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# Determination of (methylcyclopentadienyl)manganesetricarbonyl in gasoline by capillary gas chromatography with alternating current plasma emission detection

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## Abstract

(Methylcyclopentadienyl)manganesetricarbonyl (MMT) commonly used as an antiknock agent in gasoline is determined by capillary gas chromatography with an alternating current plasma (ACP) detector. The ACP selectivity, the ratio of the peak area response of MMT per gram Mn to the peak area response for a hydrocarbon per gram of carbon, was found to exceed five orders of magnitude. Detection limits for MMT and a closely related organomanganese analyte, bis(pentamethylcyclopentadienyl)manganese (BPM), were calculated to be 62 and 69 pg/s (as Mn), respectively. Precision of the methodology was 6.6% relative standard deviation ( $n = 10$ ) for both MMT and BPM.

## 1. Introduction

(Methylcyclopentadienyl)manganesetricarbonyl (MMT),  $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$  and chemically similar compounds are currently used as substitutes for tetraethyllead to improve the octane rating of unleaded gasoline [1,2]. MMT is also used in aircraft fuels and in the production of heating oil to reduce flue-gas smoke [3]. Build up of  $\text{Mn}_3\text{O}_4$  deposits may also decrease the efficiency of catalytic converters. Although 1 g of Mn as MMT is as effective in improving octane rating as 3.22 g of Pb as tetraethyllead [4], atmospheric manganese emissions are unfavor-

able and may offer a potential health risk. Levels above 5  $\mu\text{g Mn/l}$  have been reported to lead to chronic manganese poisoning and manganese-induced pneumonia [5].

Because of the underlying toxicological properties of MMT and other closely related compounds, sensitive chromatographic detectors have been employed. One common method for the determination of MMT and other gasoline additives has been to interface various element-selective detectors with gas chromatography (GC). Uden et al. [6] reported a detection limit for MMT of 3 ng Mn by utilizing a direct GC interface to a d.c. plasma emission detector. Aue et al. [7] used a commercially available flame photometric detector resulting in the determi-

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nation of MMT at the 0.6 ppm (w/w) level in gasoline. With a hydrogen atmosphere flame ionization detector, Dupuis and Hill [4] reported a MMT detection limit of  $1.7 \cdot 10^{-14}$  g/s. Coe et al. [8] were able to analyze MMT in air samples from underground parking garages achieving detection of 0.05 ng MMT  $m^{-3}$ . Atmospheric pressure microwave plasma detection has also been utilized for the determination of MMT [9]. Other approaches that have been investigated in the analysis of MMT include atomic absorption spectroscopy (AAS) with a nitrous oxide–hydrogen flame [10], AAS with a heated vapor technique [11], carbon-filament AAS [3], neutron activation analysis, spark source mass spectrometry and X-ray fluorescence [12], and GC with flame ionization detection [13].

In this report an alternating current plasma (ACP) detector developed in our laboratory [14–18] is described for the selective determination of MMT in gasoline. A gas chromatograph is interfaced with an ACP detector through a quartz discharge tube which encloses a helium-sustained plasma. Observation of the optical emission spectrum resulting from the fragmentation and excitation of the organomanganese species entering the plasma affords sensitive, elemental-selective detection. A further advantage offered by the present design is the capability to view light emitted from the plasma axially with an appropriate light-collecting lens. With the earlier work in which the helium plasma was viewed transversely through the walls of the discharge tube, deposition of materials on the walls of the discharge tube and devitrification of the quartz resulted in gradual attenuation of detector response with time.

## 2. Experimental

### 2.1. Materials

Stock solutions of MMT and bis(pentamethylcyclopentadienyl)manganese (BPM) (Strem Chemical, Newburyport, MA, USA) were prepared by dissolving the appropriate amount of the analyte in acetone and subsequent

standard solutions were prepared by serial dilution of the stock solution. The selectivity response mixture contained *n*-dodecane (Aldrich, Milwaukee, WI, USA) and MMT in acetone. Gasoline samples obtained locally were stored in amber bottles until needed. Gasoline samples were diluted 1 to 10 with acetone prior to GC in order to avoid saturation of the detector with hydrocarbons.

### 2.2. Instrumentation

The GC–ACP detector system has been described in detail elsewhere [14,18] and its experimental arrangement is illustrated in Fig. 1. Table 1 lists the components, model/type, manufacturer and the corresponding optimum operating conditions used throughout the study, unless otherwise noted. A megabore fused-silica capillary column employed for the entire study was a HP-1 30 m  $\times$  0.530  $\mu$ m I.D. column with a film thickness of 0.25  $\mu$ m (Hewlett-Packard, Avondale, PA, USA). The detector interface employed featured the megabore capillary column as the interface tube which extended from the GC oven, through a heated column jacket, into the ACP detector. The column jacket was clamped to a mount on the optical bench to

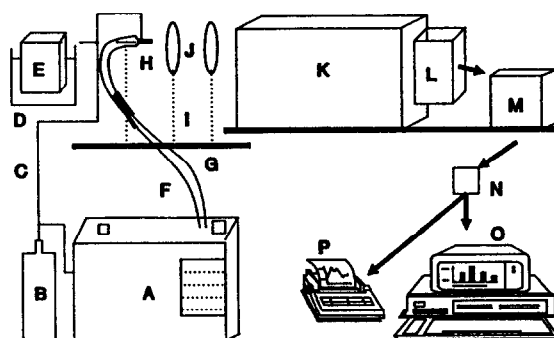


Fig. 1. Schematic representation of the GC–ACP detector instrumentation. A = Gas chromatograph; B = helium make gas; C = helium gas conduit; D = transformer water cooling jacket; E = transformer; F = GC–ACP detector interface column jacket (flexible tubing); G = optical bench; H = discharge tube; I = optical mount; J = focusing lens; K = monochromator; L = photomultiplier tube; M = picoammeter; N = resistor/capacitor low pass filter; O = data acquisition system; P = integrator.

Table 1  
Components and operating conditions for GC-ACP detector

Components	Model/manufacturer	Experimental conditions
Gas chromatograph	Hewlett-Packard 5890A	Injector temperature: 160°C, interface temperature: 170°C, linear velocity: 30 cm/s, split ratio 10:1
ACP Power supply	Webster ignition transformer, Sta-Rite, Frankfort, KY, USA	Output: 285 W; 14 000 V, 23 mA
Monochromator	EU-700, 0.35 m; McPherson, Acton, MA, USA	Slit width: 30 $\mu$ m, slit height: 5 mm
Photomultiplier tube (PMT)	R758, Hamamatsu Co., Middlesex, NJ, USA	Voltage: -1000 V d.c.
PMT Power supply	Model 7640, McPherson, Acton, MA, USA	
Picoammeter	414-S, Keithley Instruments, Cleveland, OH, USA	$3.0 \cdot 10^{-6}$ – $10 \cdot 10^{-6}$ A
Focusing lens	Fused silica, Plano convex, Oriol Corp., Stratford, CT, USA	25.4 mm dia., 150 mm f.l.
Discharge tube	Laboratory constructed	End-on configuration, 2 cm $\times$ 1 mm I.D. $\times$ 6 mm O.D.
Data acquisition Software	LabCalc, Galactic Industries, Salem, NH, USA	5 Hz
Computer	IBM-AT Compatible	
Resistor/capacitor low pass filter	Laboratory constructed	Time constant: 0.2 s

permit easy alignment and also to prevent any possible shift in optical alignment due to vibration. The capillary column was inserted through the center of one of the electrodes. Approximately 0.5 cm of the capillary column extended into the 2 cm  $\times$  6 mm O.D.  $\times$  1 mm I.D. quartz discharge tube which contains the plasma. The polyimide coating from this 0.5 cm segment was removed prior to insertion. In this arrangement, the column effluent was introduced directly into the plasma plume, minimizing band broadening.

The plasma was viewed in an axial position and focused on the entrance slit of the monochromator by means of two serial fused-silica biconvex lenses (25.4 mm diameter, 150 mm focal length). The output of the picoammeter was electrically filtered (time constant 0.2 s) and collected by the data acquisition system at a sampling rate of 5 Hz.

The total helium flow-rate through the discharge tube (column flow-rate plus plasma sup-

port flow-rate of helium) was adjusted slightly higher than the optimum value. The plasma was initiated by momentarily inserting the tip of a small diameter piece of copper wire, which acted as the second electrode, a few millimeters into the end of the discharge tube. After 2 min this combined helium flow-rate was readjusted to the optimum flow-rate of 1800 ml/min. The ACP detector was allowed to equilibrate after ignition for approximately 5 min to ensure stable, reproducible behavior.

### 3. Results and discussion

The analytical emission lines of manganese were focused on the monochromator by two methods. First, an ultrasonic nebulizer (a common room humidifier) was used to generate a headspace vapor of MMT which was transported to the ACP by helium flow. This procedure

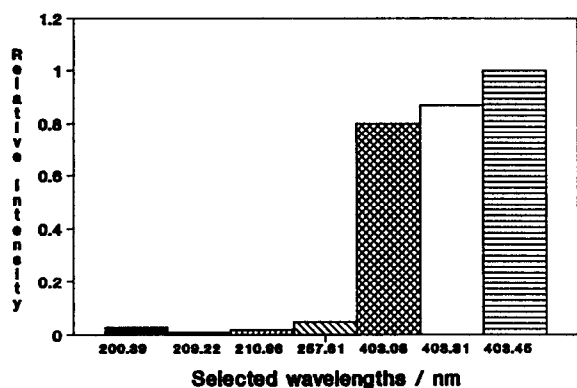


Fig. 2. Relative intensities of prominent Mn emission lines.

provided a constant mass introduction of manganese vapor into the plasma and the corresponding emission wavelengths of manganese were observed, as illustrated in Fig. 2. The 403.45-nm line was selected as the analytical

wavelength for this study because of its favorable relative intensity and location with respect to the background emission spectrum where no interference from OH, N<sub>2</sub>, NH, He and O is observed. Secondly, a manganese hollow-cathode lamp, typically employed in AAS, was employed to confirm the analytical emission line (403.45 nm) by positioning the lamp such that its emission lines were incident on the entrance slit of the monochromator. The carbon backbone of MMT was eliminated as the source of molecular emission in this spectral region because a scan of *n*-dodecane vapor in the ACP did not produce any major emission bands.

The ACP emission response at 403.45 nm resulting from a 0.5- $\mu$ l injection of a standard solution of MMT in acetone solution (230 ng/ $\mu$ l) at a column temperature of 130°C is shown in Fig. 3A. On the other hand, BPM proved to be rather air-sensitive. When standard solutions of

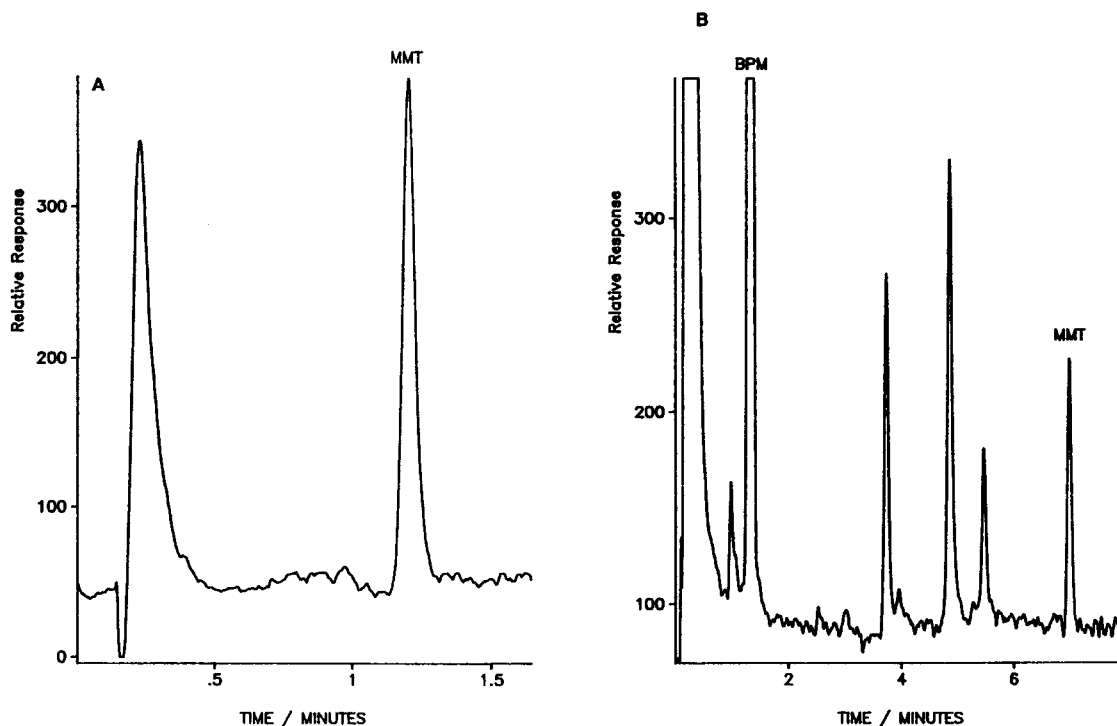


Fig. 3. (A) Isothermal separation at 130°C with ACP detector system of a standard solution of MMT in acetone; MMT peak corresponds to 1.15 ng Mn. (B) Temperature-programmed separation of BPM solution in acetone; conditions: 50°C (1 min) to 130°C at 10°C/min.

BPM were prepared in acetone, the formation of a brown flocculent precipitate was noted and suggestive of degradation. Fig. 3B illustrates a temperature-programmed separation of a acetone solution of BPM and its organomanganese degradation products which interestingly include MMT. In the chromatograms the pronounced negative response immediately after injection is associated with perturbation in the plasma due to the passage of a large volume of solvent through the plasma. The ACP detector can tolerate large volumes of eluted solvent without extinguishing and, thus, requires no venting valve, important advantages which suggest that an ACP detector can also be employed with packed GC columns.

### 3.1. Linearity and detection limits

A calibration plot of MMT and BPM for the ACP detector was constructed for the determination of the linear dynamic range, linearity and detection limits by making repetitive injections of known amounts of analyte into the GC-ACP system. The linear dynamic range for MMT and BPM extended over 3.5 orders of magnitude. Correlation coefficients of the log-log plots were found to be 0.9999 for both MMT and BPM. The detection limits of MMT and BPM were estimated based on integrated baseline noise [19,20]. Detection limit may be defined as the amount of analyte needed to produce a signal that is three times the standard deviation of the baseline noise divided by the sensitivity whereas sensitivity is defined as the slope of the calibration plot [21,22] multiplied by the peak-width at half height of the analyte peak to account for  $k'$  [23]. The detection limit was calculated to be 62 and 69 pg/s (as Mn) for MMT and BPM, respectively. The precision in response at twice the detection limit was under 6.6% relative standard deviation ( $n = 10$ ) for MMT. The detection limit of BPM should be viewed cautiously in lieu of the inherent instability of BPM.

### 3.2. Selectivity

A mixture containing MMT and *n*-dodecane in acetone was used to establish the detector selec-

tivity for MMT at a slit width of 30  $\mu\text{m}$ . The selectivity can be defined as the ratio of the peak area response of the ACP detector toward MMT at 403.45 nm per gram of elemental manganese to the response of the detector to *n*-dodecane per gram of carbon. The selectivity toward manganese was then established by means of a response mixture that contained 1150 ng/ $\mu\text{l}$  of *n*-dodecane as internal standard and 1.74 ng/ $\mu\text{l}$  of MMT. A 0.2- $\mu\text{l}$  aliquot was injected using a split ratio of 10:1 and a column temperature of 130°C, after which the responses at 403.45 nm of the hydrocarbon probe and MMT were compared. The average selectivity ratio for MMT resulting from a series of ten injections was  $5.2 \cdot 10^5$ . The ACP selectivity obtained in this study for MMT compares favorably with selectivity obtained by GC-flame photometric detection [7], even in the absence of background correction.

### 3.3. Analytical applications

Two applications were performed in order to demonstrate the selectivity of the ACP detection towards MMT in gasoline which represents a potentially interfering matrix. Old commercial regular unleaded gasoline containing no detectable amount of MMT was diluted one to ten with acetone. A 400- $\mu\text{l}$  portion of this diluted gasoline sample was then spiked with a 200- $\mu\text{l}$  aliquot of a solution containing 92  $\mu\text{g}$  MMT and 142  $\mu\text{g}$  BPM; a 0.2- $\mu\text{l}$  volume of the resulting solution was injected into the chromatographic system. Several illustrative chromatograms appear in Fig. 4 which depict the ACP selectivity. Fig. 4A and B show chromatograms with ACP detection at 403.45 nm of unspiked and spiked regular grade unleaded gasoline, respectively, whereas a parallel chromatogram with flame ionization detection is displayed in Fig. 4C. The rapid coelution of many hydrocarbons is responsible for the irregular appearance at the beginning of the chromatogram in Fig. 4A, resulting in plasma instability and carbon background emission [15–18]. Commercial fuel samples were purchased locally and analyzed for MMT content; these results are presented in Table 2. The

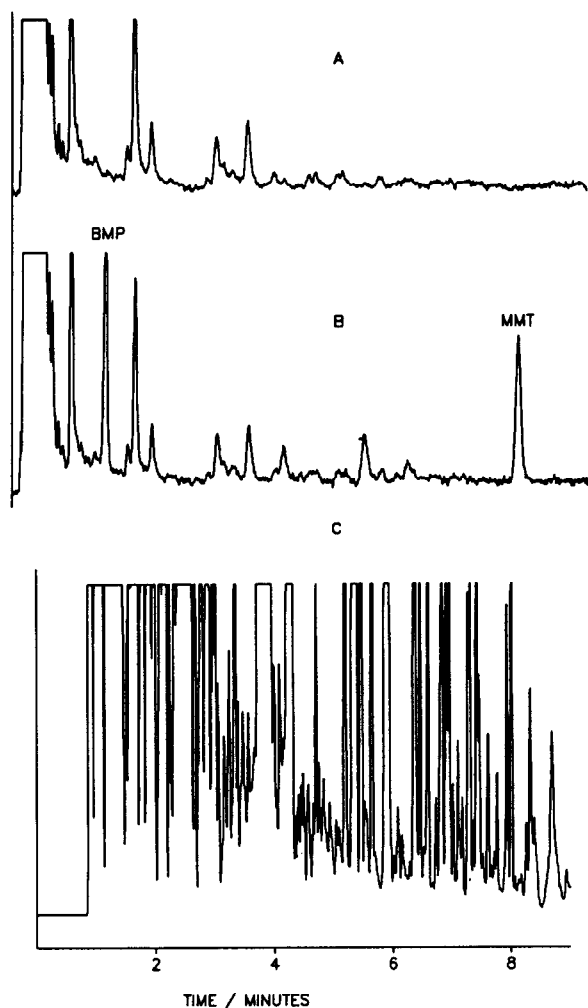


Fig. 4. (A) Chromatogram of unspiked old regular gasoline with ACP detection at 403.45 nm; (B) chromatogram of same gasoline spiked with MMT and BPM with ACP detection; (C) parallel flame ionization detection chromatogram of same sample as in (B); conditions: 30°C (1 min) to 130°C at 10°C/min.

MMT levels in the examined samples ranged from 9.74 to 16.9  $\mu\text{g}/\text{ml}$  and compare favorably with the value of 7  $\mu\text{g}$  MMT/ml in premium unleaded gasoline reported in a recent study [7].

#### 4. Conclusions

The system described here provides a versatile element-selective detector for the determination

Table 2  
Measured level of MMT in fuels

Fuel	$\mu\text{g}/\text{ml}$
Premium unleaded gasoline	9.73 (1.9) <sup>a</sup>
Regular unleaded gasoline	16.9 (2.3)
No. 2 Fuel Oil	16.4 (0.9)

<sup>a</sup> Values in parentheses represent average relative standard deviation of five replicate injections for six samples of each type of fuel obtained locally.

of organomanganese additives in gasolines. Although the commercial GC–atomic emission spectroscopy system offers a more favorable organomanganese detection limit of 1.6 pg/s [24], the detector described here is easily assembled and interfaced with chromatographic equipment at moderate cost. The ACP detector exhibits a remarkably stable signal because the plasma is self-seeding, reigniting itself every half cycle which is 120 times per second for the 60-Hz power supply. A tesla coil is not required to commence operation of the plasma if the a.c. voltage is greater than the breakdown voltage. As a result, the ACP can tolerate high mass of solvent without extinguishing and, thus, requires no venting valve which lends itself to a less complex interface design and minimizes band broadening. The inclusion of signal-to-noise enhancement devices such as background correction components and more elaborate signal filtering could greatly improve the performance of the detector.

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