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TECHNICAL EXPERIMENTAL STATION.

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

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SUMMARY: A method is described for detecting the individual products of decomposition of lead tetraethyl in naturally or artificially aged leaded fuels together with a method for the quantitative determination of triethyl-lead compounds in the presence of compounds of diethyl-lead and divalent lead compounds. Furthermore and by way of supplement to DVL Research Report No. FB.1292, a method is described for the direct standardisation of dithizone solutions.

CONTENTS.

I. INTRODUCTION.

In following the ageing or oxidation of leaded fuels, the products of decomposition of the lead tetraethyl have also been examined. Since the detection or the determination of the various stages of decomposition are of interest, further details will be given below as to the method of analysis.

II. PRINCIPLES OF THE METHOD OF DETERMINATION.

For the decomposition of lead tetraethyl in fuels under conditions of natural and artificial ageing, it could be shown that, of the separated lead sludge, only a small part consists of bivalent lead compounds, and that, moreover, the fuel itself contains decomposed lead tetraethyl in solution. In the lead sludge, diethyl-lead compounds predominate (in order to obviate misunderstandings: By a triethyl- and diethyl-lead compound we always mean here compounds in which lead is linked by 2 or 3 bonds with 1 or 2 "free valencies".), while triethyl-lead compounds are mainly to be found in solution. These substances occur, to a large extent, as the salts of carbonic acid and acids present in the fuel. Their solubility in the fuel decreases very sharply in the order: triethyl-lead - diethyl-lead and bivalent lead compounds.

All products of decomposition of lead tetraethyl are relatively highly ionised in water. To detect them, diphenyl-thiocarbazone (dithizone)is

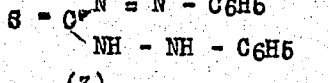
used, which gives quantitatively characteristic coloured compounds.

The fundamentals of this method of determination have already been reported[1]. To sum up briefly, the procedure is as follows: Dithizone, alkali and the lead compound to be determined are first added to a non-miscible pair of liquids. The two liquids are to be selected so that one of them, as far as possible, possesses great solubility for the ammonium salt of diphenylthiocarbazone and practically no ability to dissolve dithizone or lead dithizonate (e.g. water). The other liquid should have, as far as possible, a relatively great ability to dissolve lead dithizonate, a relatively low degree of solubility for the free dithizone and practically none at all for the ammonium salt (e.g., carbon tetrachloride). If too little dithizone is present, there is formed quantitatively (if necessary, after the two liquids have been well shaken together), the corresponding lead dithizonate; the aqueous layer remains colourless. If the dithizone is present in excess, the aqueous layer is tinged a brownish yellow by the ammonium dithizonate formed. This point is taken as being the end-point of the titration.

The divalent lead dithizonate is sparingly soluble in carbon tetrachloride (red colour), while the diethyl-lead dithizonate (orange colour) and the triethyl-lead dithizonate (yellow colour) dissolve readily in carbon tetrachloride. The solubility of the divalent lead, and the diethyl and triethyl-lead dithizonate in the aqueous phase could not be ascertained direct. When a triethyl-lead salt is titrated with dithizone (in the presence of the faintly alkaline-aqueous solution), it shows, in daylight, a relative high instability in the reaction mixture, which is indicated by the appearance of a yellow tinge in the aqueous layer and an orange tinge (diethyl-lead dithizonate) in the carbon tetrachloride phase. In the absence of light, these phenomena practically do not occur. The same applies, to a completely negligible extent however, in the titration of diethyl-lead and divalent lead salts.

In a mixture of triethyl-lead, diethyl-lead and divalent lead salts, the lead compounds react distinctly in a faintly alkaline solution (0.1% NH_3) in the above sequence, and thus permit a qualitative determination to be made. Conclusions as to the absolute stability of the dithizonates in a determined pH range cannot, however, be drawn without an exact knowledge of the solubility relationships.

Not very much can be said regarding the structure of the dithizonates (and the matter is of no further interest here) as no detailed investigations have been carried out in this direction. E. Fischer[2] assumes for diphenylthiocarbazone the formula



while E. Bamberger[3] suggests a mercaptane structure for dithizone which does not readily ketonise. H. Fischer,[4] in his published work, refers to E. Fischer's formula. He indicates that according to whether one works in an alkaline or an acid solution, dithizonates having 2 or 1 atoms of a monovalent metal per mol of dithizone (e.g. with Ag) can be obtained, and this he explains, in the case of actual determined dithizonates, by the occurrence of keto-enol tautomerism. For divalent lead dithizonates he assumes (in alkaline solution) the keto form. A test with silver showed that the same consumption of dithizone solution occurred both in alkaline and in acid solution, and in fact half the consumption as with a divalent lead solution. Moreover, on the addition of up to half the required amount of dithizone solution to a strongly alkaline silver solution, the reddish-violent precipitate mentioned by H. Fischer (1 mol Dithizone/2 atoms silver) is formed, which is insoluble in carbon tetrachloride; (in dilute solutions this takes place almost quantitatively.) On further titration, this precipitate however dissolves quantitatively in the carbon tetrachloride with a yellowish-orange colour until the end-point is reached, and until the appearance of a discolouration in the aqueous layer by excess

dithizone (consumption 1 mol dithizone/1 atom silver). If the titration is first carried out in an acid solution, only half the required amount of dithizone solution being added, then made alkaline and shaken, the carbon tetrachloride solution will immediately be discoloured, and the reddish-violet precipitate will form. If this is really a keto-enol tantomerism it would have an extremely rapid attainment of equilibrium to be assumed. The point of equilibrium would probably be determined by the ability of certain metals to give very stable, (i.e., only faintly ionised) salts with the SH group.

The properties of the diethyl- and triethyl-lead dithizonates and the divalent lead dithizonates are similar, so that for all three dithizonates, fundamentally the same structure can be assumed. The bond ratio between dithizone and triethyl-lead compounds (as shown by the example with silver) is 1 mol per molecule, whereas 2 mols of dithizone per molecule of diethyl-lead and divalent lead compounds are required. The "secondary valency link" can be caused, in principle, both by the single electron-pair of the azo-nitrogen carrying the phenyl group, and by that of the sulphur. Perhaps later on there will be an opportunity of discussing the dithizonates in greater detail.

The possibility of a direct quantitative determination of the triethyl-lead compounds in the presence of diethyl-lead and divalent lead compounds is afforded by the fact that the former compound requires half the quantity of diphenylthiocarbazone for forming the dithizone salt than that required by the diethyl-lead and divalent lead compounds. It is, therefore, only necessary to determine the total lead-content of the fuel by the DVL method[5] then, by direct titration of the fuel (see Section IV of this report), to determine its lead content as dissolved or suspended ionised lead compounds, and finally, by washing the fuel with dilute nitric acid, to remove quantitatively the decomposition products of the lead tetraethyl and re-determine the lead content of the fuel. If c cubic centimetres of dithizone solution were used in the determination of total lead d cubic centimetres in the direct titration and e ccs. after the removal of the decomposed lead tetraethyl, and if u is the number of cubic centimetres of dithizone solution corresponding to the triethyl-lead, and v the number of cubic centimetres corresponding to the diethyl-lead compounds (together with divalent lead compounds), we thus have:

$$\begin{aligned} u + v &= d \\ 2u + v &= c - e \end{aligned}$$

$$\begin{aligned} u &= c - e - d \quad (cc) \\ v &= 2d - c + e \quad (cc) \end{aligned}$$

The number of cubic centimetres of dithizone solution consumed naturally refers throughout to the same amount (in this work, $\frac{1}{2}$ cc.) of the fuel.

III. EXPERIMENTAL SECTION

In order to ascertain the behaviour of the triethyl-lead compounds with dithizone, it was necessary to prepare this compound in as pure a form as possible. The attempt to prepare triethyl-lead bromide by the method of G. Grüttner and E. Krause[6] did not produce satisfactory results, owing to simultaneous formation of diethyl-lead bromide. On the other hand, by the double decomposition of dry hydrochloric acid gas and lead tetraethyl[7], a very pure product was obtained. The tetraethyl lead chloride was prepared as follows: Hcl gas was passed at 0°C into a 5% solution of lead tetraethyl in dry petroleum ether, until no further precipitation could be observed. The white needles that formed were rapidly filtered off by suction, dissolved in a little benzene and treated with petroleum ether until a slight precipitation just re-appeared. It was then allowed to stand for 5 minutes, treated with a trace of benzene and quickly filtered through a fluted filter. By the slow addition (with a dropping funnel) of 200 ccs petroleum ether (to the filtrate), the triethyl-lead chloride was again re-precipitated,

filtered through a sintered-glass crucible and rinsed slightly with benzene-petroleum ether mixture (1 : 3). It was then twice recrystallised from benzene-petroleum ether (heat to maximum of 50°C) and dried in a desiccator over $CaCl_2$, evacuating about 5 times during a period of two hours and letting dry air in. The needle-like crystals are stored in a vacuum away from the light.

The triethyl-lead chloride is dissolved in benzene-standard gasoline (30 : 70) or a synthetic aromatic fuel, and titrated after the addition of 2 ccs. of 0.1% ammonia and carbon tetrachloride. The end-point is difficult to recognise, as even after the addition of 50% of the requisite amount of dithizone, the aqueous layer begins to be tinged yellow. This yellow colouration is not, however, due to incomplete reaction of the triethyl-lead ions with the dithizone because - if the yellowish aqueous layer is removed before the estimated end-point is reached - it gives no reaction for dithizone. In contradistinction to divalent lead dithizonate, the triethyl-lead dithizonate is still fairly stable in solutions containing up to 5% ammonia. The triethyl-lead dithizonate is also insoluble in the aqueous layer, as can be proved, if the yellow, aqueous layer is shaken up with fresh carbon tetrachloride. The carbon tetrachloride remains colourless, a thing that would not be possible for distribution of equilibrium between triethyl-lead dithizonate - carbon tetrachloride - water. Discolouration of the aqueous phase increases sharply towards the end of titration, and occurs repeatedly in diffused daylight even after replacing it by a 0.1% ammonia solution and shaking vigorously. At the same time the carbon tetrachloride layer is coloured orange (diethyl-lead dithizonate). In nitrogen the discolouration is less, and in the total absence of light, titration is normal, i.e., no discolouration takes place.

It is accordingly a question of a change in the triethyl-lead or ammonium dithizonate, the latter depending upon the presence of triethyl-lead ions; this change is caused or accelerated by light (and oxygen). By the addition of CN ions, this instability can be somewhat lessened.

In order to secure really practical results, the work must be carried out in very dim daylight, or else the titrations must be started very close to the end-point. For practical fuel analyses, i.e., in the presence of greater or smaller quantities of oxidising substances (peroxides), it is an advantage, especially if the effect of light is difficult to avoid, to work in the presence of KCN, which at the same time renders harmless any alien metals that may be present (except Bi, Sn++,Tl). It is true that the cyanogen ion has the drawback that it reacts so readily with lead, that the equilibrium of the reaction is somewhat displaced; however, this drawback is of little consequence in the presence of KCl (which suppresses the dissociation of the KCN). The results obtained under the various conditions are collated in Table 1 A.

In the case of divalent lead and diethyl-lead compounds the end-point is also slightly displaced by the addition of KCN, but this occurs to a lesser extent, the purer the dithizone solution. Nothing can be said here as to the exact position of the reaction equilibria (which lie practically entirely on the side of the formation of dithizonate) under the titration conditions in question. Difficulties arise owing to the different types of the dithizonate solvents, and to secondary reactions with products of decomposition of dithizone, etc. Since the decrease of the required amount of dithizone, produced by the concentration of hydrogen ions and potassium cyanide, gives practically the same value for divalent lead, diethyl-lead, and, more or less, for triethyl-lead compounds, (in the latter case in a saturated KCl solution) and, since quite good results are obtained when using suitably diluted lead solutions with quite a low lead content, a more exact understanding of the situation was dispensed with. Further details may be obtained from the Tables 1A, B and C. The accuracy and use of the analytical methods are clearly demonstrated by these tables. The margin of error in the determinations (by using a pure solution of dithizone) would be about

± 0.1cc. of dithizone solution, allowing for possibilities of error in the standardisation with divalent lead (v. Section V). The relative values between each of the three types of compound are naturally more accurate. Regarding tests for the purity of the dithizone solution see Section V. For examples of the effects of oxidising materials, see Page 13.

The occurrence of ethyl-lead compounds, i.e., lead with three free valences, has not yet been observed. The stability of these materials is probably extremely low.

IV. CARRYING OUT THE ANALYSIS.

1 cc. of the fuel is mixed in a shaking vessel with 2.5 ccs. of carbon tetrachloride (very pure) and 2.5 ccs. of a concentrated solution of chemically pure potassium chloride; the latter solution also containing 0.1% of ammonia (NH_3), 0.5% Rochelle salt and 0.5% sodium thiosulphate. After adding 0.25 cc. of a 2.5% KCN solution, the mixture is titrated with standardised dithizone solution until the appearance of a slightly brownish colour. On the addition of a further 0.10 cc of dithizone solution (with a high content of a triethyl-lead compound 0.20 cc), a marked deepening of the brown colour should be seen. Contrary to the determination of diethyl-lead and divalent lead compounds, the end-point is not well defined. On titrating without the addition of KCN and KCl, the end-point at once becomes clear and sharp.

The titration should always be carried out in well-diffused daylight, especially in the absence of KCN and Kcl. The time of shaking, after the addition of the first major portion of the dithizone solution, should be about 20 secs.; titration is then carried out with 0.1 cc. portions and each time the mixture should be shaken for approximately 5 seconds. In the presence of rather large quantities of peroxides, titration should be commenced as close as possible to the expected end-point. (See also Table 2).

If the carbon tetrachloride solution remains yellow or brownish yellow near the end of titration, the calculation of the lead content is carried out exactly as in the case of the normal lead determination (see also Section V of this report), except that, since the triethyl-lead compounds require only half the amount of dithizone, the amount of dithizone solution consumed by 1 cc. of fuel (x cc) must be allowed for in the calculation.

Triethyl lead compound = x. F* Vol.% (calc. as TEL).

If the carbon tetrachloride solution does not remain yellow, but becomes orange to red, or if an orange tinge was present from the beginning, the analysis is carried out as already indicated in Section II. Thus:

Determination of the total lead by DVL method (Titre = c ccs dithizone solution)

Determination of the total triethyl- and diethyl-lead (and divalent Pb) compounds with dithizone, is carried out exactly as stated for the triethyl-lead compounds, but in relation to ½ cc fuel (Titre = d cc dithizone solution)

Shake the fuel with 15% of a ½% nitric acid solution (1 part by volume 25% HNO_3 (Analar), 49 pts. by volume H_2O) for 5 mins. Decant off

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* See Section V of this Report.

the aqueous layer (after settling), shake twice for 3 minutes with 5% water; decant, dry quickly with Na_2SO_4, and after the Na_2SO_4 has settled, determine the lead by the DVL method: (Titre = b ccs dithizone solution).

Calculation:

In determining the amount of triethyl- and diethyl-lead and divalent lead compounds, u cc correspond to triethyl-, and v cc to diethyl-lead and divalent lead compounds. Thus:

u	=	c - e - d cc		Dithizone solution
v	=	2d - c plus e cc		dithizone solution

From this we have the content of:

Triethyl-lead compound =

(c - e - d). 2 F ccs/100 ccs (calc. as TEL)

Diethyl-lead (plus divalent lead) compound =

(2d - c plus e). F.ccs/100 ccs (calc. as TEL)

If the fuels contain many oxidising substances, (e.g. peroxides after bomb ageing), they must be well shaken for 3 minutes with the stated solution before the titration (after addition of KCN) - in order to determine d.

The accuracy with which the analysis can be carried out also depends (in the case of the DVL lead determination method) on the extent to which the decomposed lead tetraethyl, in solution, is converted quantitatively by the sulphuryl chloride into a compound that is insoluble in fuel. In Table 2 examples are given from which it may be seen that decomposed lead tetraethyl in solution is actually completely precipitated by SO_2Cl_2. Firstly, all the experiments are given which were made in the course of 6 months (bomb experiments), in which practically only one triethyl-lead compound was present. (Experiments 1-4). In these experiments, the difference in the lead values before and after DVL treatment may be compared with the directly determined figures. It will be appreciated that the agreement is very good indeed. For non-bomb-treated fuels, it must of course be still better. In Experiment 5 practically only diethyl-lead salts were formed in the bomb-ageing process. The agreement is good. As a general rule it is found that, after artificial ageing, mainly triethyl-lead and some diethyl-lead salts are found in solution. At the end of the Table (Experiment 6), a further experiment is given in which, by the double decomposition of diethyl-lead chloride with silver acetate, diethyl lead acetate is formed and is dissolved in the fuel. This value also provides good agreement between the values ascertained by direct titration and by the DVL lead determination method.

A separate determination of divalent lead salts and diethyl-lead compounds was not carried out, as it was not required. A photometric process would be the best for this purpose. An approximate and useful picture is, however, provided by the direct titration, since the triethyl- and diethyl-lead compounds will react before the divalent lead compounds in the order given. Examples which illustrate these possibilities may be seen in Table 3.

V. SUPPLEMENT TO DVL REPORT FB 1292

If really pure materials are used for the preparation of the dithizone solution standardisation can be carried out with a solution of known lead content, independently of other methods. Whether the dithizone solution is suitable for this type of standardisation will be seen by the fact that in titrating 2.50 ccs of the "test solution" given below or a solution of a diethyl-lead salt, without the addition of KCN, the extra consumption of dithizone (as opposed to that with KCN) is not appreciably greater than 0.5% (≈0.05 cc). If it is greater than 0.5% the

standardisation of the dithizone solution can only be carried out by the earlier method mentioned above (cf. the above DVL report), and the test solution can only be used for an approximate check of the time variation of the solution.

Since the impurities in the dithizone solution react proportionally in the titration, such solutions, if their titre is frequently checked, can be used for one and the same type of compound, but not, if any claim to accuracy is made for analysing triethyl-, diethyl- and divalent lead salts together or for comparison one with another; e.g., when one compound is used for standardisation. A test for impurities in the dithizone solution may also be carried out as follows: a diethyl-lead or divalent lead salt solution corresponding to approximately 0.10 - 0.12 vol. % TEL is titrated up to the end-point, and then, by repeated shaking with "the solution" ("the solution" is the aqueous solution containing 0.1% NH_3, 0.5% Rochelle salt and 0.5% sodium thiosulphate), and the usual addition of KCN, the carbon tetrachloride layer is freed from "excess dithizone". The brownish colour formed in the aqueous layer should not be more than that corresponding to about 0.5 cc dithizone solution.

1. Standardisation of the dithizone solution:

About 0.10 to 0.12 gr. metallic lead ("Kahlbaum" - sheet 1 mm. Analar) is weighed to the nearest 0.1 mg. in a 100 cc wide-necked Erlenmeyer flask, a mixture of 2 ccs concentrated HNO_3 (65% Analar) and 4 ccs dist. water is added and the flask placed on the boiling water-bath. After the lead has dissolved, the flask is allowed to remain on the water-bath until completely dry. (about 2 hours.)

The lead nitrate obtained is washed quantitatively into a calibrated 500 cc measuring flask with an aqueous solution containing 0.20% NH_3, 0.5% Rochelle salt, and 0.1% sodium thiosulphate, and topped up to 500 cc. (The solution and washing will be more advantageously carried out with 250 ccs of a solution containing 0.1% NH_3 and the whole of the Rochelle salt (2.59) and thiosulphate (0.59); it is then topped up with a 0.3% NH_3 solution to make 500 cc.) The solution is stable (if well sealed in the dark in a Jena measuring flask) and is sufficient for 150-200 titrations.

The standardisation is carried out as follows:-

For the preliminary experiment 2.5 ccs. of the divalent lead solution are mixed with 4 ccs of chloroform, and, after adding 0.25 ccs. of a 2.5% KCN solution, are titrated with the dithizone solution until the brown tinge just appears. The end-point can be verified by over-titration. (Thus after the addition of another 0.10 cc a considerable deepening of the colour should appear in the aqueous layer). The experiment is then repeated, taking, as the quantity of chloroform, exactly half of the dithizone solution that was used up.

The titre is checked once a week for reasons of safety. If the dithizone solution is freshly made and is to be used at once, it should have additional checks during the first seven days. Duration of check determination: about 3 minutes.

Standardisation:

If a grams of metallic lead were used for making the lead solution, and if 2.50 ccs of this solution react with b ccs of dithizone solution, the factor F, by which the ccs of dithizone solution used up must be multiplied, in order to obtain vol.% TEL in actual analysis, is given by:

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

The concentration of the dithizone solution should be so selected that 2.50 ccs of the test solution correspond approximately to 8-10 cc of dithizone solution.

In the factor 0.95, allowance is made for the fact that when standardising with the divalent lead solution, a mixture of carbon tetrachloride-chloroform should be taken owing to the poor solubility of the lead dithizonate. Disregarding the addition of chloroform and assuming the completely identical behaviour of (triethyl-,), diethyl- and divalent lead salts, the calculated factor is 0.9409 (the specific gravity of the TEL has been established as 1.659 at 20°C.) The increase of about 1% was effected by the addition of chloroform, in comparison with the behaviour of the diethyl-lead compounds (See Table 4). The extent to which this increase is justified will be found in the fact that other determinations (e.g., analysis of triethyl-lead chloride, determination of lead in paraffin base fuels by the chromate method) likewise require correction of approximately this amount. The (polar) chloroform, in the quantity employed here, only slightly influences the distribution equilibrium between dithizone and ammonium dithizonate under the conditions chosen; the change in position of the appearance of the brown tinge in the aqueous layer occurs only in the presence of the lead dithizonates and is actually proportional to the quantity present.

Practical Example.

(1) Standardisation:

Weighed portion (a) = 0.1079 gr. Pb; consumption (b) =9.05 ccs dithizone solution.

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

(2) Analysis.

Consumption (x) = 10.60 ccs dithizone solution
TEL = 10.60 x 0.01132 = 0.120 vol.%

(2) General.

Cleaning the filter apparatus: After dissolving out the lead precipitate the filter should be cleaned at once with distilled water and then with alcohol, and allowed to dry at 100° in a drying oven. With filters treated in this manner, about 20 determinations can be carried out, according to the fuel, before they have to be cleaned again with fuming nitric acid or warm chromosulphuric acid.

The sulphuryl chloride used for precipitation must be obtained in sealed bottles. (Schering).

The delivery tube must be kept dry. KCN solution added must be exactly 2.5%.

The dithizone solution must be shaken vigorously with the aqueous lead solution. In titrating the diethyl-lead and divalent lead salts, it is sufficient to shake for about 30 secs. after adding the main quantity of the dithizone solution, then, on further titration (from 0.05 to 0.20 cc) for about 10 secs. If there is difficulty in recognising the commencement of the appearance of the brown tinge in the aqueous layer, one can titrate to a stronger colour intensity without further trouble and deduct from the titre obtained, the necessary amount of dithizone solution as found from experience.

For diluting the individual samples of fuels for analysis prior to precipitating with sulphuryl chloride, fuels with a paraffin base (plus chloroform (2 : 1)) are suitable, e.g., the type in the table of the DVL Report FB 1292, under No. 1, are suitable.

Errata in the DVL Report FB 1292: Page 10, Line 13:

instead of 2 ccs, read 2.5 ccs. Page 14 (diagram of the general arrangement): in the diagram the glass cock above the burette on the siphon tube has not been drawn.

VI. SUMMARY.

A method is indicated, which makes it possible to determine qualitatively, and in part quantitatively, the products of decomposition of lead tetraethyl in the presence of each other.

A rapid process, independent of other methods, is given for standardisation of the dithizone solution.

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TABLE 1A

Exper. No.	Type of Lead Compound	Quantity Used.	NH_3 Content.	Addition of KCN Sol. 2½% cm^3	Addition of KCl	Light Effect	Dithizone Solution cm^3 Found	Dithizone Solution cm^3 Calculated *
1				0.25	Plus		11.20	
2			0.1	-	Minus	Exclusion of Light	11.30	
3	Triethyl lead chloride dissolved in Benzol-gasoline (paraffin base) 3:7	2.5			Plus		11.20	11.20
4			0.25	0.25	Plus		11.20	
5			1.0		Plus	Highly diffused daylight	11.20	
6				-	Minus		11.30	
7	0.08555 g/100cm^3	0.50		0.25	Plus		2.20	2.24
8				-	Minus		2.30	
9		0.25	0.1	0.25	Plus		1.10	1.12
10				-	Minus		1.20	

*The values given are calculated from the weighed-out portion (Column 2) and from the consumption of dithizone solution by divalent lead salts (test solution). The correction required by the addition of chloroform has been allowed for (see Table 4).

A lead determination of triethyl-lead chloride solution by the DVL method, is shown in the above table and gives a lead content of 0.0500 against the calculated value 0.0506, expressed as vol.%TEL.

Colour of the carbon tetrachloride layer: Experiments 1-6 - brownish yellow
" 7-10 - yellow.

On the addition of KCN without KCl, a light brown colouration is already observed at about 10% before the end-point, and occurs both with exclusion of light and in dim daylight. The end-point is not well defined & is also quite hard to recognise by over-titration.

In order to examine the behaviour on slow titration with and without KCN and KCl in very dim daylight, titration was commenced with 5 ccs of dithizone solution. Practically no yellow colouration of the aqueous layer occurs, and there is likewise no orange tinge in the tetrachloride layer. The end-points correspond to those of rapid titration. In diffused or bright daylight, a yellow colour is observed in the aqueous layer together with a rapidly deepening orange colour in the tetrachloride layer; the values obtained are more or less high according to the effect of the light.

TABLE 1B

Exper. No.	Type of Lead Compound.	Quantity used. cm^3	Addition of KCN Solution $2\frac{1}{2}\%$ of cm^3.	Alkali Content	Dithizone Solution cm^3	
					Found	Reference Value
1	Diethyl lead salt obtained from the DVL-lead determination method	2.50	0.25	0.1% NH_3	10.75	10.75
2				0.25% NH_3	10.75	
3				1% NH_3	10.75	
4				0.1% NH_3 0.1% KOH	10.70	
5			0.05		10.75	
6			-		10.80	
7		0.50	0.25	0.1% NH_3	2.15	2.13
8			-		2.15	
9		0.25	0.25		1.05	1.07
10			-		1.05	

In Experiments 3 and 4 a slight yellow tinge may be observed just before the end-point.

Colour of the tetrachloride layer: orange.

For examining behaviour of slow titration, with and without the addition of KCN and in diffused daylight, titration was commenced with 5 ccs dithizone solution. A slight yellow colouration occurred in the aqueous layer before the end-point only when titrating without KCN. The end-point corresponds in both cases to that found with rapid titration.

TABLE 1C.

Exper. No.	Type of Lead Compound.	Quantity used. cm³	Addition of KCN Solution 2½% cm³	NH_3 Content %	Dithizone Solution cm³ Found	Dithizone Solution cm³ Ref. value.
1	Divalent lead salt corresponding to 0.09360 gm Pb in 500 cc of a solution containing 0.1% $Na_2S_2O_3$ 0.5% $KNaC_4H_4O_6$ and NH_3 (Quantity see Col. 5)	2.50	0.25	0.05	7.97	7.95
2				0.10	7.97	
3				0.25	7.95	
4				0.50	7.92	
5				1.0	7.90	
6				2.0	7.80	
7			0.05		8.00	
8			-		8.00	
9		0.50	0.25		1.55	1.69
10			-	0.25	1.60	
11		0.25	0.25		0.75	0.80
12			-		0.80	

Experiment 4 shows a yellow colour from 7.80 ccs onwards, Experiment 5 from 7.60 ccs. and Experiment 6 and 7 30 ccs.

Colour of the tetrachloride layer - red.

For examining the behaviour with slow titration, the procedure adopted was that given below Table 1B. Without the addition of KCN a slight yellow colour occurs towards the end of the titration, the end-point is ill defined and is about 0.05 cc lower than with rapid titration. In the presence of KCN no difference can be seen compared with normal titration.

TABLE 2

Exper. No.	Content Dissolved. Decomposed TEL		Colour of Carbon Tetrachloride Layer	
	Direct Titration	Difference Method	Beginning	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" should be understood the analytical process described in Section IV for pure triethyl-lead compounds; however, the titration took place in diffused daylight. The figures in the column "Difference Method" show the differences of the lead values before and after washing the fuel with dilute nitric acid. (See Section IV).

Experiment 6 illustrates the complete precipitability of dissolved diethyl-lead salts with sulphuryl chloride.

Experiments 1 to 5 show that even fuels which have undergone ageing in the bomb, i.e., containing oxidising matter,(in some cases the time for treatment was less than 240 minutes), produce good, practical results under the conditions of direct titration.

Direct titration in highly diffused daylight should give an even better agreement of the results obtained. Prior to ageing, the fuels had a TEL content of about 0.120 vol.% If a fuel is filtered (with fluted filter 9 cms diameter), a concentration of 1% of TEL or soluble decomposed TEL can usually be assumed, (according to temperature and type of fuel) and allowance should be made for this.

An experiment with heptylene, which had been stored for 5 years, gave useless values with "direct titration". Highly acidified fuels must of course be more or less neutralised before direct titration is carried out.

TABLE 3.

Exper. No.	MIXTURE CONTAINS: Triethyl Lead Salt Corresponding to ....cc Dithizone	MIXTURE CONTAINS: Diethyl Lead Salt corresponding to ..... cc Dithizone	Divalent Lead Salt corresponding to ...cc Dithizone	Addition to Titration.	COLOUR OF CARBON TETRACHLORIDE LAYER: Yellow up to ~cc	Orange tinted from ~cc	Orange from ~cc	Orange-red from ~cc	Red from ~ cc	TOTAL CONSUMPTION ccm 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	"	-	"	KCN	"	"	"	-	1.8	-	-
3	"	-	"	0	1.0	1.0	1.1	-	1.7	8.30	8.35
4	9.50	-	0.60	KCl) KCN)	7.0	8.0	Turns into brownish-orange			10.20	10.10
5	"	-	"	0	9.3	9.4	ditto			10.10	10.10
6	0.25	10.30	-	0	0.1	0.1	Turns into orange			-	-
7	1.00	9.95	-	0	0.5	0.6	Turns through yellow-orange to orange			10.90	10.95
8	4.60	4.05	-	0	4.0 Yellow brownish yellow	4.0	Turns into brown-orange to orange			9.00	8.65
9	4.60	4.05	-	KCl) KCN)	1.5 Yellow brownish yellow	1.5	Turns into yellow orange to orange			8.70	8.65
10	7.10	10.40	-	KCl) KCN)	Impure Yellow colour	0.5	Turns into brown orange to orange			-	-
11	9.40	0.80	-	0	9.0 brownish yellow	9.0	Turns into orange			10.50	10.25
12	9.40	0.80	-	KCl) KCN)	0.9 yellow brownish yellow	0.9	Turns through brown orange to orange			10.30	10.25
13	-	1.05	7.40	KCN	-	+	Up to 0.90	0.90	2.0	-	-
14	-	2.00	7.90	KCN	-	-	" 2.10	2.1	3.0	9.85	9.90
15	-	2.00	7.40	-	-	-	" 1.80	Turns into orange red & soon passes into red		-	-
16		10.40	0.15	KCN	-	-	" 10.55	-	-	10.55	10.55

(Continued overleaf)

TABLE 3 (Contd.)

The titrations were carried out in diffused daylight avoiding the action of strong light. The aqueous solution used (about 2.5 ccs) contained 0.1% NH_3, 0.5% $KNaC_4H_4O_6$ and 0.5% NA_2SO_3. In experiments, in which KCN or KCN plus KCl was added, this was carried out with the quantity given in Section IV.

A thick line surrounding the figures means that the colour change was clearly seen. In the penultimate column (11), under "Found", the end-points given for titration were ill-defined and inaccurate, as the work was carried out in diffused daylight. The last column (12) under "Calculated", gives the sum of the values that were obtained for the individual materials (before mixing) according to the normal method of determination given in the report; the titration of the triethyl-lead salts was, however, carried out in diffused daylight. (Columns 2 to 4).

It will be seen that without the addition of KCN and KCl, some very practical values were obtained direct with mixtures of triethyl-lead and divalent lead salts. (This type of analysis is nevertheless only really possible in the absence of large quantities of oxidising materials (peroxides, etc.)). With mixtures of triethyl- and diethyl-lead salts, the prospects of differentiation are very poor, while with mixtures of diethyl-lead and divalent lead salts, useful values are obtained for the individual components after a little practice.

TABLE 4

Exper. No.	Type of Lead Combination	Ratio Between Carbon Tetrachloride	Ratio Between Chloroform	End-Point cc Dithizone Solution
1		1	0.5	7.85
2	Lead Salt	1	1	7.92-7.93
3	Diethyl Lead Salt obtained from the	1	0	10.65
4	DVL lead determination method plus	1	0.5	10.75
5	0.1% NH_3	1	1	10.85

The chloroform was added prior to titration. In the absence of lead salts and using the same quantities of tetrachloride as in Experiment 1 (i.e., about 8 ccs), a well-defined brown colour in the aqueous layer was given by 0.05ccs of dithizone solution using tetrachloride and chloroform up to the ratio 1 : 1. Experiments with chloroform, purified by fractional distillation, showed the same behaviour. The displacement of the end-point caused by chloroform is, as already mentioned, proportional to the amount of lead to be titrated. With diethyl-lead salts, the addition of carbon tetrachloride during titration (in amounts up to that equal to the volume of dithizone solution required), hardly alters the end-point at all. In the case of divalent lead salts on adding the quantity stated (together with the required amount of chloroform), a very slight rise (~ 0.0 cs) of the end-point will be observed.