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# Speciation and Quantification of Organic Manganese Compounds in Gasoline by Gas Chromatography Atomic Emission Spectroscopy

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In the 1950's an organic manganese fuel additive was developed that demonstrated good antiknock properties combined with engine and spark plug compatibility similar to tetraethyl lead (Brown and Lovell 1958). This compound, methylcyclopentadienyl manganese tricarbonyl (MMT), was originally referred to as AK-33X (antiknock agent 33X). MMT has had long-term use in Canada. It was introduced into Canadian gasoline in 1976 and its use increased substantially to the point when in 1990 it completely replaced tetraethyl lead (TEL) (Loranger et al. 1995). Canada is the only country in the world to have made exclusive use of MMT as an antiknock agent in unleaded gasoline (ULG). However in April 1997 Canada placed a restriction on MMT due to the automobile manufacturers claims about its effects on the latest emission control systems (C&EN 1995a, C&EN 1996b). The Canadian senate passed a bill to prohibit import and interprovincial transport of MMT, but the bill did not ban its use. The manufacturer of MMT, Ethyl Corp., Richmond, Va., in response filed a $250 million-plus lawsuit against the government of Canada (C&EN 1997). This situation was likely to violate the North American Free Trade Agreement given that Health Canada, the government agency that provides health protection and consumer product safety, has ruled that MMT does not cause health risks as used in gasoline (C&EN 1996b). On July 20, 1998 Canada withdrew its ban on MMT and settled with Ethyl Corp, but could still ban MMT under its Environmental Protection Act if studies in progress indicate public health and environment problems (C&EN 1998).

In October 1978 the use of MMT in US unleaded gasoline was banned by the US Environmental Protection Agency (EPA). The US EPA, having accepted reports that MMT increases hydrocarbon emissions, together with concerns over health problems, restricted the use of MMT through the Clean Air Act amendments of 1977. The use of MMT in leaded fuel however continued in the USA (Egyed and Wood 1996). The automobile manufacturers claim that MMT interferes with automotive catalytic converters and sensors in cars, compromising the capability of those devices to reduce emissions. Ethyl Corporation, however claims that the automotive manufacturers want to "tune" their cars for just one type of gasoline in both the USA and Canada to reduce their warranty costs (C&EN 1995a). After years of federal court appeals and legal battles the US EPA was found to have acted unlawfully in banning MMT in US ULG and was directed in 1995 to register it for use as an antiknock additive (C&EN 1995c). This decision allows MMT to be used at up to 0.031 g Mn/US gallon in all states except California where it remains banned (Hamilton 1998). This ruling has come about due to numerous independent studies that conclude MMT has no real effect on engine emissions such as NO and CO (C&EN 1995b), and studies in Canada show that after 18 years of MMT use occupational and environmental levels of Mn in air are well within accepted limits (Zayed et al. 1994, Loranger and Zayed 1994, Egyed and Wood 1996). North American oil companies have however been slow to adopt the use of MMT since the ruling for its unrestricted use in the US (C&EN 1996a, C&EN 1998).

The combustion of MMT results in the formation of Mn oxides, the principle product being $Mn_3O_4$ aerosols. Chronic inhalation of Mn dust is capable of producing neurotoxicity with symptoms of mild poisoning similar to Parkinson's Disease (Egyed and Wood 1996). Occupational exposure limits for Mn established by industrial hygienist organisations (ACGIH, NIOSH, OSHA) indicate that a greater measure of safety is expected for exposure to Mn than Pb in the form of dusts and fumes but studies on the effects of long-term exposure to low concentrations of Mn are lacking. The US EPA claims that this lack of toxicological data is the basis for its health concerns, and that this has contributed to the limited use of MMT throughout the world (Loranger and Zayed 1994).

Cyclopentadienyl manganese tricarbonyl (CMT or cymantrene) and its methyl derivative MMT have an essentially equal antiknock effect based on weight of metal, and have a synergistic octane effect with TEL (Brown and Lovell 1958). These and other organomanganese compounds were separated, and MMT was quantified, with the gas chromatograph atomic emission detector (GC-AED). The GC-AED (C&EN 1989) has the advantage of being able to speciate organometallics rather than just measure total elemental response as carried out with inorganic analysis techniques. It is therefore possible by GC-AED to detect the active organomanganese components in an organic solution that may also contain manganese resulting from synthesis derivatives and breakdown products. Considerations for quantitative analysis of MMT by GC-AED are presented to assist process studies and environmental monitoring programs.

## MATERIALS AND METHODS

A 5890II gas chromatograph and 5921A atomic emission detector were used with a 35920C pascal ChemStation (Hewlett Packard, Avondale, PA, USA). Oxygen and hydrogen reagent gases were used at the standard pressure settings of 25 psi and 70 psi, respectively. The helium plasma make-up gas flow solenoid was set to "high". GC operating conditions were: 50°C (2 mins), 15°C/min to 200°C. The injector and AED cavity temperatures were 250°C. The solvent vent period was 2.5 minutes. A fused silica capillary column, DB-5 MS, 15 m x 0.32 mm x 0.25 µm film (J&W Scientific Inc., Folsom, CA, USA) was used with a 7 psi column head pressure. The following chemical standards were obtained: MMT ($C_9H_7MnO_3$) 97%, and CMT or cymantrene ($C_8H_5MnO_3$) 98% (Strem Chemicals Inc., Newburyport, MA, USA). A variety of gasolines and octane booster additive products containing MMT were obtained from local outlets. Standard solutions were stored in the dark at 4°C and samples were contained in amber autosampler vials during analysis. All solvents used were analytical grade.

A selective recipe was generated by the choice of a range of emission wavelengths to include a Mn "triplet" in the 260 nm region; 257.6 nm, 259.4 nm and 260.6 nm, as well as the 279.5 nm emission line for Mn. This 22 nm wavelength span fitted well within the 40 nm active photodiode array working window (a "snapshot" window), and included many target pixels to improve the signal to noise. Interference from carbon and silicon in the 248 nm to 252 nm region was subtracted out of the recipe. To determine the helium plasma make-up flow rate for optimum Mn response on the AED, a 1.25 mg/L MMT solution was prepared and repetitively injected with 15 mL/min increments of the make-up gas flow rate measured at the cavity vent. The starting point was the standard high flow setting (with the hydrogen and oxygen reagent gases on) of 200 ml/mm. An optimum peak area response for Mn was obtained at a flow of 305 mL/min which was used for all Mn analyses.

One drop of the MMT standard was weighed into a 100 mL A-grade volumetric flask to produce a 165 mg/L stock solution in 95% hexane. This solution was diluted to between 0.33 and 1.65 mg/L in hexane (10-50 µL diluted to 5 mL). The effect of various hydrocarbon matrix backgrounds on the response of the AED to organic Mn over this concentration range was examined. Methyl tertiary-butyl ether (MTBE), methyl isobutyl ketone (MIBK), and organic Mn free ULG were added at l/500 dilutions to the solutions of MMT in hexane to produce four analysis sets over this concentration range. The GC-AED instrument precision for organic Mn at low µg/L concentrations was examined by analysis of two sets of MMT standards prepared between 0.66 and 16.5 µg/L in hexane (20-500 µL diluted to 5 mL), where one set contained organic Mn free ULG at a l/l00 dilution. The instrument precision was also determined for CMT and MMT solutions prepared at 1.65 mg/L in hexane. The quantification of MMT in fuel additives was performed by an initial l/l67 dilution (30 µL diluted to 5 mL) of the products in organic Mn free ULG, which was the median of the manufacturers' recommended dilution ranges. These samples were then serially diluted in hexane by the same ratio of 1/167. The amount of ULG in the hexane was therefore 1/167 while the gasoline additive formulations had been diluted by 1/27778. To quantify these samples two sets of MMT external standards were prepared in hexane between 0.33 and 3.30 mg/L (10-100 µL diluted to 5 mL). To one set organic Mn free ULG was added to provide a l/l67 dilution of ULG in each standard.

## RESULTS AND DISCUSSION

A major advantage of using the AED for organometallics analyses is its high selectivity and sensitivity. Therefore sample preparation can be kept to a minimum. This is preferable to using analyte from matrix separation procedures as often these result in the inability to obtain satisfactory and consistent recovery of the analyte. Thus a clean-up step in an analytical procedure generally contributes the greatest uncertainty to the quantitative determination. Where sample preparation is kept to a minimum it is important that matrix effects are well characterised for reliable quantitative analysis by GC-AED. The addition of various hydrocarbons (such as ULG) to hexane was found to produce a systematic positive bias on the response of the AED to Mn in comparison to standards prepared in hexane alone (Table 1). This feature of the AED assists trace level analysis of organometallics in complex hydrocarbon matrices. The limit of detection (LOD, 4 times noise) for MMT was improved by a factor of 5 when ULG was present in hexane compared to that obtained when in hexane alone. However, the response was dependent on the composition of the hydrocarbon matrix and was also analyte concentration dependent, such that the lower the analyte concentration, the greater the matrix effects were on the response. A degradation of linear response for Mn due to addition of oxygenates (eg MTBE, MIBK) and ULG was observed in the concentration ranges examined. A significant instrument bias was observed with these background hydrocarbons as shown by a more linear correlation coefficient for n=5 than n=6 which includes a zero point (Table 1).

Zeng et al. (1992) have reported that the AED response for Mn was found to increase by a factor of 1000 when the helium make-up flow rate was increased from 200 to 325 mL/min. This was also found in this study, however the increase in sensitivity may come at the expense of a degraded linear dynamic range. They have reported that at a plasma flow rate of 325 mL/min a linear range of at least two orders of magnitude was achievable for Mn analysis by AED using a recipe similar to this work that detected Mn emission in the 260 nm region. However, linearity could not be repeated in this study, especially when Mn was in the presence of a petroleum hydrocarbon background in hexane. Addition of ULG to hexane over the range 1/100 to 1/500 produced little difference in Mn response which indicated that the amount of hydrocarbon background was not as important as the composition of the background for accurate trace quantification by AED.

**Table 1.** Relative normalised peak area response (each response/ ULG response) for a low mg/L MMT concentration range with various hydrocarbon backgrounds.

| MMT (mg/L) | Hexane alone response | Hexane with 1/500 MTBE response | Hexane with 1/500 MIBK response | Hexane with 1/500 ULG response |
|---|---|---|---|---|
| 0.33 | 0.25 | 0.80 | 0.82 | 1.00 |
| 0.66 | 0.46 | 0.88 | 0.92 | 1.00 |
| 0.99 | 0.61 | 0.91 | 0.94 | 1.00 |
| 1.32 | 0.69 | 0.93 | 0.97 | 1.00 |
| 1.65 | 0.79 | 0.98 | 1.00 | 1.00 |
| mean | 0.60 | 0.91 | 0.94 | 1.00 |
| $r^2$ (n=6) | 0.9952 | 0.9320 | 0.9330 | 0.8738 |
| $r^2$ (n=5) | 0.9923 | 0.9773 | 0.9735 | 0.9541 |
| LOD (µg/L) | 0.5 | | | 0.1 |

Quantification of organic Mn was possible at very trace levels by GC-AED but matrix effects had to be taken into account for reliable results. The AED response to Mn tended to be polynomial when background hydrocarbons were added to the hexane solutions. For low µg/L MMT standards between 0.66 and 16.5 µg/L, the response was still polynomial over this range but was reasonably linear up to 3.3 µg/L. Between 0.66 and 16.5 µg/L, the response of the MMT standards with a ULG background was 10 times greater than for those prepared in hexane alone. Thus a MMT standard at 3.3 µg/L was observed to have a response 10 times greater when a ULG background was present, while at 330 µg/L the response was 4 times greater with a ULG background than when in hexane alone (Table 1). Hexane blanks containing 1/500 ULG, MTBE and MIBK were each found to contain less than 0.5 µg/L MMT.

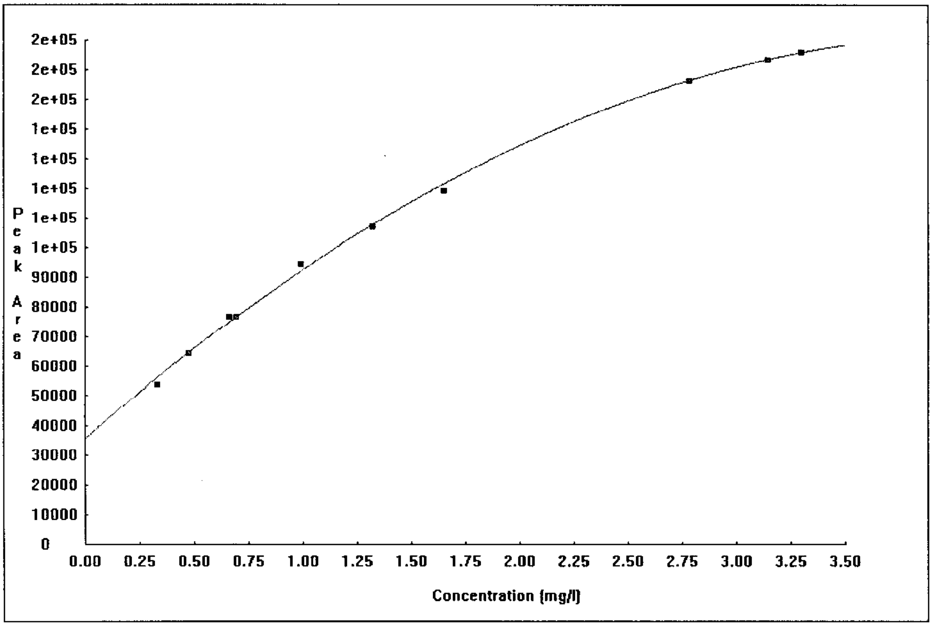

**Figure 1.** AED calibration curve for the determination of MMT concentrations in gasoline additives using MMT standards prepared with an equivalent petroleum hydrocarbon background to the samples.

The instrument precision was much better for the low µg!L standards when in the presence of a ULG background (Table 2). However, at low mg/L organomanganese concentrations, the presence or absence of a hydrocarbon background in the sample affected the instrument precision much less than for the analysis of low µg/L concentrations. For MMT at 1.65 mg/L, prepared in hexane alone, the instrument precision (n=10, from peak area) gave a coefficient of variation (CV) of 2.5%. A MMT standard at 1.65 mg/L with a 1/100 ULG background in hexane gave a CV of 2.3% (n=8). A 1.65 mg/L CMT standard in hexane alone produced a CV of 1.4% (n=lO).

**Table 2.** Instrument precision (as *CV)* for MMT by AED at low µg/L concentrations with and without a ULG background in hexane (n=7).

| MMT (µg/L) | Hexane alone | Hexane with 1/100 ULG background |
|---|---|---|
| 0.66 | 50.1% | 3.9% |
| 3.30 | 17.4% | 2.6% |
| 16.50 | 3.8% | 1.3% |

Quantification of MMT in the octane booster additive concentrates using both sets of standards is shown in Table 3. The amounts are corrected for the stated purity of the MMT standard as 97% minimum. The most reliable determination was achieved using standards prepared in an equivalent hydrocarbon background to the samples. Standards prepared in hexane alone produced a sample quantification error of 20-30% above that obtained from standards prepared in hexane with ULG. A non-linear response required that the samples were fitted to a first order polynomial expression obtained from the standard curve (Fig. 1). Reasons for non-linear and variable response by the AED are presented by Janák et al. (1994, 1995). Factors such as changes in element residence time in the plasma, variations in the excitation efficiency, and incomplete decomposition of solutes affect AED response. Reactions of excited elements with the wall of the plasma discharge tube can affect peak shape and response.

**Table 3.** Quantification of MMT in gasoline additive formulation concentrates using standards prepared with and without an equivalent hydrocarbon background.

| Sample | MMT (g/L) from standards prepared in hexane alone | MMT (g/L) from standards prepared in hexane with a 1/167 ULG background |
|---|---|---|
| 1 | 99 | 80 |
| 2 | 111 | 90 |
| 3 | 29 | 20 |

Zeng et al. (1992) analysed a sample of Canadian Shell gasoline by GC-AED and report that the sample contained approximately 200 mg/L of Mn as MMT in addition to several other Mn-containing species. Their published chromatogram for MMT in gasoline is virtually identical to those produced in this study (Fig. 2) which identified five organic Mn species in the commercially available petrol additives. They report a LOD for Mn of 0.1 pg on-column using a similar AED recipe, equivalent to the LOD found in this study. They filtered and diluted the gasoline 1:1 with toluene but do not describe a calibration procedure to account for matrix effects. In contrast to their finding, the maximum allowable application of MMT to Canadian gasoline is 72 mg MMT/L (Egyed and Wood 1996).

Based on the concentrations of MMT determined in additive concentrates 1, 2 and 3 (and their specified dilution in gasoline) 455, 353 and 108 mg MMT/L of gasoline is recommended respectively for each product. It is expected that the high application amounts specified for samples 1 and 2 is because they are marketed as additives for automobile racing. A diminishing octane return would apply however after addition of about 100 mg MMT/L of fuel. Fig. 3 shows the 1/167 diluted ULG carbon background in the 1/27778 diluted MMT additive sample 1 (Fig. 2).

Manganese response on the AED could be confirmed by the presence of the characteristic emission triplet at 257.6, 259.4 and 260.6 nm (Fig. 4). This "snapshot" shows emission spectra obtained from cymantrene. The emission spectra obtained from MMT produced the same characteristic Mn lines. Background subtracted emission from carbon at 247.9 nm is also shown in the 40 nm "snapshot" window.

*Abbreviations for key words*:
GC-AED = gas chromatograph - atomic emission detector, ULG = unleaded gasoline,
MMT = methylcyclopentadienyl manganese tricarbonyl, MTBE = methyl tertiary butyl ether
CMT = cyclopentadienyl manganese tricarbonyl (cymantrene), MIBK = methyl isobutyl ketone.,
TEL = tetraethyl lead, LOD = limit of detection

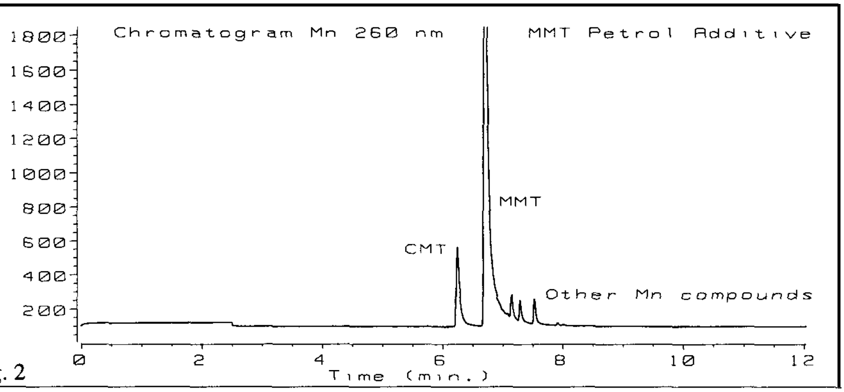

Fig. 2

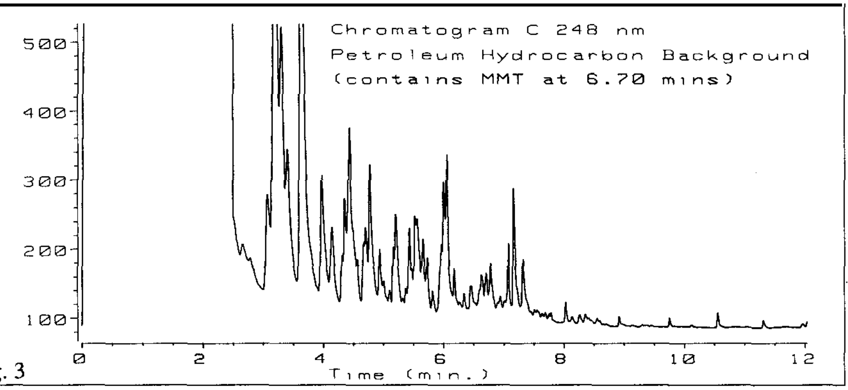

Fig. 3

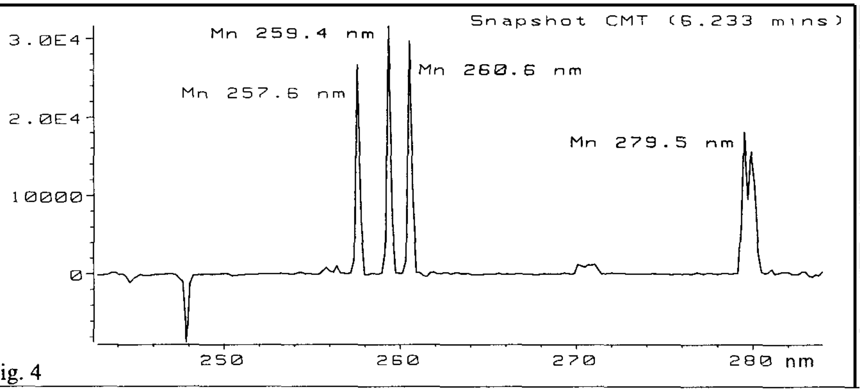

Fig. 4

**Figure 2.** (top) GC-AED Mn 260 nm chromatogram of organomanganese species present in a petrol additive concentrate. **Figure 3.** (middle) Carbon 248 nm response from ULG background in the same sample. **Figure 4.** (bottom) AED "snapshot" of cymantrene (CMT) showing the characteristic emission spectra for Manganese.

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