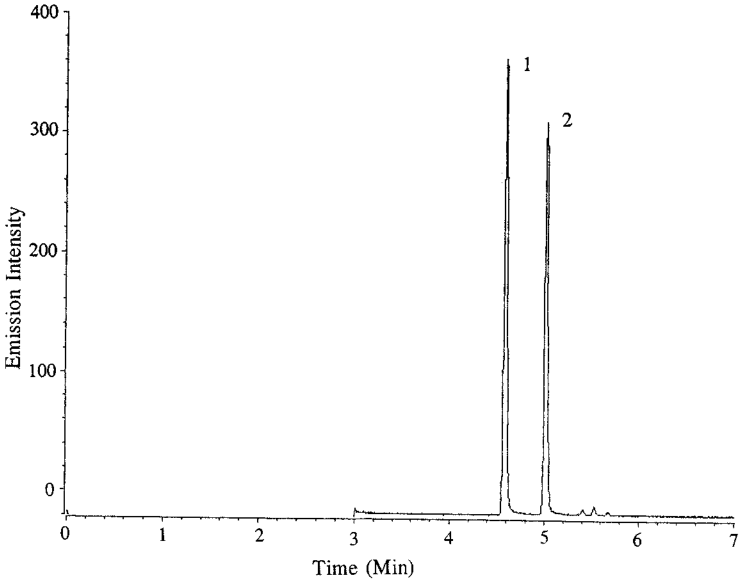

Figure 4 GC–AED chromatograms of MMT and CMT: 1, CMT; 2, MMT; 1 μl injection (10 pg Mn).

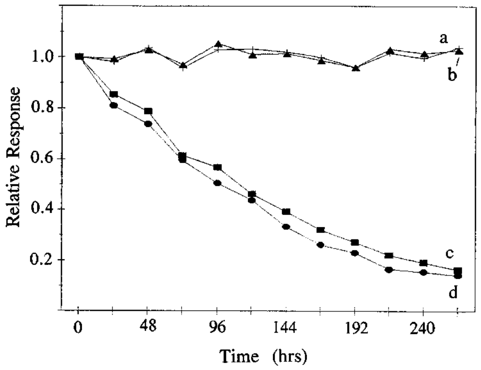

Figure 5 Stability of MMT and CMT on storage: a—MMT, b—CMT, in amber glass bottle, in freezer (−25°C); c—MMT, d—CMT, in clear bottle under normal light and temperature (20 °C) in the laboratory. Relative response = emission intensity of test solution/emission intensity of standard.

RESULTS AND DISCUSSION

Calibration curve, precision and detection limit

The linear range for the AED responses to manganese extended over 3.3 orders of magnitude from 0.005 pg to 10 pg with correlation coefficients of 0.995. The relative standard deviation (RSD) for replicate injections ($n=5$) of an MMT standard solution (10 pg Mn) was 2.8%. The absolute detection limit for MMT was obtained by injecting 1 μl of a diluted MMT standard (5×10^{-4} ng Mn ml^{-1}) into the GC–AED system. The absolute detection limit at 3σ (σ = standard deviation of background noise) was 0.5 fg (0.5×10^{-15} g), expressed as manganese.

The detection limits of the plasma atomic emission technique are generally in the picogram range for most elements. For manganese, sub-picogram detection was already achieved in the first prototype GC–microwave atomic emission system in 1978.[3] Since then, continuous improvements of the instruments and optimized operation software for manganese have been made available by the manufacturer. The low detection limit was obtained by further refining of the parameters given by the instrument manufacturer. A summary of the detection limits for manganese by various types of atomic emission detectors is given in Table 2.

Interferences

Table 3 Determination of MMT in commercial unleaded gasoline[a]

	Concentration (μg ml^{-1}	
Brand	Expressed as Mn	Expressed as MMT
Brand 1, regular	4.73	18.80
Brand 1, premium	5.63	22.37
Brand 2, regular	10.03	39.80
Brand 3, regular	7.90	31.34
Brand 4, regular	8.14	32.30

[a] Sample dilution 1000 ×; 1 μl injection; $n=3$; averaged SD = 2.8%; MMT = 3.97 × Mn value

As tetramethyl-lead (Me_4Pb), tetraethyl-lead (Et_4Pb) and MMT are common antiknocking agents used in gasoline, possible interferences in the MMT determination due to the presence of the alkyl-lead compounds were investigated. No interferences were observed when 1 μl of a standard solution of MMT (0.25 ng Mn ml^{-1}) was determined in the presence of alkyl-lead at a concentration 4000 times that of MMT, i.e. 500 ng Pb ml^{-1} of each of Me_4Pb and Et_4Pb. Inorganic manganese compounds, even if they were present in gasoline, are not expected to interfere as they cannot pass through the gas chromatograph to reach the detector. No interferences due to the high concentrations of various hydrocarbons in gasoline were observed after 1000-fold sample dilution. A related compound, cyclopentadienylmanganese tricarbonyl (CMT), present in both the MMT standard and in gasoline, appeared in the chromatograms at a different retention time and was suggested for use as an internal standard by some investigators.[2] Since CMT is present in all gasoline samples we analysed, but not in constant amounts, it may cause interference in MMT concentration calculations. A chromatogram of MMT and CMT is shown in Fig. 4. Because of the extremely high sensitivity for manganese determination by the AED technique, all glassware should be carefully cleaned before use. MMT, although it has a relatively high boiling point (232–233 °C), has a high vapour pressure which causes it to leak out from containers, possibly to contaminate adjacent laboratory ware. An iso-octane solvent standing next to a bottle of liquid MMT inside a fume cupboard was found to contain MMT. It has also been observed that a bottle of MMT standard solution stored inside a refrigerator contaminated other reagents. It is imperative that the liquid MMT or standard solutions be stored in double containers and in a locking plastic bag and placed inside a fume cupboard. They should not be left on any open bench in the laboratory for extended periods of time. Containers that have been used for MMT work should be sequentially cleaned with iso-octane, then water, then soaked in acid bath.

Stability of MMT and CMT

The stability of MMT and CMT was investigated by placing aliquots of 1.5 ml of an MMT solution (10 ng Mn ml^{-1} in two separate 2 ml GC vials (CMT was present in the MMT chemical). One vial was of amber glass and was kept in the freezer; the other was of clear glass and was kept under ambient lighting conditions and room temperature. The samples were analysed at 24 intervals for 11 days against a freshly prepared standard solution of the same concentration. The results (Fig. 5) indicated that both MMT and CMT decomposed rapidly under light at room temperature with half-lives of about 3–4 days. On the contrary, they were stable over the 11-day test period when stored in amber glass bottles and kept in the freezer. The rates of decomposition for MMT and CMT are similar.

Recovery of MMT and CMT from air

An artificial air sample containing MMT and CMT was prepared. Five drops of liquid MMT was added to a 100 ml screw-capped flask, wrapped in aluminium foil and placed inside a fume cupboard for 24 h to achieve equilibrium. A 50 μl sample of the headspace vapour was taken by a gas syringe and injected into a 2-litre separatory funnel, the walls of which had been wetted with 20 ml of iso-octane. Another 50 μl aliquot of the MMT headspace vapour was injected into 3 ml of iso-octane sealed in a 4 ml GC vial which served as a standard for evaluation of recovery. By the water displacement method, the air in the separatory funnel was transferred slowly to pass through a bubbling tower containing 50 ml iso-octane. The iso-octane originally present in the separatory funnel was combined with that in the bubbling tower and was evaporated in a rotary evaporator at room temperature to 3 ml, from which 1 μl was injected in the GC–AED. Recoveries of MMT and CMT from air averaged from four replicated runs were 74.2 ± 3.5% and 82.3 ± 9.4% respectively.

Recovery of MMT and CMT from fine sand examples

Most roadside dirt is sandy, consisting of fine sand and dusts as a result of the blowing winds,

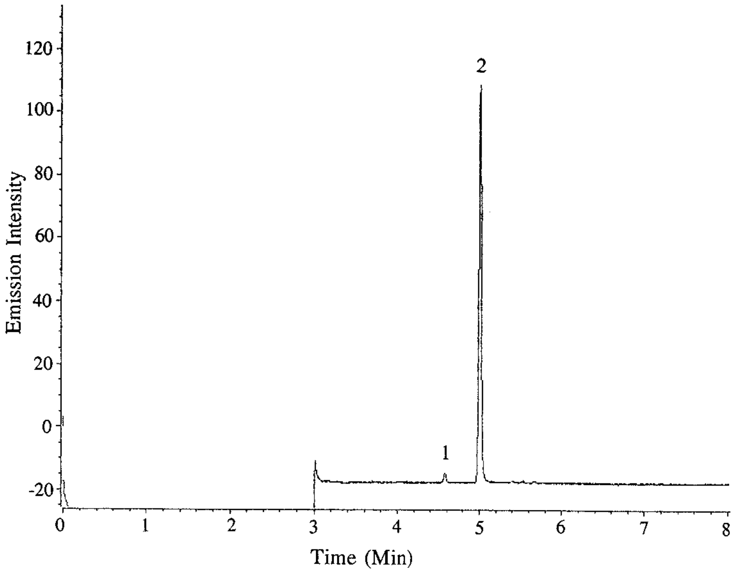

Figure 6 GC–AED chromatogram of gasoline analysis: 1, CMT; 2, MMT; sample dilution 1:1000 with iso-octane; 1 μl injection.

Table 4 Concentration of MMT and CMT in air and roadside dirt

Sample	CMT (pg Mn l^{-1})	MMT (pg Mn l^{-1})
Underground car-park		
Air no. 1	d[a]	8.8
Air no. 2	5.5	18.7
Air no. 3	7.4	22.9
	CMT (pg Mn g^{-1})	MMT (pg Mn g^{-1})
Roadside dirt		
Highway no. 1	—[a]	d
Highway no. 2	—	—
Highway no. 3	—	—
Dirt near gas station	d	41.7

[a] —, not detected; d, detected, but not quantified.

with very little soils in the composition. The recoveries of MMT and CMT from this type of sample were investigated by spiking 4 g of fine sand with 100 μl of an MMT standard solution (10 ng Mn ml^{-1}). The sample was air-dried, and shaken with 10 ml of iso-octane for 1 h, after which 5 ml of the iso-octane was removed to a test-tube and evaporated to 1 ml at room temperature by nitrogen, and 1 μl was injected into the GC–AED system against a freshly prepared standard. The recovery from sand averaged from four replicate runs was 100.5 ± 4.5% and 96.9 ± 12.3% respectively for MMT and CMT.

Analysis of gasoline

The technique was applied to the determination of the MMT content of four common brands of gasoline purchased locally. Since the analytical procedure for gasoline analysis is simple, without any extraction or preconcentration processes, the use of external standards will therefore suffice. The gasoline samples were diluted 1000-fold with iso-octane, from which 1 μl was injected into the instrument. The results are summarized in Table 3. Figure 6 shows a typical chromatogram of MMT and traces of CMT in gasoline.

Determination of MMT in roadside dirt and air samples

The technique was applied to roadside dirt and air samples for investigation of the environmental occurrence of MMT. Roadside dirt samples (4 g) on busy highways and at gas stations were collected and extracted by shaking with 10 ml of iso-octane in a 50 ml Erlenmeyer flask for 1 h. An aliquot (5 ml) of the extract was removed to a test-tube and evaporated to 1 ml at room temperature with N_2. A 1 μl portion was injected into the GC–AED system.

Air samples were collected at a city underground car-park using the water displacement technique, by first filling a 2-litre separatory funnel with distilled water, and then draining out the water slowly at a suitable location inside the car park. After the water had been emptied, the funnel was closed at both ends after 20 ml of iso-octane had been added. The funnel was swirled to allow the iso-octane to wet the walls. The sample was transported back to the laboratory in

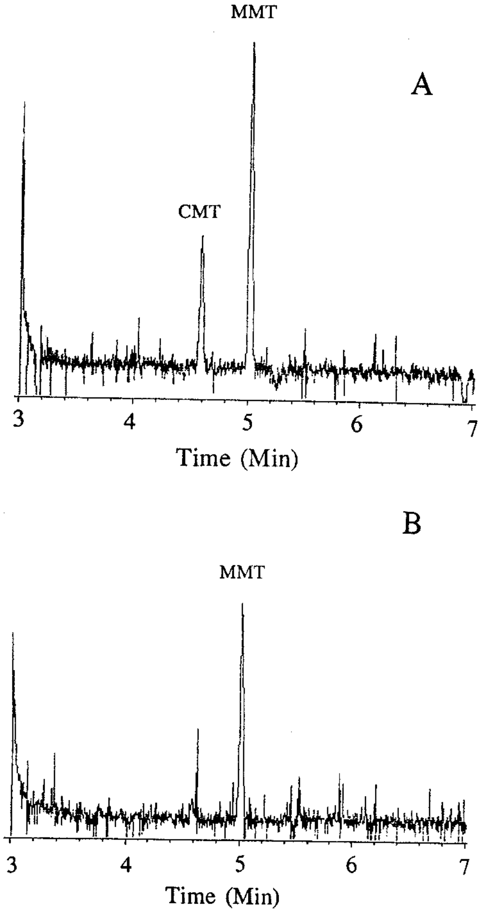

Figure 7 GC–AED chromatograms of analysis of air and roadside dirt: A, air sample in city underground car-park, sample no. 3; B, dirt near gas station.

a cooler for immediate analysis as described in the preceding paragraph for the recovery study.

Distinct peaks of MMT and CMT were observed in the chromatograms of soil and air samples. The presence of the CMT peak could serve to verify the identity of MMT because CMT has been found in the MMT standards and in all brands of gasoline. There is no known chemical interconversion reaction between CMT and MMT although they are similar in structure. Its presence may simply be due to impurities in the MMT manufacturing process.

The sampling and extraction procedures for soil and air sampling, although simple, have been successfully applied to environmental samples. Preliminary results summarized in Table 4 demonstrate that this analytical technique has the sensitivity required for such samples. MMT was present in all air samples collected at the underground car-park, but it was not found in roadside dirt samples on highways. A soil sample taken at a location near a gas station contained MMT. Figure 7 shows typical chromatograms of analyses of air collected in a city underground car-park and soil samples collected at a location near a gas station.

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