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DETERMINATION OF "I-T" AND ITS
AGEING PRODUCTS IN AERO-ENGINE FUELS

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In an earlier communication (1), a description was given of a
rapid method of lead determination. The method is further simpli-
fied, and a rapid method of determining the ethylene bromide content
of aero-engine fuels is given. The nature of the tetraethyl lead
decomposition products which form during the ageing of leaded fuels,
and the manner in which they are identified, is described.

CONTENTS.

I.   INTRODUCTION:

Of the substances so far tested which strongly influence the
thermal oxidative mechanism of decomposition during combustion, in
practice tetraethyl lead is - as far as is known - the only tetra-
alkyl lead additive used to raise the knock rating of aero-engine
fuels. Since tetraethyl lead forms a deposit when burned in the
engine (on plugs, rings, etc.) halogen in the form of halogen
hydrocarbons is also added to the fuel to increase the volatility
of these reaction products. Other common additives are dyes, for
purposes of identification, and stabilisers (patents are known for
amines and inorganic fluorides). The mixture "I.T." Fluid, which
is used in the Reich, contains two gramme-atoms of bromine as ethylene
bromide to each gramme-atom of lead, dye, petroleum, and "other
ingredients".

The increase in knock resistance produced by tetraethyl lead is not a simple function of its concentration in the fuel, and it decreases, relatively speaking, as the volume of additive increases. It depends on the fuel, and on the impurities in it. In general, tetraethyl lead - especially in highly aromatic fuels - has an unfavourable effect on the storage life of aero-engine fuels. The lead content falls with solid substances separating out (lead mud), and in unfavourable circumstances, this can lead to obstruction of the fuel system. The sensitivity of the fuel to oxygen (tendency to gum formation), also increases.

The additive in the tetra-ethyl lead - ethylene bromide - has a slightly corrosive effect in the presence of water (or alcohol), the ethylene bromide being decomposed. Below -10°C. it crystallises out of the fluid mixture in an increasing degree as the temperature falls, while tetraethyl lead remains liquid till below -55°C., so that if the leading is done below -10°C., there is a danger of too little ethylene bromide being added to the fuel.

These properties of ethyl fluid and of leaded fuels were the reason for the work to be described.

•II - AN ACCURATE RAPID METHOD FOR DETERMINING THE AMOUNT OF LEAD IN FUELS (SIMPLIFIED PROCESS).

1. **Principles:** In the description, published (2) in the Year Book for 1941, of a rapid method of determining the composition of fuels, it was proposed to make a rapid standardisation of the dithizone solution used, and this is described here. Also, to exclude the possibility of errors arising from the use of unsuitable gasoline additives, a chemically defined additive is suggested as an alternative to "paraffin-based natural gasoline" (3), and the process is simplified and shortened.

If really pure substances are used in the production of the dithizone solution, it can be titrated with lead (Pb^{++}) solution of known content, independently of other methods. The dithizone solution is, practically speaking, suitable for this type of titration if, on titrating 2.50 ccs. of the "test solution" described below, or diethyl lead salt solution, without addition of KCN, the increase in dithizone consumption (compared with that with KCN) is not above 0.25% (i.e., about 0.25 ccs.). If the increase in consumption is greater, the volume of dithizone solution can be more accurately determined by the process already described, and the test solution used for the rough checking of temporary variations in it.

Since the impurities in the dithizone solution have a proportional effect in titration, such solutions can be used for one and the same class of compound (see Section IV), if their titration volume is frequently checked. But, if accuracy is demanded, it cannot be used for the comparative analysis of triethyl - diethyl and lead (Pb^{++}) salts, e.g., use of a class of compounds for standardisation.

Since the direction to use "paraffin-based natural gasoline" as a component of the mixture may result in the use of various unsuitable gasoline fractions (synthetic gasolines), this disadvantage will have to be overcome by using chemically pure methyl cyclohexane, which is suitable both in boiling characteristics and in its influence on the dissolving capacity and form of precipitation of diethyl

lead dichloride in the fuel. To accelerate the precipitation and make the deposit more easily soluble, pyridine is added. The simplified process for aviation fuels differs from that described earlier as follows:- The additive consists of 50 parts by volume of methyl cyclohexane [1], 25 parts by volume of chloroform, and 1 part by volume of a 1% by volume solution of pyridine in methyl cyclohexane. Boil for about two minutes, and then cool for 1 minute.

The test takes 20 minutes[2]. The accuracy is the same as with the original method (see Year Book of German Aeronautical Research, 1941, II, p.459, Table I). All the aviation fuels and mixture constituents tested, including aviation gasoline, gave reliable values. The absolute accuracy was improved by the new titration method.

2. Titration of the dithizone solution: About 0.10 to 0.12 grammes of metallic lead (Kahlbaum A.R. 1 mm. sheet) is weighed into a 100 ccs. wide-necked Erlenmayer flask to an accuracy of 1/10 mg., treated with a mixture of 2 ccs. of concentrated HNO_3 (65% A.R.) and 4 ccs. of distilled water, and placed on a boiling waterbath. When the lead has dissolved, it is evaporated to dryness on the waterbath (about 2 hours).

The resulting lead nitrate is quantitatively washed into a calibrated 500 ccs. measuring flask with an aqueous solution containing 0.20% NH_3, 0.5% Rochelle salt, and 0.1% sodium thiosulphate, and then made up to 500 ccs.[3]. The solution is stable (being kept sealed in a Jena measuring flask in the dark), and is sufficient for 150 to 200 titrations.

2.5 ccs. of the lead (Pb^{++}) solution are mixed for the initial test with 4 ccs. of chloroform, 0.25 ccs. of $2\frac{1}{2}$% KCN solution, and titrated with the dithizone solution until the brown colouring appears. The limit is determined by over-titration (addition of 0.10 ccs. excess gives pronounced darkening of the aqueous layer). The test is then repeated, using exactly half as much chloroform as the dithizone solution.

The factor of the solution is checked every 8 days for safety. This check takes three minutes.

The dithizone solution, if covered with dilute sulphuric acid, is sufficiently stable, even if not sealed off from atmospheric oxygen, provided that it is protected from light while in storage.

Calculation:- If a grammes of metallic lead were used in the preparation of the lead solution, and if 2.50 ccs. of this solution require b ccs. of dithizone solution, then the factor F by which the volume of dithizone solution used must be multiplied in the actual analysis, to give the percentage by vol. of tetraethyl lead, is :-

$$F = \frac{a \times 0.95}{b}$$

The concentration of the dithizone solution should be such that 2.50 ccs. of test solution correspond to 8 to 10 ccs. of dithizone solution.

The factor 0.95 takes into account that in the titration with lead (Pb++) solution a mixture of carbon tetrachloride and chloroform must be used, because of the difficulty of dissolving lead (Pb++) dithizonate. Neglecting the addition of chloroform, and assuming that triethyl, diethyl, and lead (Pb++) behave completely identically, the calculated factor is 0.9432 (the specific gravity of tetraethyl lead is put at 1.655 (at 20°C.). The increase of 0.3% was made by analogy with the behaviour of diethyl lead compounds when chloroform is added (see Table 1.).

This increase is also justified by the fact that in the analysis of (recrystallised) lead triethyl chloride, a correction by this amount is also required (practically speaking, the polar chloroform in the amount used here hardly influences the equilibrium of distribution between dithizone and ammonium dithizonate at all; the shifting of the moment at which the brown coloration of the aqueous layer appears only occurs in the presence of lead dithizonate, proportionally to the volume which is present).

Example:

1. Standardisation

   Lead used (a) = 0.1079 gms.

   Dithizone solution used (b) = 9.05 ccs.

   $$F = \frac{0.1079 \times 0.95}{9.05} = 0.01132$$

TABLE 1.

Test No.	Type of lead compound	Ratio between		End point ccs.dithizone solution
		Tetra	Chloroform	
1		1	0.5	7.85
2	Lead (Pb++) salt	1	1	7.92-7.93
3	Diethyl lead salt obtained by D.V.L. lead content method 0.1% NH₃	1	0	10.65
4		1	0.5	10.75
5		1	1	10.85

The chloroform was added before titration. In the absence of lead salts, and using the same volumes of carbon tetrachloride, i.e., about 8 ccs., as in test 1, 0.05 cc. of dithizone solution cause a pronounced brownish coloration of the aqueous layer up to a 1:1 addition of chloroform. Experiments with chloroform purified by fractional distillation gave the same result. The delay in the end point caused by chloroform is, as already mentioned, proportional to the volume of lead to be titrated. The addition of

carbon tetrachloride in titration (in an amount equal to the dithizone solution needed) practically does not change the end point for diethyl lead salts at all. With lead (Pb^{++}) salts the addition of the above volume (and of the volume of chloroform prescribed) causes a slight rise (about 0.02 ccs.) in the end point.

2.   Analysis

Dithizone solution used (x) = 10.60 ccs.

Tetraethyl lead = 10.60 x 0.01132 = 0.120% by volume.
Note on the analysis: The filter should be cleaned with distilled water and alcohol directly the lead deposit has been removed, and dried at 100°C. After about 20 estimations it should be cleaned with fuming nitric acid. Carbon tetrachloride, and sulphuryl chloride, can be obtained from Schering A.G., and dithizone from Merck.

III.- RAPID METHOD OF DETERMINING ET~LE~~ BROMIDE CONTENT OF AERO-
ENGINE FUELS.

    1. Principles: The possible methods formerly in use for this
                       test are too laborious, and in some cases too
inaccurate.

The basis of the process is the conversion of the bromine to ionic form by means of zinc [4] in the presence of alcohol, water, acetic acid and pyridine, and volumetric analysis of the halogen by the Volhard method.

    2. Method: 25 ccs. of fuel are treated in a 200 cc. Erlenmeyer
                   flask (e.g. Jena narrow-necked ground glass stoppered
(18, 8/38) Erlenmeyer flask fitted with an 18, 8/38 ground glass jointed reflux condenser), with 10 ccs. 96% alcohol, 2 ccs. of pyridine, 1 cc. glacial acetic acid, and 1 gramme of powdered zinc [5] and heated to boiling for twenty minutes under reflux, the flask contents being shaken round several times.

After cooling, the remaining zinc is completely dissolved (cooling it if necessary) by adding 75 ccs. of 10% nitric acid (halogen-free for analytical purposes), and finally the sample is thoroughly shaken up for a short while. After adding exactly 10 ccs. N/20 silver nitrate solution, and shaking thoroughly, about $2\frac{1}{2}$ ccs. of cold saturated ferric ammonium sulphate is added, and the mixture titrated with N/20 ammonium thiocyanate solution until the first lasting brown coloration of the aqueous layer appears. The mixture is then shaken thoroughly for a short while.

The end point can be checked by adding excess (it is an advantage to use a 10 ccs. burette calibrated to 0.02 cc.).

Calculation:-

10 cc. N/20 $AgNO_3$ added.

Back titration:-

a ccs. N/20 NH_4SCN

Required:-

x gm/100 ccs. $C_2H_4Br_2$

or y ccs./100 ccs. (% by volume) $C_2H_4Br_2$.

1 cc. N/20 $AgNO_3$ corresponds to: 0.004697 gms.

$CH_2H_4Br_2$ or: 0.002155 cc. $C_2H_4Br_2$ (D_4^{20} : 2.180)

Consequently:-

x = (10 - a). 0.01879 grammes/100 ccs.
y = (10 - a). 0.00862 ccs/100 ccs. (% by volume).

The estimation can also be done without a flame or cooling water, by shaking hard for 20 minutes in a ground glass jointed Erlenmeyer at room temperature (above 15°C.), instead of boiling under reflux for 20 minutes.

The same method can be used with 5 ccs., if slight alterations are made.

The reaction times specified (20 minutes) are twice as long as really necessary with the less active zinc (catalogue No. 74113), to make sure of complete reaction. The density given for ethylene bromide in the literature on the subject varies greatly (2.177 to 2.182). The Ethyl Company uses, according to verbal information, ethylene bromide from D_4^{20} : 2.17 to 2.19.

The slight errors inherent in the Volhard method are not considered any further here, since they are of no importance from the point of view of this test, and the process should be as clear and simple as possible. For further details see Kolthoff-Menzel, "Volumetric Analysis", Springer 1931.

Ethylene bromide content of "I.T" Fluid.

100 grammes = 56.98 ccs. of "I-T Fluid" (D_4^{20} : 1.755) should contain: 61.42 grammes = 37.11 ccs. of Pb $(C_2H_5)_4$(D_4^{20} : 1.655) and 35.68g = 16.37 cm³ $C_2H_4Br_2$ (D_4^{20} : 2.18).

(Accordingly, the volumetric ratio of tetraethyl lead to ethylene bromide is 2.267:1; "I.T" fluid to tetraethyl lead is 1.535:1).

Results.

Fuel	Mixed with ethylene bromide (Schering, purest) g/100 ccs.	found:	
		20 mins.under reflux	shaken for 20 mins.
		g/100 ccs.	
B4 215/41	0.11422	0.1140	0.1140
63 223/41	0.11722	0.1175	0.1170

	Treated with "I.T." fluid, corresponding to 0.1185% by vol.TEL(n.DVL) corr.to ethylene bromide. % by vol.	found:	
		20 mins. under reflux	shaken for 20 mins.
		% by vol.	
Rumanian distilled gasoline (21/40)		0.0515	0.0515
B4(215/41)		0.0515	0.0520
C3(223/41)	0.0525	0.0515	0.0515
T52(isop)		0.0520	0.0515
329/41			
DHD(3/42)		0.0515	0.0515

Blanks done on C3 and B4 were within the limits of error. The standard solutions used were "Fixanal substances" of Riedel de Haën.

An exploratory test with a strongly unsaturated fuel (Russian cracked gasoline, 157/40, J.Z.82) gave a brownish coloration of the aqueous layer before titration, so that it was necessary to titrate in steps of 0.1 cc. to get an accurate end point.

Content of T.E.L.:- 0.1185 gms./100 ccs.* = 0.0525 cc./100 ccs.
Found:- 0.0515 cc./100 ccs. after 20 minutes refluxing
0.0510 cc./100 ccs. after 20 minutes shaking.

IV - DETECTION AND DETERMINATION OF AGEING PRODUCTS OF TETRAETHYL LEAD IN FUELS.

1. Principles of the method of determination: In tracing the ageing or oxidation of leaded fuels, a more minute investigation was made of the decomposition products of tetraethyl lead. The detection or determination of the individual stages of decomposition being of general interest, some details are given here about the analytical method.

As regards the decomposition of tetraethyl lead in fuels under conditions of natural and artificial ageing, it could be proved that of the separated lead sludge only part consists of lead (Pb⁺⁺) compounds, and also that the fuel itself contains already affected tetraethyl lead in solution. In lead sludge diethyl lead⁶) compounds predominate, while the solution contains mainly triethyl lead compounds. These substances are present in part as salts of carbonic acid, and of the acids present in the fuel. Their solubility in fuel is in descending order as follows, falling off very rapidly :-

Triethyl-, diethyl lead, and lead (Pb⁺⁺) compounds.

All the decomposition products of tetraethyl lead are relatively strongly ionised in water. In order to identify them, use was made of diphenylthio-carbazone (dithizone), which gives, quantitatively, colours which are typical of the stages of decomposition.

The principle of the determination has already been discussed (4), and can be briefly summed up as follows :-
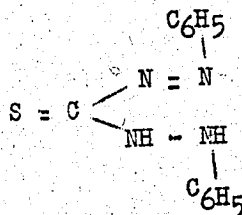
Primarily, dithizone, ammonia, and the lead compound to be determined should be present in a pair of fluids which do not mix. The two fluids should be such that as far as possible one of them (water) will dissolve the ammonium salt of diphenylthiocarbazone to a great extent, and practically speaking will not dissolve the dithizone or lead dithiazonate. The other fluid (carbon tetrachloride) should as far as possible have a large solubility for lead dithiazonate, and should dissolve relatively little of the free dithizone, and practically none of the ammonium salt. If there is too little dithizone present, then, after shaking up the two fluids well, lead dithiazonate will form quantitatively, and the aqueous layer remain colourless. As soon as there is excess dithizone present, the aqueous layer is coloured brownish yellow by the ammonium dithiozonate which forms. This is taken as the end point of the titration.

* Translator's note: The text gives this as 0.1185 vol.% = 0.0525 vol.%.

Lead (Pb^{++}) dithiazonate dissolves slightly in carbon tetrachloride (giving a red colour), while diethyl lead dithiazonate and triethyl lead dithiazonate dissolve easily in carbon tetrachloride, giving orange and yellow respectively.   There was no evidence that all three were soluble in the aqueous phase.   When a triethyl lead salt is titrated with dithizone (in the presence of weakly alkaline aqueous solution) in daylight, it shows considerable instability in the reaction mixture, which is expressed in a yellow coloration of the aqueous layer and an orange coloration (diethyl lead dithizonate) of the carbon tetrachloride phase. If light is excluded, these phenomena practically speaking do not occur. The same is true, though to a negligible extent, of the titration of diethyl lead and lead (Pb^{++}) salts.

In a mixture of triethyl-, diethyl lead, and lead (Pb^{++}) salts, the lead compounds clearly react in a weak alkaline solution (0.1 (NH$_3$), in that order, and so make a qualitative assessment possible. But it is impossible to draw conclusions from this about the absolute stability of dithizonates in a certain p$_H$ range without knowing exactly the conditions of solubility.

It is not possible to say much here about the structure of the dithizonates - which are of no further interest here - since no thorough investigations have been made into this question.   E. Fischer assumes for diphenylthiocarbazone the formula :-

$$S = C \Big\langle \begin{array}{c} \overset{\displaystyle C_6H_5}{\underset{\displaystyle |}{}} \\ N = N \\ \\ NH - NH \\ \underset{\displaystyle C_6H_5}{\overset{\displaystyle |}{}} \end{array}$$

while E. Bamberger (6) regards dithizone as a mercaptan without a tendency to revert to keto form.   H. Fischer (7) uses E. Fischer's formula in his publications.   He states that, according as one is working in an alkaline or acid solution, dithizonates with 2 or 1 gramme atoms of mono-valent metal per molecule of dithizone (e.g. with Ag) will be obtained, and explains it by the occurrence in certain dithizonates of keto-enol tautomerism.   He assumes the keto form for lead (Pb^{++}) dithizonate (in alkaline solution).   On checking with silver, the consumption of dithizone solution was found to be the same, in an alkaline or acid solution, being half that for lead (Pb^{++}) solutions.   When up to half the required volume of dithizone solution is added to a strongly alkaline silver solution, the reddish-violet precipitate (1 mol. dithizone/2-gramme/atoms of silver) mentioned by H. Fischer, forms (almost quantitatively in a weak solution).   This is insoluble in carbon tetrachloride.   When further titrated, this deposit dissolves quantitatively in carbon tetrachloride, giving a yellow-orange colour, until the end point is reached, without discoloration of the watery layer by excess dithizone (1 mol. dithizone used per gramme-atom of silver).   By titrating first in acid solution, adding only half the required volume of dithizone solution, and then making it alkaline and shaking, the carbon tetrachloride solution is immediately decolourised, and the red-violet precipitate forms.   If it were actually a question of keto enol tautomerism, then an extremely rapid readjustment of equilibrium would have to be assumed.   The position of equilibrium would largely be determined by the capacity of metal present to give very stable, that is, only weakly ionised salts, in combination with the SH-group.

The properties of diethyl and triethyl lead dithizonate and of lead (Pb⁺⁺) dithizonate are similar, so that the three may be assumed to have the same structure. The combining ratio between dithizone and triethyl lead compounds is (as the example with silver shows) 1 molecule per molecule, whereas 2 molecules of dithizone are required for each molecule of diethyl lead and lead (Pb⁺⁺) compounds. The "secondary valency linkage" may be brought about in principle either by the single electron pair of the azo nitrogen attached to the phenyl group, or by that of the sulphur.

A direct quantitative estimation of triethyl lead compounds in presence of diethyl lead and Pb⁺⁺ compounds is therefore possible, as formation of triethyl lead dithizonate requires only half as much diphenylthiocarbazone as formation of the salts of the others. It is thus only necessary to determine the lead content of fuel (by the D.V.L. method), then determine its content of dissolved or suspended ionised lead compounds by direct titration (see section 3 of this report), and finally to remove the tetraethyl lead decomposition products quantitatively by washing the fuel with dilute nitric acid, and again carry out a lead determination. If c ccs. of dithizone solution were required in the total lead determination, d ccs. in the direct titration, and e ccs. after removal of the tetraethyl lead decomposition products, then, if n is the number of ccs. required for triethyl compounds, and v that for diethyl lead (and divalent lead) compounds :-

$$n + v = d$$
$$2n + v = c - e$$

$$n = c - e - d \text{ (ccs.)}$$
$$v = 2d - c + e \text{ (ccs.)}$$

The number of ccs. of dithizone solution used must of course refer throughout to the same volume of fuel ($\frac{1}{2}$ cc. in the test).

2. **Experimental work:** To ascertain the behaviour of triethyl lead compounds towards dithizone, it was necessary to produce them in as pure a form as possible. The attempt to prepare triethyl lead bromide by the method of G. Grüttner and E. Krause (8) proved unsatisfactory owing to the simultaneous formation of diethyl lead bromide. On the other hand, a largely pure product was obtained by reaction of dry hydrogen chloride gas with dry tetraethyl lead (9).

The triethyl lead chloride was prepared as follows :-

HCl gas was passed into a 5% solution of tetraethyl lead in dry petroleum ether at 0°C. until no more precipitate is observed to form. The white needles produced were rapidly filtered off, dissolved in a little benzene, and treated with sufficient petroleum ether to cause slight precipitation. It was then left to stand for five minutes, treated with a trace of benzene, and filtered rapidly through a folded filter. The triethyl lead chloride is reprecipitated from the filtrate by slowly adding 200 ccs. of petroleum ether (from a dropping funnel); it was then filtered through a sintered glass crucible, and washed for a short while with benzene/petroleum ether (1:3). It was then recrystallised twice from benzene/petroleum ether (heated to a maximum of 50°C.), and dried in a dessicator over Ca Cl₂ (evacuating 5 times in the course of two hours, and letting in dry air again). The needle-shaped crystals so obtained were stored under vacuum in absence of light.

The lead triethyl chloride was dissolved in benzene/standard gasoline (30:70) or in a synthetic aromatic fuel, and titrated after adding 2 ccs. of 0.1% of ammonia and carbon tetrachloride. The end point is difficult to determine, as the aqueous layer begins to turn yellow when 50% of the volume of dithizone required has been added. The yellow colour is not, however, due to complete reaction of the triethyl lead ions with dithizone. In contrast to lead (Pb^{++}) dithizonate, triethyl lead dithizonate is even fairly stable in solutions containing up to 5% of ammonia. Triethyl lead dithizonate is also insoluble in the aqueous layer. The colour in the aqueous layer fades sharply towards the end of the titration, and on addition of 0.1% of NH_3 solution and vigorous shaking in diffused daylight, always reappears.

Simultaneously the carbon tetrachloride layer becomes orange-coloured (diethyl lead dithizonate). In the presence of nitrogen there is less discoloration. In absence of light, the titration is normal, that is, there is no discoloration.

It is thus a question of a change caused or accelerated by light (and oxygen) in the triethyl lead - (or ammonium dithizonate - the latter caused by the presence of triethyl lead ions). This instability can be somewhat reduced by adding CN ions.

To obtain useful results, it is necessary to work in very subdued daylight, or to titrate as rapidly as possible. In practical fuel analysis, when greater or smaller amounts of oxidation products (peroxides) may be present, it is an advantage to work with an addition of KCN, especially when the effect of light can hardly be excluded. This also prevents interference by any extraneous metals (except bismuth, stannic tin, and thallium). The cyanide-ion has the disadvantage of being so firmly attached to the lead that the equilibrium is somewhat displaced by it, but in presence of K Cl (which represses the dissociation of KCN) this effect becomes negligible. The values found under the various conditions are shown in Table 2a.

With lead (Pb^{++}) - and diethyl lead compounds the addition of KCN causes a displacement of the end point, which decreases with increasing purity of the dithizone solution. Under the titration conditions selected, nothing can be predicted about the exact position of the equilibrium of the reaction tending towards the formation of dithizonate. The difficulty is caused by differences in the solvents used for the dithizonates, by secondary reactions giving decomposition products of dithizone. As it was found that consistent values could be obtained by using pure dithizone, no further investigations were made into the reduction (due to the concentrations of hydrion and KCN used) in the volume of dithizone solution required with Pb^{++}, diethyl lead, and (to a certain extent and in saturated K Cl solution) with triethyl lead compounds. Good results were also obtained with solutions of low lead content at corresponding dilutions. The results can be seen in more detail in Tables 2a, b, and c. They show with sufficient clarity the accuracy and usefulness of the analytical methods. The margin of error in this determination would be about ± 0.1 ccs. of dithizone solution, with Pb^{++} salts, if a pure dithizone solution is used and the possibility of error in titration is taken into account (see Section II). The relative values (those of the three types of combination by themselves) are of course more accurate. See Section II for the tests on the purity of the dithizone solution. See Table 3 for the influence of oxidation products.

The behaviour of ethyl lead compounds, that is, of lead with three free valencies was not observed. The stability of these substances is probably very low.

Method of Analysis.

1 cc. of fuel is treated in a shaking flask with 2.5 ccs. of purest carbon tetrachloride, and 2.5 ccs. of a concentrated solution of chemically pure potassium chloride, containing 0.1% of ammonia (NH_3), 0.5% of Rochelle salt, 0.5% of sodium thiosulphate. 0.25 ccs. of 2.5% KCN solution is then added and the mixture titrated with the standard dithizone solution, until there is a faint brown colouration of the aqueous layer. If a further 0.10 cc. of dithizone solution (0.20 cc. if there is a high content of a triethyl-lead compound) is added, the brown colouration should become noticeably darker. In contrast to the results with diethyl lead and lead (Pb^{++}) compounds the end point cannot be clearly identified. If the titration is done without adding KCN and KCl, the end point can be clearly seen.

The titration must always be done in very subdued daylight, especially in absence of KCN and KCl. After adding the first main volume of the di - solution, shake for about 20 seconds; then titrate 0.1 ccs. at a time, shaking for about 5 seconds each time. In the presence of large amounts of peroxide, the titration is begun shortly before the expected end point, or before the end point determined in a preliminary test (see Table 3).

If the carbon tetrachloride solution remained yellow to brownish yellow right up to the end point, the lead content is calculated exactly as for the normal lead determination, except that, since the triethyl lead compound only requires half the volume of dithizone, the basis of the calculation is the volume of dithizone solution used (x ccs.) per 1 cc. of fuel.

Triethyl lead compound = x x F % by volume (·7)
$\qquad$ (calculated as tetraethyl lead).

If the solution of carbon tetrachloride did not remain yellow, but became orange to red, or if the orange colour was present initially, the analysis was done as already described in Section IV, 1. Thus :-

Estimation of total lead by the D.V.L. method :-

Consumption: c ccs. of dithizone = solution.

The sum of triethyl, diethyl lead and lead (Pb^{++}) compounds is determined with dithizone as just described for triethyl lead compounds, but related to $\frac{1}{2}$ ccs. of fuel; consumption; d ccs. of dithizone solution.

The fuel is shaken with 15% of a half per cent solution of nitric acid (1 volume of A.R. 25% H NO_3, to 49 volumes of H_2O), the aqueous layer drained for 5 minutes (after settling), shaken twice every three minutes with 5% of its volume of H_2O, drained, dried for a short while with Na_2SO_4, and when the Na_2SO_4 has settled, the lead content determined by the DVL method; consumption: e ccs. of dithizone = solution.

Calculation:-

In determining the sum of triethyl lead, diethyl lead and lead (Pb^{++}) compounds; u ccs. is the amount of triethyl lead, and v ccs. that of diethyl lead and lead (Pb^{++}) compounds. As was proved :-

$\qquad$ u = c - e - d ccs. dithizone solution.
$\qquad$ v = 2d - c + e ccs. = solution.

Hence the content is :-

triethyl lead compound
(c - e - d). 2F ccs./100 ccs. (calculated as tetraethyl lead)
diethyl lead - (+ lead (Pb^{++}) - compound :-
(2d - c + e). F ccs./100 ccs. (calculated as tetraethyl lead)

If the fuels contain many oxidation products (e.g., peroxides after ageing in a bomb), then to determine d, add KCN before the titration, and shake well with the given solution.

The accuracy with which it is possible to carry out the analysis depends on the extent to which in the D.V.L. lead determination the tetraethyl lead already decomposed in solution is converted quantitatively by the sulphuryl chloride to a compound which is insoluble in fuel. Table 3 shows examples which prove that decomposed tetraethyl lead in solution is actually completely precipitated by $SO_2 Cl_2$.

Firstly all the bomb tests are reported which were made with only a triethyl lead compound present, over a period of 6 months (Tests 1 to 4). In these tests, the difference in lead content before and after the D.V.L, treatment are comparable with the values determined directly. It will be seen that the results agree very well. They would agree even better with fuels not treated in the bomb. In Test 5, practically only diethyl lead salts were formed during the bomb ageing, and the agreement is good. Generally speaking, after artificial ageing mainly triethyl lead and some diethyl lead salts are found in solution. At the end of the Table (test 6) is shown still another test in which diethyl lead acetate was produced by the reaction of diethyl lead chloride with silver acetate, and dissolved in a fuel. This fuel also gives good agreement between the values found by direct titration and those by the D.V.L. lead determination.

It was considered unnecessary to develop the estimation of Pb^{++} compounds in presence of diethyl lead compounds any further. A photometric method should prove most suitable.

A useful idea was given by direct titration as Triethyl lead- and Diethyl lead compounds can be made to react in a definite order before Pb^{++} compounds. Examples are given in Table 4 showing the practicability of this.

V - REFERENCES.

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2. loc. cit.

3. loc. cit., p.456.

4. loc. cit.

5. E. Fischer, Liebigs Ann. 212, 216 (1882).

6. E. Bamberger, R. Padova and E. Armerod. Liebigs Ann.446, 271 (1925).

7. H. Fischer, Angen. Chemie 50, 919 (1937); W.Prodinger "Organic Precipitants in Quantitative Analysis."

8. G. Grüttner, E. Krause, Ber.deutsch.chem. Ges. 49, 1426 (1916).

9. G. B. Buckton, Liebigs Ann. 112, 227 (1859).

Table 2a.

Test No.	Type of lead compound	Vol. used ccs.	Aqueous solution			Effect of Light	Dithizone solution	
			NH$_3$ content %	Addition of KCN solution 2½% ccs.	Addition of KCl		found	calculated *
1	Triethyl			0.25	+	Light	11.20	
2	lead chloride		0.1	-	-	excluded	11.30	
3					+		11.20	11.20
4	dissolved in	2.5	0.25	0.25	+	Very	11.20	
5			1.0		+	sub-	11.20	
6	gasoline-benzene			-	-	dued	11.30	
7	(paraffin-based) 3 : 7			0.25	+	day-	2.20	2.24
8	0.08555 g/100 ccs.	0.50	0.1	-	-	light	2.30	
9				0.25	+		1.10	1.12
10		0.25			-		1.20	

*These values are calculated from the weighing (column 2) and from the consumption of the dithizone solution with lead (Pb^{++}) salts (test solution). The correction caused by the addition of chloroform is taken into account (see Table 4).

A lead estimation by the D.V.L. method on the above triethyl lead chloride solution gives a content of 0.0500% by volume of tetraethyl lead compared with the calculated figure of 0.0506.

Colour of the tetra layer: Tests 1 - 6 - brownish-yellow
" " " " " " 7 -10 - yellow.

If KCN is added without KCl, a slight brown colouration is observed 10% before the end point in the aqueous layer. This occurs in darkness or in subdued daylight. The end point is not clearly defined, and even with over-titration it is difficult to identify.

To test the behaviour under slow titration in very subdued daylight, with and without KCN and KCl, titration was first done with 5 ccs. of dithizone solution. There was practically no yellow colouration of the aqueous layer, and no orange colouration of the carbon tetrachloride layer. The end points correspond to those for rapid titration. In diffused or bright daylight there is a yellow colouration of the aqueous layer, and a rapidly progressing orange colouration of the carbon tetrachloride layer; the values obtained are higher or lower according to the effect of light.

Table 2b.

Test No.	Type of lead compound	Vol. used. ccs.	KCN solution added 2½% ccs.	Content of bases	Dithizone solution ccs. Found	Ref.value
			Aqueous solution		Dithizone solution	
1				0.1% NH$_3$	10.75	
2	Diethyl lead			0.25% NH$_3$	10.75	
3	salt		0.25	1% NH$_3$	10.75	10.75
4	content by the	2.50		(0.1% NH$_3$ (0.1% KOH	10.70	
5	D.V.L.		0.05		10.75	
6	method				10.80	
7	of	0.50	0.25		2.15	2.13
8	lead			0.1% NH$_3$	2.15	
9	estimation	0.25	0.25		1.05	1.07
10					1.05	.07

In tests 3 and 4, the light yellow colour appeared shortly before the end point.

Colour of the C Cl$_4$ layer = orange.

To test the behaviour on slow titration in diffused daylight with and without KCN addition a titration was first done with 5 ccs. dithizone solution. A very slight yellow colouration of the aqueous layer before the end point occurs only when the titration is done without KCN. The end point corresponds in both cases to that which was found on rapid titration.

Test No.	Type of lead compound	Vol. used ccs.	Aqueous solution		Dithizone solution ccs.	
			KCN solution added (2½%)ccs.	NH₃ content	Found	Reference value
1	Lead (Pb⁺⁺) salt			0.05	7.97	
2	corresponding			0.10	7.97	
3	to 0.09360 gm.		0.25	0.25	7.95	
4	lead in	2.50		0.50	7.92	7.95
5	500 ccs.			1.0	7.90	
6	of a solution			2.0	7.80	
7	containing:		0.05		8.00	
8	0.1% Na₂S₂O₃		–		8.00	
9	0.5% KnaC₄H₄O₆	0.50	0.25	0.25	1.55	1.59
10	and NH₃		–		1.60	
11	(For amount	0.25	0.25		0.75	0.80
12	see col.5.)		–		0.80	

Test 4 showed yellow coloration from 7.80, test 5 from 7.60, and test 6 from 7.30 ccs. Colour of the C Cl₄ layer : red.

To test the behaviour under slow titration, the procedure was that given in Table 1b. With no KCN added, a slight gold coloration appears towards the end of the titration, the end point is not well-defined, and is about 0.05 cc. lower than in the rapid titration. In the presence of KCN there is no difference compared with normal titration.

Table 3.

Test No.	Content of dissolved, decomposed tetraethyl lead		Colour of the C Cl₄ layer	
	Direct titration	Difference method	At the beginning	At the end
1	0.0450	0.0445		brown-yellow
2	0.0390	0.0395		yellow-brown
3	0.0395	0.0385	yellow	brownish-yellow
4	0.0085	0.0080		yellow
5	0.0670	0.0680	orange	orange
6	0.0895	0.0900		

By direct titration is meant the analytical process for pure triethyl lead compounds given in Section IV, 3; but the titration is done in diffused daylight. The values in the column marked "difference method" give the differences in the lead values before and after the fuels were washed with dilute nitric acid (see Section IV, 3.).

Test 6 shows that the dissolved diethyl lead salts are almost completely precipitated with sulphuryl chloride.

Tests 1 - 5 show that those fuels which have been aged in a bomb (in some cases the induction period was under 240 minutes), that is to say, contain oxidation products, also give good values under conditions of direct titration. If direct titration were carried out in very subdued daylight, there would be an even better agreement between the results. Before ageing, the fuels had a tetraethyl lead content of about 0.120% by volume.

If a fuel is filtered (folded filter of 9 cms. diameter), then on the average (according to temperature and type of fuel), it can be assumed that there is an enrichment of 1% of tetraethyl lead or soluble decomposed tetraethyl lead, and this must be taken into account.

A test on heptylene which had stood for 5 years and had a high peroxide content gave unsatisfactory results on direct titration. Highly acidified fuels must of course be neutralised by direct titration.

(footnote to Table 4.)

The titrations were made in diffused daylight, strong light being avoided. The aqueous solution used (about 2.5 ccs.) contained 0.1% of NH_3, 0.5% $KNaC_4H_4O_6$, and 0.5% $Na_2S_2O_3$. In the tests in which KCN or KCN + K Cl was added, the volumes added were as given in Section IV, 3.

Where the values are sharply outlined, this indicates that the change in colour could be clearly seen. In the penultimate column (11), under "found", the end points given for the titrations are necessarily badly defined and inaccurate (since they were done in diffused daylight). The last column (12) shows, under "calculated", the sum of the values obtained for the individual substances (before mixing) by the normal type of determination given in the report; the titration of the triethyl lead salts was, however, done in diffused daylight (columns 2 to 4). It will be seen that if KCN and K Cl are not added to mixtures of triethyl lead, and lead (Pb^{++}) salts, good values are obtained (This type of analysis is, however, actually only possible in the absence of large amounts of oxidation products (peroxides, etc.)). With mixtures of triethyl and diethyl lead salts the possibility of differentiation is very slight, while with mixtures of diethyl lead and lead (Pb^{++}) salts, good values are obtained (with some practice) for the individual components.

Table 4.

Test No.	mixture contains Triethyl lead salt corresponding to ccs. Dithizone	Diethyl lead salt corresponding to ccs. Lithizone	Lead(PbS) salt corresponding to ccs. Dithizone titration	Additions to one titration	Colour of the tetra layer yellow up to ccs.	orange tinge from ccs.	orange from ccs.	orange-red from ccs.	red from ccs.	Total consumption ccs. Dithizone found	calculated
1	1.00	-	7.35	(KCl (KCN	0.4	0.6	1.0	1.2	2.0	8.35	8.35
2	1.00	-	7.35	KCN	0.4	0.6	1.0	-	1.8	-	-
3	1.00	-	7.35	0	1.0	1.0	1.1	-	1.7	8.30	8.35
4	9.50	-	0.60	(KCl (KCN	7.0	8.0	shading to brown orange			10.20	10.10
5	9.50	-	0.60	0	9.3	9.4	shading to brownish orange			10.10	10.10
6	0.25	10.30	-	0	0.1	0.1	shading to orange			-	-
7	1.0	9.95		0	0.5	0.6	" via yellow orange to orange.			10.90	10.95
8	4.60	4.05		0	4.0	4.0	shading via brown orange to orange.			9.00	8.65
9	4.60	4.05		(KCl yellow,brownish-yellow (KCN yellow,brownish-yellow	1.5	1.5	shading via yellow orange to orange			8.70	8.65
10	7.10	10.40		(KCl no pure yellow (KCN colour	0.5		shading via brownish orange to orange.			10.50	10.25
11	9.40	0.80		0	9.0	9.0	shading to orange			10.50	10.25
12	9.40	0.80		brownish-yellow (KCl 0.9 0.9 (KCN yellow,brownish+yellow	0.9	0.9	shading via brownish			10.30	10.25
13	-	1.05	7.40	KCN	" up to 0.90	" to 0.90	2.0			-	-
14	-	2.00	7.90	KCN	" 2.10	" 2.10	3.0			9.85	9.90
15	-	2.00	7.40	-	" 1.80 shading to orange red, changing soon					-	-
16	-	10.40	0.15	KCN	" 10.55 to red.					10.55	10.55

Footnotes not inserted in
Report.

1) For the above, it is sufficient to have "purest methyl cyclo hexane" of Deutsche Hydrierungswerke" Rodleben. The chloroform need not be further alcohol-freed

2) For this estimation 12 G 4 sintered glass crucible of 20 -25 secs. filtering time for water should be used.

3) The solution and washing are best done with 250 ccs. of a solution containing 0.1% NH_3 and the whole of the Rochelle salt and thiosulphate; this is then made up to 500 ccs. with 0.3% Ammonia solution.

4) Production of ethylene from ethylene bromide by means of zinc and alcohol; Gladstone and Tribe, Ber. 7(1874) p. 364 with zinc and acetic acid: Zelinsky, Schlesinger, Ber. 41 (1908) p. 2431.

5) Zinc dust contains oxide and halogens, and must therefore be purified as follows (100 grammes are sufficient for 100 tests) : Zinc powder is shaken with about 10 times its weight of $2\frac{1}{2}$ per cent acetic acid for about 10 minutes. After the zinc powder has settled the acetic acid is poured off as completely as possible. This is repeated twice - three minutes shaking is now sufficient - and finally the zinc is poured into a sintered glass crucible and washed with dilute acetic acid followed by alcohol. The alcohol is sucked out, and then the remainder of the acetic acid displaced or washed out by pouring on and sucking through at least 5 lots of alcohol. The alcohol is then displaced by ether, and the zinc is dried in a vacuum dessicator (without Ca Cl_2) aired two or three times, and then stored in a well -sealed flask. Of course, all the chemicals and apparatus used must be tested to make sure that they are halogen-free.

    (The substances used for the test were : A.R. Zinc powder, Schering, Catalogue number 74,104, and Zinc powder Schering, Catalogue number 74113.)

6) To avoid misunderstanding:- Triethyl and di-ethyl lead compounds always mean in this text doubly or trebly covalently linked lead with 1 or 2 "residual valencies."

7) See section II,2.