# POLAROGRAPHIC DETERMINATION OF TETRAETHYL LEAD IN GASOLINE

by

C. R. Viswanatham* and S. S. Vats

Defence Research Laboratory (Stores), Kanpur

## ABSTRACT

The polarographic determination of tetra-ethyl lead in gasoline by the hydrochloric acid extraction method of Borup and Levin has been critically studied and an improved procedure employing a solution of hydrogen chloride in ether is described.

## Introduction

The determination of tetra-ethyl lead (TEL) in gasoline constitutes one of the most important routine determination handled by control laboratories all over the world dealing with petroleum products. Since the official methods (A.S.T.M.-D526-48 and I.P.-116/49) are laborious and extremely slow, there is need for a rapid and economical method. Among the various rapid methods proposed in recent years, the polarographic methods [1, 2, 3, 4], particularly those of Borup and Levin[2] and Hansen *et al*[3] appeared to possess accuracy, simplicity and speed. However, on close examination, the method of Hansen *et al* was found to suffer from the following defects. It gave erroneous results with aged gasolines high in unsaturated compounds and peroxides. The diffusion currents were small and the diffusion waves obtained were more or less flattened, the rise being spread over a greater voltage range than in aqueous media. The method did not take into account the effect of the loss of solvent in the course of heating on the determination. Heating for periods less or greater than 15 to 20 minutes was found to give low results. The method of Borup and Levin[2], on the other hand, appeared to be free from any defects and eminently practicable, though it also appeared, like the method of Hansen *et al*[3], to be purely empirical in as much as the chemistry of the method was not understood and no attempt had been made to explain some of the observations and results. It was, therefore, decided to subject this method (of Borup and Levin)[2] to a critical study to effect any possible improvements in the procedure, and to find explanations for the unexplained results recorded by its authors and also to elucidate the chemistry of the process so as to place it on a firm scientific basis.

## Experimental Procedure

*Materials and apparatus*—The gasoline samples used were selected at random from the large number of samples of motor and aviation gasolines received for routine testing in this laboratory. The polarographic determinations were carried out with a sargent Heyrovsky Model XII polarograph. Wave heights were obtained from photographed curves.

*At present with the Geological Survey of India, Calcutta.

The following series of experiments were carried out :—

*Series 1*—10 ml. of leaded gasoline were shaken with 10 ml of hydrochloric acid (Sp.gr. 1·16) for 5 minutes in a 50 ml volumetric flask at room temperature (20°—25°C) taking care to avoid splashing on the stopper. The liquid was then allowed to drain off the neck and the gasoline was washed (while in the flask itself) with distilled water. The washed gasoline was withdrawn by means of a pipette into a separating funnel and its TEL content determined by the Institute of Petroleum method (I. P. 116/49). The solution in the volumetric flask was made up to 50 ml with distilled water after adding 10 drops of a 0·05 per cent gelatin solution, and the lead determined polarographically as described by Borup and Levin[2]. The lead content of this solution was also determined by precipitation as $PbCrO_4$ after evaporation to dryness with Schwartz solution. The results of these experiments are given in Table I.

*Series 2*—The same procedure as in Series 1 was adopted except that the flask was heated on a steam bath for 30 minutes. The TEL content of the gasoline was determined separately by the I.P. method for purpose of comparison. The results of these experiments are given in Table II.

*Series 3*—Same as Series 1 except that a saturated solution of hydrogen chloride in dry ether at room temperature was used in place of hydrochloric acid (Sp. gr. 1·16) and shaking was done only for 3 minutes instead of 5 minutes. The results of these experiments are given in Table III.

*Series 4*—10 ml. of leaded gasoline were shaken in a 50 ml dry volumetric flask with 10 ml of a saturated solution of hydrogen chloride in dry ether at room temperature for 3 minutes, 10 ml of hydrochloric acid (Sp. gr. 1·16) were added, the mixture shaken for 2 minutes and then heated on a steam bath for 30 minutes . The results of these experiments are given in Table IV.

*Series 5*—The procedure was as in Series 4 except that no gelatin was added and the determination of the lead content of the treated and washed gasoline was omitted. The results of these experiments are given in Table V.

**Discussion**

The results recorded in Table I show that when the gasoline-hydrochloric acid mixture was merely shaken but not heated, all the lead present in the gasoline was not brought into the aqueous solution and, further, most of the extracted lead in the aqueous solution was present in a form in which it did not undergo reduction at the dropping mercury electrode as evidenced by the low values obtained for the lead polarographically. The results given in Table II show that heating the mixture (after shaking for 5 minutes) for 30 minutes resulted not only in extracting the lead almost completely from the gasoline into the aqueous layer but also led in to the conversion of the extracted lead into a form in which it underwent polarographic reduction. However, even this treatment failed to extract all of the lead from the gasoline. This proves that the procedure of Borup and Levin[2] was not entirely satisfactory though this was not reflected to any noticeable extent in their determinations because the quantities of unextracted lead were negligible, and the results were calculated with reference to a gasoline sample containing a known quantity of (TEL) which was subjected to the same treatment as the test samples.

## RESULTS

TABLE I

| Expt. No. | Lead content of untreated gasoline (ml of TEL/I.G.) | Lead found in the extracted gasoline (ml of TEL/I.G.) | Lead found in the aqueous acid extract | |
|---|---|---|---|---|
| | | | Chemically | Polarographically |
| 1 | 2·81 | 0·70 | 2·09 | 0·12 |
| 2 | 2·81 | 0·78 | 2·06 | 0·14 |
| 3 | 2·81 | 0·79 | 2·01 | 0·16 |

TABLE II

| Expt. No. | TEL content of the gasoline (I.P. method) (ml/I.G.) | TEL content of the gasoline by the polarographic method of Borup & Levin, (ml/I.G.) | TEL left in the gasoline after the extraction with HCl (ml/I.G.) |
|---|---|---|---|
| 1 | 2·81 | 2·78 | 0·01 |
| 2 | 3·14 | 3·09 | 0·02 |
| 3 | 3·25 | 3·20 | 0·02 |
| 4 | 4·80 | 4·82 | 0·03 |
| 5 | 5·18 | 5·12 | 0·03 |
| 6 | 5·36 | 5·29 | 0·03 |

TABLE III

| Expt. No. | Lead content of the untreated gasoline (ml of TEL/I.G.) | Lead found in the extracted gasoline (ml. of TEL/I.G.) | Lead found in the aqueous acid extract | |
|---|---|---|---|---|
| | | | Chemically | Polarographically (ml of TEL/I.G.) |
| 1 | 2·81 | *Nil* | 2·78 | 0·10 |
| 2 | 2·81 | *Nil* | 2·80 | 0·68 |
| 3 | 2·81 | *Nil* | 2·78 | 0·12 |

TABLE IV

| Expt. No. | TEL content of the gasoline (I.P. method) (ml/I.G.) | TEL content of the gasoline found polarographically (ml/I.G.) | TEL left in the gasoline after extraction with ether-HCl (ml/I.G.) |
|---|---|---|---|
| 1 | 1·28 | 1·26 | *Nil* |
| 2 | 1·50 | 1·53 | *Nil* |
| 3 | 2·70 | 2·68 | *Nil* |
| 4 | 3·43 | 3·38 | *Nil* |
| 5 | 4·84 | 4·81 | *Nil* |
| 6 | 5·31 | 5·25 | *Nil* |

TABLE V

| Expt. No. | TEL content of the gasoline (I. P. method) (ml/I.G.) | TEL content of the gasoline found by the polarographic method (ml/I.G.) |
|---|---|---|
| 1 | 1·82 | 1·78 |
| 2 | 2·76 | 2·78 |
| 3 | 0·53 | 0·51 |
| 4 | 3·37 | 3·32 |
| 5 | 4·96 | 4·91 |
| 6 | 5·11 | 5·05 |
| 7 | 5·48 | 5·41 |
| 8 | 5·55 | 5·58 |

The failure of the procedure of Borup and Levin might be due to the fact that the reaction between TEL and the hydrochloric acid was more or less confined to the water-gasoline interface due to the very low solubility of hydrogen chloride in gasoline. The results of the experiments under Series 3 presented in Table III show that replacing the aqueous hydrochloric acid solution with a saturated solution of hydrogen chloride in ether enabled the total extraction of the lead from the gasoline by merely shaking without heating; the lead however, remained in a form in which it did not undergo polarographic reduction. The results given in Table IV show that the procedure used for Series 4 was entirely satisfactory in that both the extraction of lead and its conversion into a polarographable form were complete.

The quantity of gelatin used by Borup and Levin[2] as maxima suppressor was too low (being only 10 drops of a 0·05 per cent gelatin solution in 50 ml of the lead solution as against the 0·01 to 0·02 per cent overall concentration of gelatin usually employed in polarographic determination of lead). Inspite of this,

the actual polarographic curves obtained were perfectly free from maxima. Apparently the procedure adopted by Borup and Levin resulted in the extraction of some suppressors which were either present originally in the gasoline or were formed as a result of the action of hydrochloric acid on the gasoline. This view is confirmed by the results obtained by us in Series 5 in which the curves were entirely free from maxima although no gelatin was used. Hensen (loc. cit) obtained curves free from maxima without using any gelatin but did not realise the significance of this fact.

Taylor and Smith[5] found that high concentrations (of the order of 0·04 per cent and above) of gelatin used as maxima suppressor in polarographic determinations of lead decreased the diffusion current thus giving low values for the lead. They also found that this effect was shown by other maxima suppressors like tyloze. It therefore, appears that this is a characteristic of maxima suppressors in general. This observation is of importance as will be explained further below.

Since TEL itself is insoluble in water, its extraction depends on its conversion into products which are soluble in water as a result of the treatment with hydrochloric acid. The reaction between HCl and TEL under different conditions, and the properties of the products formed as a result were studied by Heap and Saunders[6]. This reaction gives rise to three products, depending on the conditions, namely triethyl lead chloride ($(C_2H_5)_3PbCl$), diethyl lead chloride ($(C_2H_5)_2PbCl_2$) and lead chloride ($PbCl_2$) all of which are soluble in water. At low temperatures, $(C_2H_5)_3\ PbCl$ is the main product which is fairly stable even in contact with excess $HCl$. But as the temperature rises, this is converted in the presence of HCl into $(C_2H_5)_2PbCl_2$ which itself, being less stable than $(C_2H_5)_3PbCl$, is quickly changed into $PbCl_2$. From this it will readily be seen that on shaking leaded gasoline with hydrochloric acid in the cold (that is, at room temperature) the bulk of the lead extracted into aqueous solution will be in the form of $(C_2H_5)_3PbCl$ which does not appear to undergo polarographic reduction as evidenced by the very low polarographic values obtained without heating.

On heating in $HCl$ solution for a sufficiently long time this compound is completely converted into $PbCl_2$ as already mentioned which can then be determined polarographically. If the heating time is too short, the conversion into $PbCl_2$ will be incomplete giving rise to low results. If, however, the heating is carried on for too long a period, not only is the conversion of the organo-lead compounds to $PbCl_2$ complete, but due to the longer interaction of the $HCl$ and the reactive compounds in the gasoline at the high temperature, excessive quantities of the maxima suppressor compounds (gums) are formed which reduce the diffusion currents resulting in low values for the lead. It is well known that interaction between gasoline and various reactive chemicals including acids, halogens and halogen compounds results in increased gum content especially if the gasoline contains unsaturated compounds (as cracked gasolines invariably do) Viswanadham[7] *et al* showed that interaction between gasoline and anhydrous ferric chloride in ether solution results in increased gum contents which amount to many times the original values in the cases of cracked gasolines. Ageing and the presence of peroxides are also known to increase the gum content of gasolines especially those containing unsaturated compounds.

Thus the low values obtained by Borup and Levin[2] (as also by Hasen[3]) on heating for periods shorter or longer than those presented by them find satisfactory explanation on the basis of the above discussion.

The low values obtained in the polarographic method are due to one or more of the following causes—

(1) Incomplete extraction of the lead from the gasoline;

(2) Incomplete conversion of the organo-lead compounds into lead chloride;

(3) Excessive formation of maxima suppressor substances (gums).

The procedure developed by us for the polarographic determination of TEL in gasoline (described under experimental Series 5) was found to give good results (within the limits of accuracy imposed by the polarographic technique itself) when tested against numerous samples of motor and aviation gasolines (including both cracked and straight run varieties) with TEL contents ranging from 0·5 to 6·0 ml/gallon which were selected at random from the samples undergoing routine testing in our Laboratories. We therefore, recommend its adoption for the routine determination of TEL in gasoline.

We also found that a solution of lead nitrate in *HCl* medium (10 ml HCl of 1·16 sp. gr. in 50 ml. solution) with 0·01 per cent gelatin concentration could be used as the standard for the calculation of the TEL values instead of gasoline samples containing a known quantity of TEL, with equally good results.

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