Analysis of Gasoline for Antiknock Agents with a Hydrogen Atmosphere Flame Ionization Detector

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A hydrogen atmosphere flame ionization detector (HAFID), modified from a commercial FID, is demonstrated as a selective gas chromatographic detector for the determination of antiknock agents in gasoline. By a simple one to ten dilution of a leaded gasoline, alkyllead compounds were detected with no interference from overlapping chromatographic peaks of hydrocarbons. The two samples analyzed in this study contained 1.22 and 0.38 g/gal Pb as tetraethyllead (TEL). Similarly, methylcyclopentadienylmanganese tricarbonyl (MMT), corresponding to 6 mg/gal of Mn, could be easily detected in an unleaded gasoline sample. Detection limits were calculated to be 7.2×10^{-12} g/s of Pb and 1.7×10^{-14} g/s of Mn. Optimal operating conditions are discussed.

The hydrogen atmosphere flame ionization detector (HAFID) introduced in 1972 (1) and subsequently developed through 1976 (2-5) is a sensitive and selective gas chromatographic detector for organometallic compounds. Minimum detectable amounts for certain metal containing compounds extend to the low picogram and sub-picogram range with selectivities of 10^4 and 10^5 when compared to n-hydrocarbon responses.

Its basic design can be compared to a standard flame ionization detector modified so that oxygen enriched air is premixed with the column effluents and introduced through the jet tip while hydrogen doped with small amounts of silane is introduced directly into the detector housing so that the flame burns in a hydrogen atmosphere. For optimal response, the collecting electrode is positioned 5 to 7 cm from the flame compared to only 0.5 cm for the FID collector. Response mechanisms remain unclear but it is believed that the enhancement of organometallic response rests with a charge transfer process between the ions responsible for the flame background current and the organometallics or their combustion products to form a stable ionic species that is capable of being efficiently collected several centimeters from the flame (4).

Because of the HAFID's simple design and the high sensitivity and selectivity to organometallic compounds, it appears ideal for routine determination of volatile antiknock agents in gasolines by gas chromatography.

Alkylleads and MMT are the most common antiknock agents. TEL has been used commercially since 1920 but in recent years lead concentration in gasolines has been restricted because of environmental concerns. Since the passage of the Clean Air Act in 1970, maximum allowable lead concentrations in gasolines have dropped continually from 2.5 g/gal in 1970, to 2 g/gal in 1974, to 1.25 g/gal in 1977, 0.8 g/gal in 1978 with a new goal of 0.5 g/gal by October 1979 (6). As the use of lead was restricted, other organometallics were substituted. The most successful of these substitutes is MMT (7). One gram of Mn as MMT is as effective in improving octane rating as 3.22 grams of Pb as TEL. MMT has been used as the antiknock agent in many unleaded gasolines but since low levels of manganese in the atmosphere may lead to chronic manganese poisoning and since buildup of Mn_3O_4 deposits may decrease efficiency of catalytic converters, it has recently been banned. It is still added to some leaded gasolines and is also used as a fuel oil additive. Wherever this antiknock agent is allowed, sensitive analytical methods will be necessary to routinely monitor and ensure compliance with legal concentration limits.

One common method for the determination of antiknock agents has been to couple various spectroscopic units with a gas chromatograph. Coker (8) reported a gas chromatography/atomic absorption spectrometry technique for alkylleads in which he could analyze a sample in 5 min with a detection limit of 0.2 ppm lead, a value, he points out, suitable for determining trace lead in unleaded gasoline. Uden et al. (9) recently reported a technique for MMT with a detection limit of 3 ng of Mn utilizing a direct GC interface to an argon plasma emission detector. Alkyllead has recently been determined in the atmosphere with a GC-microwave plasma detector by Reamer et al. (10).

Other GC detection methods that have been investigated for alkyllead analysis include several electron capture procedures (11-13), a flame ionization method which requires a complicated separation and derivation step (14), and a dithiozone spectrophotometric technique (15, 16).

Potential of the HAFID for use as an antiknock detector has been pointed out by Hill and Aue. Their detector had a selectivity for tetraethyllead over dodecane of 10^4 with an MDA of 51 pg TEL injected (4). They showed a chromatogram where a peak for TEL could be easily detected in an injection of gasoline diluted 1 to 100 in hexane (5). MMT response has never been characterized in the HAFID.

The purpose of this study is to construct an optimized HAFID from a FID design different from any previously reported, to compare detection limits, response selectivity, and calibration curves for tetraethyllead with those obtained in earlier work, to report response characteristics of MMT, and to demonstrate the HAFID as a selective detector for antiknock agents in gasoline.

EXPERIMENTAL

HAFID Design. The HAFID constructed for this work was a modification, similar in design to the HAFID reported in ref. 4, of one of the FID units from a Hewlett-Packard dual FID system (Model 18812A). In this design, illustrated in Figure 1, the base of the original FID was unmodified but the FID electrode and mounting were substituted with a stainless steel cap containing a collecting electrode and an ignitor. The collector, the terminal pin of a coaxial bulkhead fitting, screwed into the stainless steel cap so that the pin was 53 mm above the jet tip. The original jet tip (0.5-mm i.d.) was bored to an internal diameter of 1.5 mm. Two 1.5-V Ray-O-Vac 900 Hobby batteries provided the current to a KB-15 glow plug for detector ignition. Ions were collected with a -90 V potential supplied from an Eveready no. 490 battery placed between the pin electrode and a Keithley Model 417 picoammeter. After amplification, the signal could be recorded directly with a Sargent-Welch Model XKR strip chart recorder or channeled via a Hewlett-Packard Model 18871A A/D converter for print out and peak integration with a Hewlett-Packard 18850A terminal. The final modification was to interchange the air and hydrogen lines from normal FID operation.

Detector Conditions. *HAFID.* Detector temperature was maintained at 250 °C. The total hydrogen gas flow was held constant at 1600 mL/min and for optimal response was doped
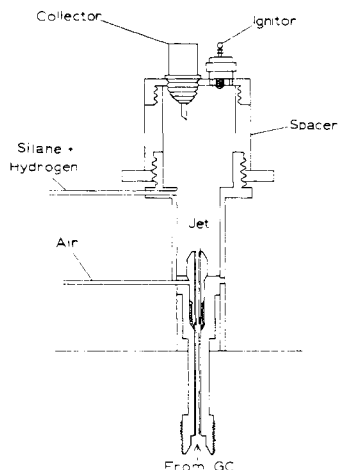
Figure 1. HAFID modified from a Hewlett-Packard FID. Air enriched with O_2 is passed down the outside of the jet through an orifice not pictured above and mixes with the GC effluent at the column exit

with 34 ppm of silane by mixing proper proportions of pure hydrogen (Airco Specialty Gases, Santa Cruz, Calif.) and hydrogen doped with 100 ppm silane (Airco Specialty Gases, Santa Cruz, Calif.). Air, 120 mL/min, was enriched with 150 mL/min of oxygen before entering the jet tip.

FID. Detector temperature was maintained at the same temperature as the HAFID. Flow rates used were those recommended by the manufacturer: Hydrogen, 30 mL/min and air, 240 mL/min.

Standards and Samples. TEL (ICN Pharmaceuticals, Inc., Plainview, N.Y.) was diluted in hexane to produce standard solutions at concentrations of 10 μg/μL, 1 μg/μL, 100 ng/μL, 10 ng/μL, and 1 ng/μL. Each concentration was sealed in a 25-mL screw cap glass sample tube with an aluminum foil liner and stored at 5 °C. They were warmed to room temperature before use. TEL was the only alkyllead standard available for use in this study. Peaks for tetramethyllead (Me$_4$Pb), trimethylethyllead (Me$_3$EtPb), dimethyldiethyllead (Me$_2$Et$_2$Pb), and triethylmethyllead (Et$_3$MePb) were identified from retention patterns reported in earlier work (8, 11, 16).

MMT (Alfa Division, Ventron Corp., Danvers, Mass.) standards were diluted in iso-octane to concentrations decreasing by a factor of 10. The concentrations ranged from 10 μg/μL to 10 pg/μL. Because MMT undergoes light induced decomposition, standards were kept in brown bottles and were prepared fresh each day. Dodecane was used to characterize the HAFID response to hydrocarbons for determination of detector selectivity. A solution of 500 ng/μL was prepared in hexane.

Gasoline samples were collected in brown glass bottles from local service stations, transferred to the laboratory, and analyzed as soon as possible.

Chromatographic Conditions. *General.* A Hewlett-Packard 5830A gas chromatograph with dual FID detection (one modified to HAFID) was used throughout this study. The column, 6 ft × $^1/_4$ in. o.d. (2-mm i.d.) borosilicate packed with 80/100 mesh Ultra-Bond 20 M (RFR Corp., Hope, R.I.), was interchanged between detectors. The injection port temperature of 225 °C and the carrier gas flow of 20 mL/min of helium remained the same throughout the study.

Silane Optimization. Injection of 1 ng MMT and 5 ng TEL was repeated as the silane mixing ratio with hydrogen was varied from 5 to 60 ppm. The total hydrogen flow was held constant at 1600 mL/min. Column temperature for MMT was 140 °C and for TEL was 90 °C.

Calibration Curves. Under optimal silane doping conditions of 34 ppm, calibration curves were obtained from TEL and MMT standards with the same isothermal column conditions used for silane optimization. Selectivities of these compounds were calculated by comparing the 5 ng TEL response and the 25 pg MMT response to that response obtained for 500 ng of dodecane.

Sample Analysis. Gasoline samples analyzed for alkylleads were diluted 1 to 10 with hexane in order not to saturate the detector with lead. The analysis was accomplished by injecting
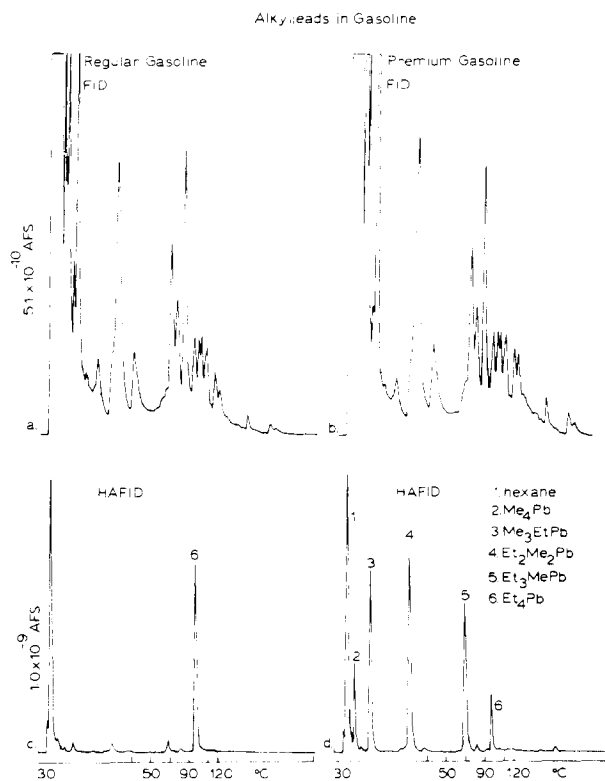
Figure 2. HAFID and FID analysis of alkylleads in gasoline. (a) FID tracing of a regular grade gasoline. (b) FID tracing of a premium grade gasoline. (c) HAFID tracing of a regular grade gasoline. (d) HAFID tracing of a premium grade gasoline. Chromatographic conditions: He (carrier gas) = 20 mL/min, injection temperature = 225 °C, temperature program: 30 °C for 5 min, 20 °C/min, 120 °C for 5 min. Column = 6 ft × $^1/_4$ in. o.d. (2-mm i.d.) borosilicate packed with 80/100 mesh Ultra-bond 20 M. Detector conditions: HAFID-H$_2$ = 1600 mL/min, SiH$_4$ = 34 ppm, O$_2$ = 150 mL/min, air = 120 mL/min, temp. = 250 °C. FID-H$_2$ = 30 mL/min, air = 240 mL/min, temp = 250 °C

0.5 μL of the diluted sample and temperature programming the column from 30 °C held for 5 min to 120 °C held for 5 min at a rate of 20 °C/min. MMT analysis was accomplished by injecting 0.25 μL of the gasoline directly into the column held isothermally at 140 °C. Both FID and HAFID detection methods were used for each sample under identical chromatographic conditions.
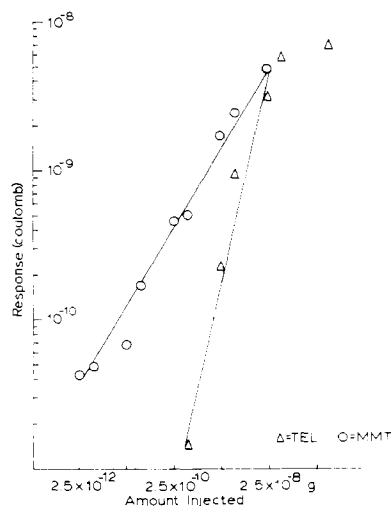
RESULTS AND DISCUSSION

Figure 2 demonstrates the effectiveness of the HAFID for analysis of gasolines for alkylleads with several illustrative chromatograms. Chromatograms a and b are respective FID tracings of a regular grade and a premium grade gasoline. The complexity of these chromatograms caused by the FID's sensitive response to numerous hydrocarbon components masks the alkyllead peaks and makes analysis impossible. Chromatograms c and d are HAFID tracings of the same samples under identical chromatographic conditions juxtaposed with the appropriate FID tracings. Alkyllead peaks contain little or no interference from hydrocarbons making them easily identified and quantified from standards.

Results for MMT were similar to those for alkylleads. Figure 3a shows MMT detection in a sample of unleaded gasoline while Figure 3b illustrates the difficulty of a FID analysis for the same sample and under the same chromatographic conditions. Figure 3c is a chromatogram obtained with the HAFID for a gasoline sample not containing MMT while Figure 3d is of a 25-pg MMT standard. Note that the retention time for the standard does not correspond with a detectable peak in the FID tracing.

The minimum detectable amount (MDA) of 30 pg obtained for tetraethyllead compares favorably with that of 51 pg reported earlier (4). The detector's minimum detectable limit
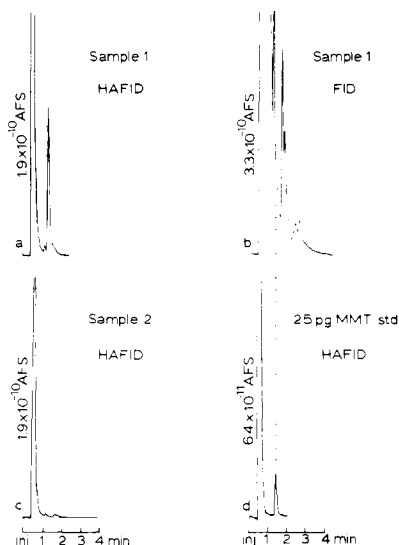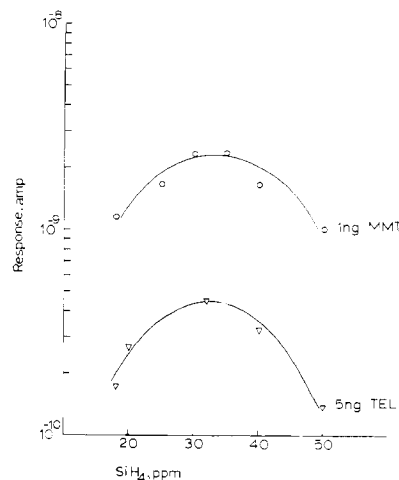
Figure 3. HAFID and FID analysis of MMT in gasoline. (a) HAFID tracing of a nonleaded gasoline containing MMT. (b) FID tracing of gasoline sample used in a. (c) HAFID tracing of nonleaded gasoline not containing MMT and (d) HAFID tracing of a 25-pg standard of MMT. Conditions are the same as in Figure 2 except column temperature was held constant at 140 °C

Figure 4. Calibration curves for MMT and TEL

Figure 5. Optimization of silane in hydrogen

Although calibration curves were linear on a log–log scale, their slope exceeded 1.0 indicating that the response was not a linear function of concentration. Specific geometrical design characteristics or thermal decomposition in the injection port may be a cause of nonlinear response, but further investigations are required before definite explanations can be proposed.

Construction of the HAFID on the H.P. 5830A was carefully patterned after an earlier model built on a Bendix 2500 (4), but three design characteristics were noticeably different. First, since both HAFIDs were constructed by modifying FIDs, internal diameters differed as dictated by original FID designs. The i.d. in the reaction zone of the HAFID on the H.P. instrument was 10 mm compared with 32 mm for the Bendix instrument. No experiments have been performed comparing internal diameter variations, and it is not clear what effects these changes have on response. Second, the platinum loop electrode was substituted with the terminal pin of an Amphenol, coaxial connector. Cursory comparisons of the pin head electrode and a platinum loop electrode indicate that electrode shape does not affect response.

The location at which hydrogen was introduced into the detector is the third and a most important design variation. In the model of this study (see Figure 1), hydrogen enters the detector 21 mm above the jet tip as a stream perpendicular to the exiting gases from the flame. In the detector on the Bendix unit, hydrogen was introduced beneath the jet through diffusers so that a laminar hydrogen flow passed by the flame. This difference is believed to be the primary reason the optimal silane doping concentration was significantly higher than in the earlier model. Figure 5 shows the response of 1 ng of MMT and 5 ng TEL as a function of the mixing ratio of silane in the hydrogen gas with an optimal value for both compounds of 34 ppm. The optimum in the earlier detector was 5 ppm and compares favorably with 7 ppm obtained for a newly constructed detector (not discussed in this paper) in which hydrogen is also introduced beneath the flame jet. When hydrogen is introduced below the flame, silane is transferred to the flame with the hydrogen flow; but when silane is introduced above the flame, it first contacts combustion products from the flame. The higher requirement for silane could then be attributed to reactions with H_2O, O_2, and other gases in the exhaust, reducing its effective concentration in the atmosphere.

As is obvious from this discussion, many questions are still unanswered concerning the mechanism of this enhanced metal ionization response. How is the doping gas transferred to the reaction zone? Why is the doping gas necessary? Do other doping agents exhibit similar effects? What is the ionic species

(MDL) for TEL was calculated to be 1.1×10^{-11} g/s or a MDL for Pb of 7.2×10^{-12} g/s. MMT produced a more sensitive response than TEL with a minimum detectable amount of 200 fg and a detection limit of 6.6×10^{-14} g/s for MMT or 1.7×10^{-14} g/s when calculated for Mn. Detection limits for Mn-containing compounds have not previously been reported for the HAFID. Selectivities, calculated for dodecane, were comparable to those reported for the earlier models (4).

Quantitative data could be interpolated easily from the calibration curves shown in Figure 4. All points, except one, fell within 10% of the standard curves. TEL was determined to be present at a concentration of 1.90 g/gal (1.22 g of Pb/gal) in the regular gasoline and at 0.60 g/gal (0.38 g of Pb/gal) in the premium sample. As expected, the amount of MMT found in the unleaded gasoline was considerably lower than TEL concentrations found in the leaded gasolines with a value of 24 mg/gal for MMT (6 mg/gal for Mn). These concentrations are about 10 times less than the maximum allowed (62.5 mg of Mn/gal). Since MMT decomposes readily, the Mn value obtained with this method accurately reflects the level of active antiknock agent but does not necessarily represent the total Mn concentration in the sample.

that is collected 53 mm from the flame? Is detector geometry of paramount importance? Yet, for practical analytical purposes, it is simple and inexpensive to modify virtually any commercial flame ionization detector to a dependable selective organometallic detector. Hydrogen doped with the appropriate amount of silane can be purchased from many of the gas supply houses. For routine operation, the only major disadvantage is the large volume of unburned hydrogen which requires an efficient hood system for venting the exiting gases. Hydrogen, however, is used in chromatography as a carrier gas and in the flame photometric detector as a detector gas. When compared to atomic absorption spectrometers and microwave emission detectors with their associated expense and respective flame flashback and high voltage hazards, the HAFID appears to be an attractive alternative for GC detection of organometallics and especially for the determination of antiknock agents in gasolines.

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Simultaneous Determination of Americium and Curium in Soil

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A method is presented for the routine determination of americium and curium in 10 g of soil. The soil is dissolved with a mixture of nitric acid and hydrofluoric acid. Insoluble sulfates and phosphates are metathesized with boiling sodium hydroxide solutions. Plutonium and iron are sorbed on anion-exchange resin from 9 M hydrochloric acid after which the plutonium can be eluted and further purified for electrodeposition. Americium and curium are purified by cation-exchange and liquid–liquid chromatography. Mean recoveries of americium and curium were 58% and 56%, respectively, for prepared soil samples. The minimum detectable activity for the individual nuclides is 0.002 pCi/g. For americium and curium activities of 0.1 to 1.0 pCi/g, the relative standard deviations for replicate analysis ranged from 3% to 8%. The deviations of the means from their known values were generally within ±3%.

The increasing demand to monitor α-emitting nuclides near nuclear facilities has led to the development of different methodology for analysis of environmental soil samples (*1–8*). In this study it was desired to develop a method to determine americium and curium in 10-g soil samples which could be combined with existing methodology to determine plutonium. Although solvent extraction techniques have been extensively used for the isolation and purification of the actinide elements (*3, 5, 6*), this method employs ion-exchange techniques as this laboratory's experience has shown that far less manpower is required to routinely process large quantities of samples by column chromatography. An additional consideration was a reluctance to use large quantities of volatile organic solvents whose use may be deemed potentially hazardous.

The 10-g soil samples are dissolved with nitric and hydrofluoric acids (*8*). The sodium hydroxide metathesis and ammonium hydroxide precipitations render the sample soluble in strong hydrochloric acid where plutonium can then be isolated by anion-exchange chromatography (*7*).

Cation-exchange chromatography is used to separate the alkaline earths from the americium–curium fraction by using dilute hydrochloric acid eluents. Remaining trace contaminants are dramatically removed by using strong perchloric acid washes.

Americium-243 was used to trace both curium and americium in soil samples which were spiked with americium-241 and curium-243, -244. As fractionation between the americium-243 tracer and the curium spike was not observed, a curium nuclide is not necessary to trace in-situ curium when using this method. For environmental concentrations, interference from other transplutonium actinides is not considered to be a problem.

EXPERIMENTAL

Test Samples. The soils analyzed were prepared by adding spikes of americium-241 and a mixture of curium nuclides, curium-243 and curium-244, to 10-g aliquots of standard plutonium soils. The nuclides added were previously calibrated by evaporation and 2π counting (*9*).

The standard soil samples contained plutonium in a refractory form and were also analyzed for plutonium to demonstrate that the dissolution procedure would solubilize and equilibrate refractory actinides with soluble tracer. The standard plutonium