

Determination of Trace Amounts of Lead in Gasolines and Naphthas

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► Two analytical methods have been developed for the determination of lead in gasolines and naphthas in the concentration range of 10 to 100 parts per billion of lead as inorganic lead or tetraethyllead. Both methods are modifications of dithizone colorimetric procedures; one is a two-color method involving the use of a spectrophotometer and the other is essentially a one-color method involving the use of either a spectrophotometer or a color comparator. The experimental work includes a complete study of systemic variables and errors in both methods. The accuracy and precision of the methods are within 10 parts per billion.

THE INCREASING USE of platinum-containing catalysts for upgrading gasoline and naphtha and the poisoning effect of heavy metal ions on these catalysts have resulted in a need for a rapid method for the determination of lead in gasoline in the concentration range of 10 to 100 parts per billion. Because the same pipelines, trucks, and tankage are used for the transport and storage of leaded and unleaded fuels, each shipment and plant feed stream must be checked before being charged to the catalyst. The analytical method must determine both inorganic lead and tetraethyllead, and it is desirable that both the elapsed and expended times be kept to a minimum.

This paper describes the development of two methods which are rapid and are sensitive to 10 p.p.b. of lead as tetraethyllead. Both are modifications of dithizone colorimetric methods (4, 9). One, developed by Griffing and Rozek, is a spectrophotometric method which involves the extraction of lead at relatively low pH, 9.5 to 10.5. The other, developed by Snyder and Henderson, is a color-comparator method which involves the extraction of lead at pH 10.8 to 11.0. The latter is rapid and can be applied in field situations.

Published methods for the determination of lead in gasoline are both chemical and instrumental. In the most

commonly used chemical methods (3, 7), lead is extracted with hot hydrochloric acid and determined by the volumetric molybdate, gravimetric sulfate, or gravimetric chromate method. Neither the chemical methods nor the various instrumental methods are sensitive enough for the analysis of the charge stocks. A modification of the gravimetric chromate method has been used for this purpose; it involves dissolution of the chromate precipitate and subsequent colorimetric determination of the lead. The sensitivity of the chromate method has not been established, and the time required for the analysis is excessive, elapsed time being approximately 8 hours.

Sandell reviewed the published data concerning the use of chloroform solutions of dithizone for trace-metal analysis (8). In determining lead by use of dithizone, the following equilibria must be controlled: the reversible reaction of dithizone with other interfering metals; the reaction of lead with anions forming stronger complexes than the dithizonate; the distribution of lead dithizonate between the chloroform and aqueous phases; and the distribution of unreacted dithizone between the chloroform and aqueous phases.

The reducing buffer solutions recommended in these procedures are designed to help control these equilibria by chemical means. The high concentration of cyanide prevents the formation of other metal dithizonates; the citrate prevents the coprecipitation of lead with group III cations; the sulfite reduces any oxidizing agents, thus stabilizing the color; and the ammonia adjusts the pH.

The distribution of lead dithizonate and of unreacted dithizone between chloroform and aqueous phases was studied first by Clifford and Wichmann (4) and later, with more attention to actual pH values, by Biefeld and Patrick (2). All of these authors have shown that the distribution of both lead dithizonate and dithizone is a function of pH and of the percentage of excess dithizone. At excessively high pH values, the dithizone distributes, primarily, into the aqueous phase;

but lead losses tend to occur. Snyder (9) has shown that lead can be completely extracted into the chloroform phase at higher pH values by use of a more concentrated solution of dithizone, and at lower pH values, by use of more dilute solutions of dithizone. The distribution of dithizone is a function of the ratio of the chloroform volume to the aqueous volume, the dithizone concentration, and the pH value. Therefore, a variety of methods of equivalent accuracy can be developed, utilizing a different balance among these three variables. By controlling experimental conditions, complete extraction of the lead and reproducible distribution of the dithizone can be obtained. Any inaccuracy of such a method is independent of the quantity of dithizone in the chloroform layer, but dependent on the changes in that quantity because of uncontrolled variables.

The development of these methods for the determination of 0.5 to 10 γ of lead has required study of procedures for the decomposition of low concentrations of tetraethyllead in gasoline, of variables involved in the dithizone extraction, and of the application of the methods to a variety of charge stocks.

EXTRACTION OF TETRAETHYLLEAD FROM GASOLINE

Existing methods for determination of tetraethyllead in organic media involve extraction either with hot hydrochloric acid in specially designed extractors (1) or with a nitric acid solution of potassium chlorate (6). A micro-method for the determination of tetraethyllead in fuels, published by Gordon and Burdett (5), used iodine to decompose the tetraethyllead. These methods have been studied only for higher concentrations of tetraethyllead, and the extracts are not suitable for direct application of the colorimetric methods.

A number of reagents were tested for their effectiveness in decomposing tetraethyllead and extracting the resulting lead salts. None of the following reagents was effective: concentrated nitric acid, concentrated hydrochloric

acid, aqua regia, hydrogen peroxide, potassium permanganate (1.0*N*), sodium oxychloride, concentrated hydrobromic acid, chlorine in acetic acid, and chlorine water (saturated). Radiation with ultraviolet light resulted in no measurable decomposition. In contrast, bromine in carbon tetrachloride (50%), bromine water (saturated), and aqueous solutions of iodine (1.0*N* and 3.0*N*) gave complete decomposition of tetraethyllead. The reaction of tetraethyllead with halogens is stepwise, forming triethyllead, diethyllead, and inorganic lead halides. These products are formed at different rates, and the quantity of each product is a function of time, temperature, halogen concentration, and solvent. Therefore, the more effective reagents were studied to obtain basic data for developing a method of converting tetraethyllead in gasoline to inorganic lead ion.

Reaction of Tetraethyllead with Iodine, Bromine, and Hydrogen Bromide.

To measure the completeness of reaction of iodine or bromine with tetraethyllead, 1 ml. of an ethylalcohol solution containing 100 γ of tetraethyllead was added to 10 ml. of the halogen solution and shaken for various periods of time at temperatures ranging from 25° to 76° C. Then the reaction was quenched by the addition of an ammoniacal solution of sulfite, cyanide, and citrate. The triethyllead, diethyllead, and lead halides reacted with dithizone and were extracted into chloroform as dithizonates. The concentrations of the dithizonates were measured spectrophotometrically at wave length settings of 420, 498, and 540 $m\mu$ respectively.

In an aqueous medium, both 1.0*N* and 3.0*N* iodine solutions convert essentially all the tetraethyllead to inorganic lead ion after a 2-minute reaction period. In an organic medium, the reaction is not complete, but tends to convert tetraethyllead to diethyllead iodide. Bromine in either water or carbon tetrachloride rapidly converts tetraethyllead to diethyllead bromide. At elevated temperatures some inorganic lead bromide is formed. These data are shown in Table I. Hydrogen bromide gas was bubbled through hexane solutions of tetraethyllead, and the effects of varying the reaction time and temperature were studied. The results, shown in Table II, indicate that hydrogen bromide at elevated temperatures is highly effective for completing the decomposition of diethyllead bromide to lead bromide.

On the basis of these studies, two procedures were established for decomposing and extracting tetraethyllead from gasoline. Both procedures employ a carbon tetrachloride solution of bromine. One uses bromine at room

temperature to convert tetraethyllead to diethyllead bromide and additional bromine at 100° C. to complete the reaction to inorganic lead ion. The other involves the addition of diisobutylene and bromine to the sample. These two reagents react to form hydrogen bromide gas, and their heat of reaction raises the sample temperature to 50° C. without external heat.

SPECTROPHOTOMETRIC METHOD

Practical volumes of aqueous and chloroform phases have been chosen, and each variable has been studied independently to establish how carefully the experimental conditions have to be controlled to obtain accurate analyses.

Apparatus and Reagents. Absorbancy measurements were made with Beckman Model DU and Model B spectrophotometers, using a 0.04-mm. slit setting and matched Corex cells 1.000 cm. thick. Measurements of pH were made with a glass electrode assembly.

All extractions were carried out using Squibb-type separatory funnels and an automatic shaking machine capable of 250 cycles per minute.

The use of self-filling pipets for the dithizone reagent and the buffer has

resulted in considerable saving of time in handling a large number of samples and has decreased the incidence of contamination difficulties.

All glassware used in the method, including the sampling bottles, must be kept free of lead. To accomplish this, the same glassware is retained for each phase of the trace-lead work and is carefully cleaned, first with chromic acid cleaning solution and then with nitric acid solution. Washing with a mixture of the buffer solution and dithizone solution is one of the most effective ways of testing for the absence of lead and for removing final lead contaminants. If the equipment has been stored for any period of time, it should be washed in this manner before use, even though it was lead-free when put into storage.

An 0.8% nitric acid solution was prepared by dissolving 8 ml. of concentrated nitric acid (specific gravity 1.42) in water and diluting to 1 liter. This nitric acid solution was used for extracting lead from fuel samples.

A stock lead solution was prepared by dissolving reagent grade lead nitrate and 8 ml. of concentrated nitric acid (specific gravity 1.42) in water and diluting to 1 liter. Standard solutions for preparing calibration data were

Table I. Reaction of Bromine with Tetraethyllead

Concn. of Bromine	Temp., °C.	Time, Min.	% TEL Converted to		
			Triethyllead bromide	Diethyllead bromide	Lead bromide
N		In Carbon Tetrachloride			
0.36	25	0.5	0	99	1
		10.0	0	87	13
0.36	60	1.0	0	89	11
		10.0	0	56	44
1.0	25	15.0	0	86	14
		60	0	56	44
2.0	25	0.5	3	33	64
	25	5.0	1	50	49
	76	1.0	3	26	71
5.0	25	10.0	0	93	7
	60	10.0	0	50	50
	76	1.0	4	19	77
		In Water, Saturated			
	25	0.5	1	99	0
		5.0	2	98	0
		10.0	1	99	0
	100	1.0	2	86	12

Table II. Reaction of Hydrogen Bromide Gas with Tetraethyllead in Gasoline

Time, Min.	Temp., °C.	% TEL ^a Converted to		
		Triethyllead	Diethyllead	Inorganic lead
1	25	13	79	8
5	25	12	55	33
5	40	11	21	68
5	50	7	7	86

^a Originally 100 p.p.b.

made by diluting the stock solution with the 0.8% nitric acid solution.

Dithizone solutions were prepared by weighing and dissolving 30, 40, and 60 mg. of dithizone in reagent grade chloroform and diluting to 1 liter. Eastman Kodak product was used without purification.

The buffer solution was prepared by dissolving 20 grams of potassium cyanide, 6 grams of ammonium citrate, and 40 grams of anhydrous sodium sulfite separately in water. The solutions were mixed, 200 ml. of ammonium hydroxide (specific gravity 0.90) were added, and the mixture was diluted to 1 liter. This buffer gave a pH of 10.0 when a 10-ml. portion was added to 50 ml. of the nitric acid solution. A second buffer solution was prepared in the same way, using 600 ml. of ammonia to give a final pH of 10.5.

Bromine solution was prepared by diluting 300 ml. of bromine to 1 liter with carbon tetrachloride.

Because many stopcock greases contain lead, clear Vaseline is recommended for lubricating all stopcocks in trace-lead determinations.

In chloroform solution, lead dithizonate is red in color and shows an absorption maximum at 510 $m\mu$, which was chosen as the analytical wave length. Dithizone is green, has an absorption peak at 600 $m\mu$, and shows appreciable absorption at 510 $m\mu$. In studying the systemic variables, unless otherwise noted, a "reading blank" containing all reagents except the standard solution of lead was prepared and used in the reference cell of the spectrophotometer. The conclusions concerning the effect of any variation are applicable only when a reading blank is used.

In the study of all variables, a total aqueous volume of 60 ml. and the following relationships between quantity of lead and volume of reagent were maintained:

Amount of Lead, γ	Volume of Dithizone, ml.
0-10	5.0
0-15	10.0
2-80	25.0

Even though readings may be obtained outside these limits, specific experiments should be designed to ascertain the applicability of the methods used before accepting the results.

Effect of Dithizone Concentration. In choosing a reagent concentration, a compromise must be reached. On the one hand, a sufficient excess must be present to assure complete lead extraction and to minimize the effect of changes in lead concentration on the absorbancy contribution of the excess dithizone. On the other hand, a sufficiently small excess should be present to minimize the change in absolute

absorbancy and therefore in the lead equivalency resulting from uncontrolled variations in pH and small variations in reagent concentration, which might occur between preparations of reagents.

For 5, 10, and 25 ml. of dithizone solution and a pH between 9.6 and 10.5, complete lead extraction is obtained with 30 to 60 mg. of dithizone per liter. The slopes of the calibration curves are independent of the reagent concentration. The more concentrated reagent gives a system which is more sensitive to pH changes.

Therefore, a reagent concentration of 30 mg. of dithizone per liter is recommended. Variations resulting from the preparation of new reagent solution do not result in a measurable error.

Effect of pH. Variations in the distribution of dithizone with pH result in two errors. Even though lead is completely extracted, the slope of the calibration curve (expressed as absorbance per microgram of lead) increases 1% for an increase of 0.1 pH unit. Therefore, this method recommends that the pH of all samples be kept within 0.3 pH unit of the pH chosen for preparation of the calibration data. This may be at any pH between 9.5 and 10.5. The range of 10.5 to 11.0 pH units was not studied. If a pH difference is obtained between the reading blank and any sample, a more significant error will result. The magnitude of this error is shown in Table III, expressed as micrograms of lead equivalent to a pH difference of 0.1 at the indicated pH.

For this reason, pH control is specified for this method. However, if an unusual sample or the sample treatment

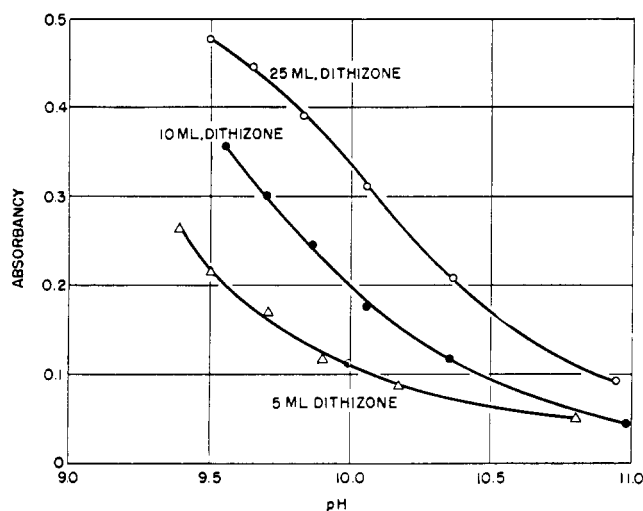


Figure 1. Change of absorbance of reading blank with pH

Reagent concentration 30 mg. per ml.
Cell thickness, 1.000 cm.
 CHCl_3 used as reference

Table III. Effect of pH Difference between Sample and Reading Blank

(Error = 0.1 pH difference for reagent volumes shown)^a

pH of Aqueous Phase	Lead, γ		
	5 ml.	10 ml.	25 ml.
10.7	0.1	0.2	1.6
10.4	0.1	0.6	2.3
10.1	0.2	0.7	3.2
9.9	0.3	1.2	3.4
9.7	0.4	1.2	2.9
9.6	0.3	1.3	2.3

^a Concentration = 30 mg. dithizone/liter.

step results in a pH difference between a sample and the reading blank, a correction can be applied using the curves shown in Figure 1. The data for plotting these curves may be obtained in the following manner:

Prepare a series of reading blanks at different pH values, using variable quantities of dilute nitric acid solution and the volume and concentration of dithizone reagent to be used in the analysis. Read the absorbancies and pH values of the blanks at 510 $m\mu$, using chloroform in the reference beam of the spectrophotometer. Plot these absorbancies against the pH values to obtain curves similar to those shown in Figure 1.

Measure the pH of the reading blank and of each sample solution. If any of these differ by more than 0.02 pH unit, a correction can be made from the data in Figure 1 in the following manner: Read the absorbancies corresponding to the pH of the sample, S_A , and to the pH of the blank, B_A , respectively; then the correction is $B_A - S_A$. Add the correction alge-

braically to the observed absorbancy of the sample.

Capacity of Buffer. Because a significant error is introduced by a difference between the pH of the sample and of the reading blank, a study was made of the capacity of two buffers. One buffer contained 200 ml. and the other 600 ml. of concentrated ammonia per liter. The change in pH for incremental additions of nitric acid was measured. These data showed that both buffers had essentially the same buffering capacity but gave different pH values. The use of a larger volume of buffer solution did not give greater buffering capacity. However, there was some evidence that the presence of a higher concentration of ammonium nitrate would give better buffering action.

Stability of Colored Solutions. For each volume of reagent, four identical lead solutions were prepared and analyzed at pH 10.0. The dithizone extractions were made, and the chloroform layers were left in contact with the aqueous phases until the absorbancies were read. Readings were made 6, 20, 35, and 50 minutes after extraction. These data showed that the solutions are satisfactorily stable for at least 50 minutes. The absorbancy of the sample using 25 ml. of dithizone reagent decreased slowly, indicating that in this range readings should be made within 30 minutes for best accuracy.

Calibration Data. Calibration curves were prepared for each volume of reagent solution, using 30 mg. of dithizone per liter of chloroform and pH 9.5, 10.0, and 10.5. Under all these conditions, the systems obeyed Beer's law. Typical calibration data, shown in Table IV, demonstrate the accuracy of the method for the determination of inorganic lead in aqueous solution when pH control is good. Calibration data were obtained by pipetting varying volumes of a standard solution of lead nitrate into separatory funnels. The volume for each funnel was made up to 50 ml. by addition of 0.8% nitric acid solution. Then, 10 ml. of the buffer and the appropriate volume of dithizone reagent were added, and the funnel was shaken for 2 minutes. The absorbancies of these solutions were read, using a reading blank prepared as described in the procedure.

Spectrophotometric Procedure. Choose the appropriate sample size from Table V and pipet it into a beaker. Add bromine solution until the bromine color persists for at least 5 minutes, and let the beaker stand for at least 10 minutes. Place the beaker on the hot plate and heat it until all the bromine is evolved. Cool the solution to room temperature and then, using 25 ml. of 0.8% nitric acid solution, transfer it

quantitatively to a separatory funnel. Shake the funnel and contents for 2 minutes, then drain the aqueous extract into a 200-ml. beaker. Repeat the extraction of the sample with a second 25-ml. portion of nitric acid solution, then combine the two extracts.

Add 1 ml. of bromine solution to the aqueous extract. Place the beaker on the hot plate and condense the contents to approximately 10 ml. to complete the decomposition of alkyllead

salts and to volatilize the excess bromine, as well as most of the hydrogen bromide.

Quantitatively transfer the aqueous solution to a 125-ml. separatory funnel, using water, and bring the total volume to 50 ml. Add 10 ml. of the buffer solution to adjust the pH and shake. Add the appropriate amount of dithizone solution (Table V) and shake for 2 minutes. If the aqueous extract is colored, extract with successive 25-ml. portions of chloroform until a colorless chloroform layer is obtained before adding the dithizone. If chloroform extraction is included in the analysis, it should be included in the calibration procedure.

Prepare a reading blank by pipetting into a separatory funnel 50 ml. of the same nitric acid solution used to extract the lead, and by treating it with the same buffer and dithizone solutions as the brominated aqueous extracts from the sample. A single reading blank may be used for 1 hour. For those samples requiring chloroform extraction, prepare a separate reading blank.

Withdraw and discard a small portion of the chloroform layer from the separatory funnel to remove any water or lead which may have accumulated in the stem. Then fill a Corex cell with the chloroform layer of the extract. Fill a Corex cell in the same manner with the reading blank. Measure, on the spectrophotometer, the absorbance of the sample with respect to the reading blank, using a wave length of 510 m μ and the normal sensitivity. Calculate the micrograms of lead from calibration data, and correct for the lead contained in the volume of bromine used.

Using 5 ml. of dithizone, analyze each new preparation of bromine solution by adding 10 ml. of the stock solution to 50 ml. of the nitric acid solution and then treating this solution in the same manner as the aqueous extracts.

Application to Gasolines and Naphthas. Blended samples were prepared by adding a known quantity of tetraethyllead to iso-octane and to two different charge stocks. These

Table IV. Typical Calibration Data for Spectrophotometric Method

(Reagent concentration, 30 mg. of dithizone per liter, pH. 9.9)

Reagent Volume, Ml.	Absorbancy	Lead, γ		
		Added	Calculated ^a	Difference
5	0.134	1.9	2.1	+0.2
	0.191	3.2	2.9	-0.3
	0.322	5.1	4.9	-0.2
	0.419	6.3	6.4	+0.1
	0.544	8.2	8.3	+0.1
	0.630	9.5	9.6	+0.1
25	0.168	15.8	15.2	-0.6
	0.244	22.1	22.1	0.0
	0.357	31.6	32.3	+0.7
	0.426	37.9	38.5	+0.6
	0.523	47.4	47.3	-0.1
	0.594	53.7	53.7	0.0
	0.699	63.2	63.2	0.0
	0.770	69.5	69.6	+0.1
	0.886	79.0	80.1	+1.1
	0.939	85.3	84.9	-0.4

^a Using average slope of calibration curve.

Table V. Selection of Samples and Dithizone Volumes^a

Limits of Analysis, P.P.B.	Sample Volume, Ml.	Dithizone Volume, Ml.
10-100	100	5
50-150	100	10
100-1,000	100	25
100-2,000	50	25
1,000-20,000	5	25

^a These volumes are suitable for reagent concentrations of 30 to 60 mg. dithizone per liter and for pH values of 9.5 to 10.5.

Table VI. Analysis of Blended Samples by Spectrophotometric Method

Sample Description	No. of Replicates	Lead, P.P.B.		
		Added	Total ^a	Found
Iso-octane	25	0	14	14
	8	25	39	37
	50	50	64	61
Reformer charge stock A	3	0	24	24
	3	26	50	53
	3	79	103	101
	3	159	183	183
Reformer charge stock B	3	0	13	13
	3	26	39	36
	3	79	92	94
	3	159	172	188

^a Based on analyses for amount of lead in blending stocks.

Table VII. Analysis of Samples for Trace Lead by Spectrophotometric Method

Description of Stock	Added	Found	Concentration of Lead, P.P.B.	
			Estimate of Lead in Stock	Mean
Naphtha	0	16	16	12
	40	48	8	
Reformer charge stock A	0	44	44	34
	50	74	24	
Reformer charge stock B	0	40	40	36
	50	81	31	
Reformer charge stock C	0	7	7	4
	50	51	1	
Reformer charge stock D	0	69	69	60
	63	115	52	
Reformer charge stock E	0	76	76	70
	63	126	63	
Reformer charge stock F	0	33	33	26
	63	82	19	
Catalytic reformer charge stock	0	42	42	40
	50	89	39	
Kerosine	0	550 \pm 50	550 \pm 50	
Iso-octane	0	400 \pm 20	400 \pm 20	
	0	1100 \pm 30	1100 \pm 30	

were analyzed by the procedure described (Table VI). The data indicate that the over-all method is considerably less precise than the colorimetric measurement.

The method has been applied to a variety of samples received from various petroleum companies for analysis. Poor precision was obtained with some samples, probably because of incomplete decomposition of tetraethyllead. Therefore, a control procedure was devised to check the completeness of the decomposition of tetraethyllead. Duplicate aliquots of the sample were taken as received, and sufficient iso-octane solution of tetraethyllead was added to two other aliquots to increase the lead concentration by 25 to 50 p.p.b. All four aliquots were analyzed simultaneously, and a mean concentration of lead in the original sample was calculated. If the average of each pair of analyses did not differ from the mean by more than 10 p.p.b., the analysis was considered to be correct. If low recoveries were obtained, additional samples were treated with more bromine at the boiling point of the sample. This control procedure is recommended for analysis in the range of 0 to 50 p.p.b.

Typical analyses controlled in this way are shown in Table VII. These data indicate that the method is applicable to a wide variety of petroleum products, and that its accuracy probably is not better than ± 10 p.p.b. in the range of 10 to 100 p.p.b. and 10% at higher concentrations.

COLOR-COMPARATOR METHOD

A method of analysis employing dithizone reagent and a visual color comparator for the determination of

lead in air (10), was sensitive to ± 2.5 γ . For the determination of trace lead in naphtha charge stocks in 50 to 100 ml. of sample, the method must be sensitive to ± 0.5 γ of lead. This paper describes the modifications made to obtain this increased sensitivity and presents analyses of blended samples using the modified procedure.

Apparatus and Solutions. Color comparisons were made using Hellige Comparator No. 605 with lead dithizonate disk No. 620 S-10. This disk is calibrated in numbers 0, 1, 2, 3, 4, 6, 8, 10, 15, and 20.

The dithizone extraction and the color measurement were made in a specially designed vessel, shown in Figure 2. This vessel may be purchased from Kessler, Inc., 3801 Barnett St., Houston, Tex., Catalog No. K-87521.

Dithizone solutions were prepared by dissolving 60, 120, and 240 mg. of dithizone in reagent grade chloroform and diluting to 1 liter. Eastman Kodak product was used without purification.

Reagent grade diisobutylene was used as received.

Bromine solution was prepared by diluting 1 pound of bromine to 500 ml. with carbon tetrachloride.

The buffer solution was prepared by dissolving 50 grams of ammonium citrate, 20 grams of potassium cyanide, and 150 grams of anhydrous sodium sulfite in 800 ml. of distilled water. This solution was diluted to 4 liters with concentrated ammonia (specific gravity 0.90).

It usually was unnecessary to delead the reagents.

Study of Variables. A total volume of 150 ml. of the aqueous phase is ex-

tracted with 2 ml. of a chloroform solution of dithizone. As the solubility of chloroform in water is appreciable (0.67 ml. per 100 ml. at 15° C.), it was necessary to saturate the aqueous phase with chloroform before extracting with the dithizone reagent.

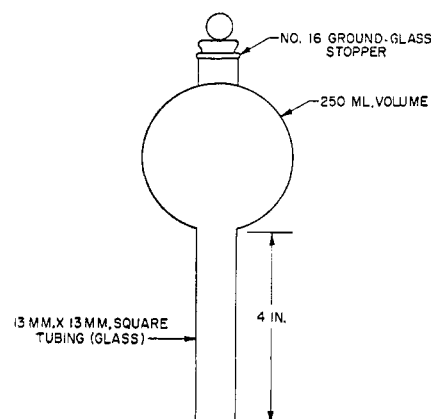


Figure 2. Color comparator

The effect of reagent concentration was studied on samples containing 10 γ of lead as lead nitrate. Identical samples were extracted with 2-ml. portions of dithizone reagent, using concentrations of 60, 120, and 240 mg. of dithizone per liter. The lead content of the dithizone layer was measured. These studies showed that a reagent concentration of 240 mg. of dithizone per liter gives complete lead extraction, but that 120 mg. of dithizone per liter gives only 84% extraction. If the volume of reagent is increased to 10 ml., complete lead extraction is obtained with 60 mg. of dithizone per liter.

The buffer used in this method is designed to control the pH at 10.8 to 11.0. If each new preparation of buffer is added to 100 ml. of the nitric acid and the pH is checked there will be no danger that the pH will be too high. If excess acid is introduced into the extracts from the sample treatment step, the pH may be too low. If this occurs, the chloroform extract will assume a greenish hue and color comparison cannot be made.

Calibration Data. A calibration curve for the visual measurements was prepared by adding known amounts of lead nitrate to 100 ml. of 1% nitric acid solution and then adding 50 ml. of buffer solution. This aqueous solution was saturated with 5.0 ml. of chloroform and the excess chloroform discarded. The lead dithizonate color was developed by shaking the aqueous solution with 2.0 ml. of dithizone solution (240 mg. per liter) for 30 seconds.

After the chloroform layer had been allowed to separate, the color intensity of the known sample was compared visually with permanent glass standards in the Hellige color comparator, estimating between standards. The results were corrected for the lead present in the reagents (blank) and plotted in the form of micrograms of lead versus color-comparator readings. A straight-line calibration curve was obtained.

Calibration data for spectrophotometric measurement may be prepared in the same way, using 5 ml. of a dithizone solution containing 120 mg. per liter, and making absorbance measurements at 510 m μ with a blank in the reference cell.

Color-Comparator Procedure. Weigh 45 grams of gasoline in a 100-ml. graduated cylinder and transfer it to a 250-ml. separatory funnel. Add 10 ml. of

separatory funnel; the resulting organic layer is heavier than the aqueous layer and separates at the bottom. Immediately shake the funnel for 1 minute and discard the organic layer. Do not allow the two layers to remain in contact for over 2 or 3 minutes, as excessive amounts of hydrogen bromide may be extracted into the aqueous phase. Wash the acid solution with an additional 25 ml. of chloroform to remove any colored oxidation products, and discard the chloroform. Add 50 ml. of buffer solution to adjust the pH, add 5 ml. of chloroform, and mix well. Allow the chloroform solution to separate completely from the aqueous portion, and discard all droplets of excess chloroform. Drain the aqueous solution into a color comparator tube (Figure 2), and add 2.0 ml. of dithizone solution (240 mg. per liter). Mix well for approximately 30 seconds, then allow the chloroform layer to settle.

Measure the color visually, as described in the section on calibration data. Correct the observed lead concentration of the unknown sample by running a blank on all the reagents used in the complete test.

Table VIII. Analysis of Blended Tetraethyllead in Gasoline Samples by Color-Comparator Method

Lead Added γ	Lead Found, P.P.B.	Difference, P.P.B.
0.00	0	0
0.45	10	+ 5
0.89	20	+ 5
1.78	40	- 6
3.54	79	+ 1
4.43	98	-12
8.86	197	-17
8.86	197	-27

diisobutylene and mix well. Add bromine solution slowly and cautiously until a marked excess of bromine persists for at least 4 minutes. The reaction of these reagents provides a constant supply of hydrogen bromide and raises the sample temperature, both of which assist the decomposition of the tetraethyllead.

Add 30 ml. of chloroform and 100 ml. of 1% nitric acid solution to the

Application to Gasolines and Naphthas. The accuracy and precision of this method were studied for lead concentrations ranging from 10 to 200 p.p.b. in a single straight-run gasoline and at 200 p.p.b. in several base stocks. The samples were blended by adding a measured quantity of a standard solution of tetraethyllead to 45-gram portions of gasoline. The samples were then analyzed by this procedure.

The results of these studies, shown in Tables VIII and IX, indicate that this method is sensitive to 10 p.p.b. of lead and gives a precision within ± 5 p.p.b. over the range of 10 to 80 p.p.b. At higher concentrations, the method tends to give low results, with somewhat poorer precision. As the tables indicate, this method is applicable to a variety of blending stocks.

DISCUSSION

Both dithizone methods are designed on the principle of pH control. Because any dithizone method is pH-sensitive, periodic pH measurement

should be included to assure the best possible accuracy. If the pH is incorrect, a correction should be applied for the spectrophotometric method or better pH control established for the color-comparator method. In many instances, the problem can be eliminated by the preparation of a new buffer. Decomposition and extraction of lead and random lead contamination seem to be the factors limiting the precision of both methods. The authors have suspected that this is caused by the presence of trace quantities of naturally occurring lead compounds which do not react stoichiometrically with bromine to form water-soluble lead salts. This explanation would account for the lower precision obtained recently in the analysis of a sample of charge stock before and after clay treatment. The clay apparently removed a few parts per billion of lead, and analyses of the treated samples gave precision equivalent to that obtained on blended iso-octane samples, whereas the untreated samples showed variations from the mean of 10 p.p.b.

The spectrophotometric method is most suitable for use in a laboratory for the simultaneous analysis of a number of samples; the color-comparator method is most suitable for use in a field or refinery situation for the rapid analysis of a few samples. It requires only 10 minutes for one sample. Both methods are accurate to 10 p.p.b. over the range of 0 to 100 p.p.b.

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Table IX. Analyses of Various Gasoline Base Stocks by Color-Comparator Method

Gasoline Base Stock Used	Lead, P.P.B.		
	Present	Found	Difference
Stabilized virgin naphtha	197	180	-17
Light catalytically cracked naphtha	197	180	-17
Thermally cracked (80% reformate and 20% visbreaker naphtha)	197	200	+ 3
Polymerized gasoline	197	180	-17
Aviation alkylate	197	200	+ 3