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ENTHALPIMETRIC DETERMINATION OF TOTAL LEAD IN GASOLINE

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Abstract

A method is descubed for the determination of lead alkyl additives in gasoline by direct injection enthalpimetry. The method is a single step process, iodine monochloride solution is injected into a sample of the gasoline diluted with an equal volume of *o*-xylene. The system can be arranged to gave a direct reading of the concentration of the permitted lead alkyls for several concentration ranges. Once calibrated the proposed method can be operated by semi-skilled workers. The precision and accuracy are within industrial limits. The main advantages of the method are those of low cost and low time of analysis.

Keywords: enthalpimetry

Introduction

The oxidation of motor fuel in internal combustion engines produces intermediates such as peroxides, aldehydes and peracids and these compounds have the ability to dissociate and promote chain reactions that accelerate preflame oxidation and lead to detonation (knocking).

In 1921 [1], tetra-ethyl lead (TEL) was found to be an anti-knock agent for gasoline used as a fuel in internal combustion engines. The increase in the number of engines, especially those with higher compression ratios, intensified the demand for fuels with a high octane value with the resultant increase in the amount of TEL used. Tetra-methyl lead (TML) has also been used due to its higher volatility (B.Pt 110°C compared with a B.Pt of 200°C for TEL) and its thermal stability. As a result of the latter, it tends to be distributed more evenly amongst the various engine cylinders.

Although the oxidation rate of TML is greater than that of TEL its oxidative degradation produces mainly formaldehyde, which is itself a powerful anti-knock agent. On the other hand, oxidation of TEL produces less formaldehyde but more acetaldehyde, which is a pro-knock agent. However, TML is more expensive and thus tends to be used in lower quantities than TEL.

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The alkyls decompose late in the combustion cycle destroying or deactivating the free radicals produced during the pre-combustion chain reaction of the hydrocarbons. The tetra-ethyl or the tetra-methyl or a mixture (methyl ethyl lead) are added to the gasoline to inhibit the knock and thereby increase the efficiency of the engine.

On combustion, organolead in motor gasoline tends to form oxides and sulphates which deposit in the combustion chamber causing fouling and corrosion of the spark plugs and valves.

It thus becomes necessary to remove these deposits which is generally achieved by the use of ethylene dichloride and ethylene dibromide as "scavengers". The mixture of scavengers and anti-knock agents, termed "ethylfluids", are added to gasoline to give the required concentration of lead alkyls.

Although there is a growing tendency to use lead-free gasoline, approximately 50% of the fuel presently used contains lead. The concentration varies from country to country. In the UK the British Standard (B.S.4040:1988) indicates a minimum requirement of 0.05 g l^{-1} and a maximum of 0.15 g l^{-1}.

Various methods have been proposed for the determination of the total lead in gasoline. Campbell and Moss [2] proposed a method for the determination of lead in gasoline based on the extraction of the lead as a dialkyl di-iodo lead complex formed by reaction of the tetra alkyl-lead compounds with iodine monochloride. The lead content of the extract was then determined colorimetrically using dithizone. They recorded a high precision using a working volume of 10 cm^3.

This forms the basis of a method (IP 224/68; Re-approved 1985) used for the determination of trace amounts of lead in aviation turbine fuels and light petroleum distillates. The suggested sample size depends on the amount of lead expected, varying from 2 cm^3 for a range of 5–25 ppm to 1 litre for 0.003–0.015 ppm.

The same authors later used the iodine monochloride extraction method followed by determination of the lead by titration using EDTA [3]. They reported a precision of 0.01 repeatability, 0.016 reproducibility and a total determination time of ca 2 h. This is essentially the same method as that applied in two proposed standard methods, (i) ASTM 3341-74 (later approved as 3341-79 and 3341-80) and (ii) IP 270-70. Campbell and Palmer used a similar extraction method and determined the lead content of the extract using AAS. They reported a precision similar to that obtained using the standard method IP 224-68 [4].

A working volume of 25 cm^3 of gasoline was required for expected concentrations of 125 ppm. The use of AAS is also the basis of a standard test method ASTM D3237-79 (re-approved 1984). A reproducibility of 0.01 g gal^{-1} would be expected to be exceeded in only 1 result in 20.

Trace concentrations of lead in primary reference fuels have been determined using bromine to cleave the alkyl lead and after extraction of the dibromodialkyl lead into aqueous solution the bromine is removed by evaporation and the lead is determined colorimetrically using dithizone. (ASTM Method ASTM D1368-83.) The lead alkyls have been separated from the gasoline using GLC and the lead determined using flame photometry [5].

In a further method the lead is extracted from the gasoline by refluxing with oncentrated hydrochloric acid and then titrated using a iodometric/chromate ethod. A working volume of 50 cm^3 is used. The working range is 250–1200 ppm of lead. A repeatability of ca 0.001 and a reproducibility of ca 20 ppm are reported. Each analysis requires ca 2 h for completion. This procedure formed the basis of an ISO international programme carried out in 1962 and the ASTM method D2547-82, originally proposed in 1966 and re-approved in 1977.

Other methods include the use of X-ray analysis (ASTM Methods D5299-82/D5299-71 and Inst. of Pet. Method. IP 228/72). A minimum working volume of 10 cm^3 is required and the range is 25–1250 ppm.

Experimental

The iodine monochloride is in an aqueous acidic solution and thus any reaction between it and the lead alkyl in a non-polar phase must occur at the solvent interface when the two solutions are brought into intimate contact during the injection and the rapid stirring of the mixture.

Preliminary experiments were made using various organic solvents to extract the iodine monochloride and then mixing the extract with a solution of a lead alkyl dissolved in a mixture of n-octane and the solvent used to extract the iodine monochloride.

There was a sensible heat change when either *o*-xylene or toluene was used as the extractant. It was decided that this heat change was of potential use for the enthalpimetric determination of the alkyl lead compounds. When the iodine monochloride was injected as an aqueous solution, a heat change was also observed.

When gasoline samples were spiked with lead alkyls and aqueous iodine monochloride was used, it was noticed that it was not easy to obtain good and rapid uniform mixing of the various phases and the heat pulse did not instantaneously reach its maximum value. Experiment showed that when *o*-xylene was used to dilute the gasoline, an adequately fast reaction occurred and reproducible results were obtained using a fixed speed of stirring.

Reagents

Iodine monochloride

This was prepared using the method of Campbell and Moss [2] for the oxidation of iodide with iodate in the presence of a high concentration of hydrochloric acid. Sufficient potassium iodide was used to give a final concentration of 1.0 *M* ICl in 6 *M* HCl.

o-Xylene

Freshly distilled *o*-xylene (B.Pt 144 °C) was used as diluent.

Lead alkyls

These were used as supplied.

Enthalpimetric apparatus

The basic construction and electronic details of the type of Direct Injection Enthalpimetric apparatus used have been previously described [6]. The thermistors used in the bridge have a nominal resistance of 10000 ohm at 25°C. The various resistances used in the other arms of the Wheatstone bridge are of the same order to ensure maximum sensitivity of the bridge. The output from the bridge was amplified using a d.c. amplifier and then connected to a potentiometric recorder having ranges from 0–1 mV to 0–1 volt for a full scale deflection of approximately 200 mm.

The overall sensitivity of the bridge and the recorder could be varied to give a full scale deflection (FSD) on the recorder for 0.005–1°C change in the temperature of the system. (For quality control work the recorder is replaced with a digital voltmeter and shunt so that a standard sample will give a reading of 100 units.)

The reaction cell consists of an insulated reaction vessel (a disposable polyethylene beaker of nominal capacity 30 cm^3 contained within a Dewar vessel) fitted with a lid holding an electrically driven glass paddle stirrer, a thermistor probe and an injection pipette of nominal capacity 1 cm^3.

Calibration studies

A series of solutions of TML and TEL in a 1:1 (v/v) mixture of *n*-hexane and *n*-octane was prepared containing between 0.25–2.25 g l^{-1} of the lead alkyl.

For each concentration, including zero concentration, of the lead alkyl, an aliquot (5 cm^3) of each solution was diluted with an equal volume of *o*-xylene and allowed to come to thermal equilibrium in the reaction vessel. An injection pipette, previously filled with the iodine monochloride solution, was placed in the lead alkyl solution. The lead alkyl solution was rapidly stirred at a constant predetermined speed and when the system had attained thermal equilibrium, (indicated by a steady reading on the recorder or the digital voltmeter) the iodine monochloride solution was rapidly injected into the sample. The heat pulse was recorded. The procedure was repeated for all the concentrations of the lead alkyls in the calibration series. The results are given in Table 1.

Table 1

Conc.* of TEL/ppm	0	2.5	5.0	7.5	10.0	15.0	20.0
Step height**	4	9	14	20	24	29	34
Conc.* of TML/ppm	0	2.5	5.0	7.5	10.0	15.0	20.0
Step height**	4	10	14	20	24	30	34

Conc.*: - Concentration of the lead alkyl in the original sample (i.e. the concentration in the reaction vessel is 1/2 this value).

** Step height:- These are arbitrary units (millimetres deflection on the recorder chart). Each value is an average of three values differing by not more than 1 mm.

Experimental statistics

Two series of 15 aliquots of separate solutions containing 50 ppm TEL and 100 ppm TEL respectively were analysed using the above procedure. Standard Deviations and Percentage Relative Standard Deviations were calculated for each series. The results are given in Tables 2a and 2b.

Table 2a A series of aliquots of a solution containing 5.0 ppm TEL analysed using the procedure outlined above

Assay number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Heat pulse	19	20	21	19	19	20	21	20	19	20	18	19	20	21	19

Mean value = 19.66; Standard Deviation = 0.94;

$$\%\text{RSD}\ \frac{\text{SD}\times 100}{\text{mean value}} = 4.6$$

Table 2b A series of aliquots of a solution containing 10.0 ppm TEL analysed using the procedure outlined above

Assay number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Heat pulse	39	40	39	39	40	39	40	41	49	40	41	39	40	42	39

Mean value = 39.8; Standard deviation = 0.90;

$$\%\text{RSD}\ \frac{\text{SD}\times 100}{\text{mean value}} = 2.4$$

Results

The electronic sensitivity used was less than 50% of the maximum practical sensitivity available, i.e. the electronic noise level is less that 50% of the signal for 0.1 ppm of TEL. Blank value:- is obtained by measuring the heat pulse caused by the heat of mixing of the sample and the injected reagent.

Range of the method

Calibration curves covering ranges from 0–25 and 0–250 and 0–2500 ppm may be obtained by suitable adjustment of the electronic sensitivity of the system. In all cases linear curves are obtained. The same proportional analytical statistics are generally obtained for all the higher ranges of concentration.

Use of the method in practice

Preparation of calibration curve

Using a stock solution of TEL (or TML) in a 1:1 v/v mixture of *n*-hexane/*n*-octane, obtain a range of concentrations of the lead alkyl covering the ranges expected in practice.

Pipette an aliquot (5 cm^3) into the reaction cell contained within the Dewar vessel and dilute with an equal volume of *o*-xylene.

Place in position a 1 cm^3 submersible pipette previously filled with the 1.0 *M* iodine monochloride reagent.

Switch on the electronic system including the recorder and the stirrer operating at a predetermined fixed rate. Allow the system to come to thermal equilibrium (indicated by the trace becoming horizontal).

Inject the iodine monochloride. Measure the step height.

Prepare a calibration curve using a range of concentrations of the lead alkyl from zero to approximately 110% of the maximum expected.

Adjust the electronic sensitivity of the system to give the maximum practical deflection for the maximum concentration.

Proposed method

1) Non-routine samples

Using an (5 cm^3) aliquot of the sample diluted 1:1 v/v with *o*-xylene, proceed as in the preparation of the calibration curve. Note the step height. Using a second sample, spike a known volume of the gasoline with an equal volume of a stock solution of the lead alkyl. Dilute a 5 cm^3 aliquot of the mixture with an equal volume of *o*-xylene. Use this as the test solution and determine the step height. Using the normal calculation processes for standard addition and the previously prepared calibration curve determine the actual concentration of the lead alkyl in the original sample.

2) Routine assay

Using the stock solutions of the lead alkyl prepare spiked solutions of the gasoline. Determine the "blank value". Adjust the zero on the millivoltmeter scale to compensate for the blank. In further routine assays it is then only necessary to use "non-spiked" samples and obtain directly the actual reading on the millivoltmeter.

Industrial samples

In order to ascertain whether the petroleum distillate and/or materials (other than lead alkyls) added as commercial additives to gasoline have any effect on the

Table 3

Conc. of TEL added (ppm)	0	2.5	5.0	7.5	10.0	15.0	20.0
Corrected Heat Pulses							
Series A	0(1)	12	23	35	47	68	96
Series B	0(2)	13	24	36	46	68	99*
Series C	0(3)	11	23	34	46	70	100

Corrected heat pulses are calculated:

Experimental Heat Pulse (With added lead alkyl) – Experimental Heat pulse on non-spiked sample. (Blank value)

(1) The blank value for Series A was 14 units.

(2) The blank value for Series B was 88 units. This indicated a lead content of approximately 8.0 ppm in the original gasoline.

(3) The blank value for Series C was 9 units.

* The reading of 99 units was obtained by calculation after decreasing the sensitivity of the recorder by 50%. (The actual experimental reading was "off-chart" necessitating a reduction in the overall electronic sensitivity of the system.)

analytical procedure, two series (A and B) of industrial samples were assayed. A third series (C) prepared using 1:1 v/v *n*-hexane:*n*-octane as the solvent was also assayed using the same experimental parameters. Each corresponding sample contained the same amount of lead alkyl added by the present authors.

Series A

A series of solutions of the lead alkyls prepared using commercially available "lead free" gasoline.

Series B

A series of solutions of the lead alkyls prepared using commercially available gasoline containing lead.

The results are given in Table 3.

Investigation of the cause of the blank value in the "non-leaded gasoline" sample

The amount of lead in the gasoline sample was determined using the ASTM method ASTM D1368-83 in which bromine was used to cleave the lead/alkyl bond. After removal of the excess bromine by boiling, the bromo-alkyl lead compound was extracted into aqueous solution and the lead determined colorimetrically using dithizone, (previously prepared standard solutions of a lead salt were used in the preparation of the calibration graph.)

The amount of lead found was between 1–1.5 ppm and was insufficient to account for the total amount of the "blank value" in the enthalpimetric method. Using the previously prepared calibration graph obtained for "pure" lead alkyl solutions the "enthalpimetric blank value" for a zero concentration of lead alkyl dissolved in the gasoline sample was calculated.

This value differed from that obtained using the lead alkyl dissolved in *n*-hexane/*n*-octane/*o*-xylene solutions by a few units, indicating that one or more of the commercial additives had contributed to the blank value. The identity of the particular additive(s) was not established.

Discussion

The overall heat change in the system used in the determination of the lead alkyls is an integrated result of all the heat changes occurring in the system during the period of measurement (the recording) of the heat pulse. Temperature changes resulting from the difference in the temperatures of the iodine monochloride and the sample solution are obviated by the use of the submersible injection pipette. Any heat change caused by the mixing of the injected solution and the sample solution is standardised by ensuring that the experimental parameters of rates of injection and stirring are practically the same throughout all the analyses. This ensures that the amount and rate of mixing of the two solutions are constant. The remaining heat changes are from heats of reaction associated with the chemical changes in the system.

It is recognised that iodine monochloride is not a specific reagent for the lead alkyls and its use does not necessarily ensure that only the heat of the reaction between the lead alkyls and the iodine monochloride is observed. Other substances present in the sample may react.

The general B.S. requirements [7] for all grades of petrol are that "the petrol shall consist essentially of volatile hydrocarbons together with additives as required". Such additives may include organic compounds containing oxygen and are used as blenders or as stabilisers. However, the type of compounds and the maximum amounts are strictly specified.

Whilst the various alcohols and ethers specified do not have a significant reaction with iodine monochloride during the time of measurement, and hence no respective heat change is observed, other materials which may be present can react. Benzene may be present up to a maximum allowable limit of 5% v/v [7]. Although the reaction between benzene and iodine monochloride does not appear to be as fast as is the reaction between the lead alkyls and iodine monochloride, at the maximum permitted concentration of benzene some reaction may occur during the time of obtaining the heat pulse. Such a reaction would result in any difference, probably an increase, in the blank value obtained. If the original base stock had a high olefine content it is possible, although not highly probable, that the sample may contain some olefines. These would also react with the iodine monochloride and contribute to the blank value.

It is essential to ensure that the proportion of the sample reacting is always the same. In the present system, completeness of reaction is ensured. The injection of the aqueous iodine monochloride into the rapidly stirred non-aqueous mixture of *o*-xylene and the gasoline sample occurs as a fine stream of liquid that rapidly breaks up into very small droplets. Thus the iodine monochloride presents a large surface area of contact. The use of a large excess of the reagent ensures that the reaction between the lead compound and the iodine monochloride is practically instantaneus and is complete. The degree of completion of the reaction is confirmed by a study of the heat changes recorded in the calibration experiments.

After the initial and nearly vertical rise, the curves become level and remain so for about 90 s before a small decrease is noted, which is the result of some slight cooling of the solution.

Comparison of the proposed method with other methods

The primary aim of the present study is to provide a rapid, low-cost method of assay for routine analytical procedures used in quality control. A comparison of the proposed method with other methods used for the analysis of lead alkyls in gasoline was thus made.

For routine quality control analysis in which a relatively large number of assays are made in a working day, the cost of each assay is of importance. The overall costs must be assessed in terms of initial costs of equipment, running costs including labour costs, the costs of reagents and the amount of sample required per assay.

An additional important factor is the time required from the receipt of the sample to obtaining a result on which a working decision may be made. With any industrial process having a large and continuous throughput this time factor assumes a high importance. Stopping the process, or having to make alterations to a large volume of product whose quality is outside accepted specifications, can be very costly and is generally to be avoided. The choice of a particular method of assay may often be determined by this factor.

The previously published methods may be divided into those which decompose the lead alkyls using iodine monochloride and those which use other halogen containing reagents such as iodine, bromine or concentrated hydrochloric acid.

In the first group the tetra-alkyl lead is decomposed to give the di-iodo di-alkyl lead. This is extracted from the system and the lead content is determined colorimetrically, by atomic absorption or by X-ray methods.

The methods of the second group use a multistage reaction sequence to obtain the lead in a form suitable for titration, either by direct or by indirect titration.

The recommended methods for the preparation of the iodine monochloride reagent are more or less standard and require the same number of reagents. Some methods using iodine monochloride involve the extraction of the di-iodo-dialkyl lead compound and require further reagents for the extraction of the lead compound and for the destruction of the excess iodine monochloride and to convert the organic lead compounds to an inorganic form. All reagents used in these processes must be treated to remove all traces of lead. The calorimetric methods reqire the provision of standard aqueous lead solutions. The methods using titration of the lead with EDTA require not only standardised EDTA but also buffer and indicator solutions. All these solutions must be prepared using lead free water. Considering the methods not requiring the use of iodine monochloride:

(i) In the ASTM method D3237-84 the gasoline sample is diluted with methyl isobutyl ketone and the lead compounds are "stabilised" by reaction with iodine. After allowing the mixture to stand for some time, the lead compounds are dissolved in a quaternary ammonium salt solution. (Aliquat 336 dissolved in MIBK) and the lead content of the sample is determined by AAS using standards prepared from reagent grade lead chloride.

(ii) In the "Volumetric chromate" method, (ASTM D2547-82) the lead alkyl is converted to lead chloride and extracted from the gasoline by refluxing the sample with concentrated hydrochloric acid. The acid extract is evaporated to dryness, any organic material present is removed by boiling with concentrated nitric acid (or conc. nitric acid /potassium chlorate). The lead is then precipitated as lead chromate and determined by the volumetric iodimetric chromate method. The precipitation requires a neutralisation step in addition to the subsequent reaction with potassium dichromate.

The titration procedure requires the dissolution of the lead chromate in a hydrochloric acid/sodium chloride solution before the sodium chromate so obtained is reacted with potassiun iodide and the subsequently liberated iodine is titrated to a starch end point using standardised sodium thiosulphate. After the preparation of the iodine monochloride and presentation of the diluted sample, the proposed method is a single stage method involving no further reagents for routine work. For non-routine work it is necessary to provide standard solutions of the lead alkyls.

Many of the published methods in which the lead component is isolated by extraction from the industrial sample and determined after destruction of possible organic interferences do not specify that lead alkyls must be used to verify the method. However, it is generally considered to be good analytical practice to test the protocol by using test samples containing known amounts of the analytes (lead alkyls) to ensure that acceptable results are being obtained on a routine basis. It is, therefore, common practice for laboratories imvolved in routine lead alkyl analysis to have "standard" lead alkyl samples available for this purpose.

Multistage reaction processes, especially those involving extraction procedures, removal of excess of reagents and destruction of organic matter before any determination of the lead can be made, are time consuming. Although, when using such analytical methods it is common laboratory practice to analyse more than one sample at a time, the elapsed time between receipt of sample and obtaining the information required for industrial use is still relatively long. Using the proposed method, the time between receipt of a routine sample and the obtaining of a result is less than 5 min and if the *o*-xylene and the iodine monochloride solution are kept in the same thermostat as is the Dewar vessel containing the reaction cell, the time may be reduced to approximately 2 min.

Using a shunted digital millivoltmeter to indicate the heat pulse enables the result obtained to be compared directly and instantly with the standard result.

The cost of the proposed apparatus is extremely low when compared with those of a u.v. spectrophotometer, an atomic absorption spectrometer with suitable scale expansion or any suitable X-ray equipment.

Labour costs per analysis using the proposed method are probably the lowest of all the methods and can be carried out by semi-skilled operators.

The calibration curves obtained using standard solutions of the two lead alkyls normally used in gasoline (TEL and TEM) indicate that the heats of reaction of these compounds with iodine monochloride do not differ by a practically significant amount. Thus it is possible to use the calibration curve obtained for either standard for the analysis of a sample containing either or both the lead alkyls. If it is necessary, for commercial purposes, to ascertain the relative amounts of the two lead alkyls in a sample, then the ASTM method D1949-79 (re-approved 1984) may be used to separate the two alkyl compounds. Their subsequent determination using either calibration curve gives acceptable results.

The range of the proposed method is as extensive as most of the other methods. It is not recommended for concentrations in the parts per billion range since, although it is possible to use thermistors with a much higher resistance and hence a greater sensitivity, using the present apparatus the electronic noise generated in the system is too great to allow acceptable precision.

The advantages inherent in the present system of being able to vary the overall sensitivity and hence the range covered make it acceptable for most routine situations.

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