ANALYTICAL REACTIONS OF TETRAETHYL LEAD[1]

Graham Edgar and George Calingaert

Ethyl Gasoline Corporation Laboratory, Yonkers, N. Y.

Analytical methods have been described for the determination of tetraethyl lead and related compounds in concentrated preparations, and of tetraethy lead in dilute solution in gasoline.

The limits of accuracy of these methods, and their applicability, under different conditions, have been discussed.

The wide distribution of motor gasoline containing tetraethyl lead has stimulated interest in the analytical methods that can be applied to organic lead compounds. Except for the publications of Krause and his coworkers several years ago (9) and the more recent article by Gilman (8), practically no methods of analysis applicable to concentrated organic lead preparations have been published. On the other hand, several methods of analysis of gasoline for tetraethyl lead have been suggested in the literature (1, 2, 4, 5, 7, 10) which, from the authors' experience, are somewhat lacking in both convenience and accuracy. Since the methods suggested by Krause and by Gilman are of only limited applicability, it may be of interest to present in detail and discuss the methods which have been developed in this laboratory and employed for several years.

The methods as described herein apply particularly to tetraethyl lead and other ethyl lead compounds. Their applicability to other alkyl lead compounds will be considered in the discussion.

For the physical and chemical properties of organic lead compounds on which the analytical methods are based, the reader is referred to a review of the subject by one of the authors (3).

Experimental Methods

Method 1. TOTAL LEAD IN CONCENTRATED PREPARATIONS

Caution--Concentrated preparations of organic lead compounds are highly poisonous. They should be handled under a hood equipped with vigorous suction, and care should be employed to prevent contact with the hands.

(a) Gravimetric.

Reactions: $PbEt_4 \longrightarrow PbBr_2 \longrightarrow PbCrO_4$

To about 25cc. of carbon tetrachloride in a 500-cc. Erlenmeyer flask add about 1cc. of tetraethyl lead or its concentrated solution, weighed in a Lunge pipet (6). Keep the Erlenmeyer flask ice cold, and add slowly and with constant shaking an excess (5 to 10 cc.) of a 30 per cent solution of bromine in carbon tetrachloride.

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Evaporate on a steam bath the carbon tetrachloride from the solid lead bromide. To the dry lead bromide add a mixture of 30 cc. of concentrated ammonia (sp. gr. 0.90) and 50 cc. of 50percent acetic acid, washing down the sides of the flask. Boil until the precipitate is completely dissolved and any remaining carbon tetrachloride removed. Filter from any insoluble matter and wash the flask out well with hot water into a beaker. Dilute the filtrate and washings to 450 cc. and heat to boiling on a hot plate. Now add slowly and with constant stirring 40 cc. of a 5 percent solution of potassium dichromate. Stir for 5 minutes while the solution is boiling, then remove from the hot plate and keep in a warm place for one hour. Collect the precipitate on a weighed and ignited Gooch crucible and wash well with hot water. Dry in a crucible air bath, or in an oven at 105 degrees C. and weigh as $PbCrO_4$.

(b) Volumetric.

Reactions: $PbEt_4$ ------ > $PbBr_2$ ------ > $PbMoO_4$

Prepare the ammonium acetate solution of lead as in section (a), boil it down to 150 cc., and titrate hot with a standard molybdate solution, until a yellow coloration is obtained with tannic acid used as outside indicator. The molybdate solution is standardized against a known weight of lead or lead chloride (11). The indicator used is a 0.5 per cent freshly prepared solution of tannic acid. Care must be taken always to use the same amount of indicator (2 drops) and solution (4 drops). A blank is run on the same amount of water and ammonium acetate, and the amount of molybdate solution used to give a distinct coloration (about 0.3 cc.) is subtracted from the result of the titration.

Method 2. TOTAL ORGANIC LEAD IN DILUTE SOLUTION (IN GASOLINE)

(a) Gravimetric.

Measure with a pipet 100cc. of gasoline containing tetraethyl lead in a 400-cc. beaker. Add slowly a solution of 30 per cent bromine in carbon tetrachloride, until the permanent brown-red color of bromine is obtained.[2] Filter promptly through asbestos in a dry Gooch crucible--or preferably through a fritted Jena glass filter crucible of No. 2 porosity--and wash with petroleum ether. Put the crucible back in the beaker where the precipitation was made and add about 3 cc. of nitric acid (sp. gr. 1.40) in the crucible. Add a warm solution of 10 per cent nitric acid in quantity just sufficient to cover the top of the crucible, bring to boiling, remove the crucible, and boil down to about 5cc. Dilute and filter the solution through soft filter paper (if a Gooch crucible was used), rinsing the beaker and crucible with warm water. Just neutralize the filtrate with ammonium hydroxide and add 5 cc. of 50 per cent acetic acid. Continue as per Method 1 (a).

Note 1 -- Gasolines containing a high percentage of unsaturated compounds absorb bromine vigorously with evolution of heat. In such cases it is highly advisable to dilute the sample with about 100 cc. of a volatile petroleum fraction fairly free from unsaturated compounds (cracked stock), to add the bromine slowly, and to keep the beaker in ice. When this precaution is not taken, the results are apt to be low. Suitable diluents are, for instance, fighting grade aviation gasoline, petroleum ether, and ligroin.

[2] This method of separating the lead from the gasoline was worked out independently in several laboratoris during the early part of the research

Note 2 -- Some gasolines, when treated with bromine, give a tarry liquid insoluble in gasoline. In such cases the precipitated lead bromide should be washed with special care with petroleum ether, in order to remove the tar thoroughly before dissolving the lead bromide in nitric acid.

(b) Volumetric.

Prepare the ammonium acetate solution as in Method (2)(a), boil down to 150 cc., and titrate hot with a standard molybdate solution as in Method 1 (b).

Note 1 -- The molybdate solution may be made to contain 2.380 grams of commercial C. P. salt, in which case 1 cc. of this solution used on an original 100-cc. sample of gasoline corresponds to 0.1 cc. of tetraethyl lead (sp. gr. 1.65) per gallon of gasoline.

Note 2 -- In some cases the lead nitrate which begins to precipitate when the solution is concentrated to 5 cc. volume is contaminated by a small amount of organic matter. It is then advisable to evaporate to dryness and treat with fuming nitric acid, repeating the operation until a clean white residue of lead nitrate is obtained.

Method 3. TETRAETHYL LEAD IN CONCENTRATED PREPARATIONS--

Reaction. $Pb(C_2H_5)_4 + I_2 = Pb(C_2H_5)_3I + C_2H_5I$

Solutions: 0.1 N iodine containing 50 grams of C.P. potassium iodide per liter; 0.1 N sodium thiosulfate; starch solution; C.P. benzene.

Apparatus: 250-cc. glass-stoppered flasks; weighing pipet (See Note 4) weighing burets or accurate volumetric apparatus.

Procedure: Weigh accurately 0.5 cc. of pure tetraethyl lead, or 1 cc. or less of its concentrated solution, and add it to 50 cc. of C.P. benzene in a 250-cc glass-stoppered flask. Add at once 0.1 N iodine solution in amount equal to 2 to 5 cc. above the theoretical. (For tetraethyl lead the weight of the sample multiplied by 15 gives very nearly the correct volume of 0.1 N iodine: for a solution its approximate concentration must be determined by a trial titration.) Shake vigorously for 2 to 3 minutes and titrate the excess iodine with 0.1 N sodium thiosulfate, using starch solution as indicator and shaking vigorously meanwhile.

The number of cubic centimeters of 0.1 N iodine required times 0.01617 equals the weight of tetraethyl lead in the sample.

Note 1 -- In order to obtain accurate results, it is important that the procedure be followed in all its details, especially in regard to the amount of benzene and the concentration of potassium iodide in the iodine solution.

Note 2 -- When titrating with sodium thiosulfate part of the iodine is in the aqueous potassium iodide layer and part in the benzene. The titration can be run rapidly until the blue color of the iodine-starch in the water layer disappears. This will reappear on shaking, and the titration is then completed by adding the thiosulfate drop by drop, shaking well between additions.

Note 3 -- If the excess iodine is less than 2 cc., the results are usually low and the analysis should be repeated. More than 5 cc. excess can usually be added safely, but 2 to 5 cc. is best. If a yellow precipitate (of lead iodide) appears, the analysis should be rejected.

Note 4 -- For a convenient type of pipet devised primarily for this use, see Reference (6).

Method 4. MIXTURES OF TETRAETHYL LEAD AND DILEAD HEXAETHYL

Such mixtures are usually obtained in the preparation of alkyl lead compounds by the Grignard reaction. If no other substance is present, the specific gravity will indicate the composition of the mixture, the specific gravity of the two compounds being approximately 1.65 and 1.94, respectively. More accurate information will, however, be obtained by analysis. Both substances react with iodine:

$$Pb(C_2H_5)_4 + 2I = Pb(C_2H_5)_3I + C_2H_5I$$

$$Pb_2(C_2H_5)_6 + 2I = 2\ Pb(C_2H_5)_3I$$

The total lead present can be determined by Method 1.

From the results of the iodine titration and the determination of total lead, performed as per Methods 1 and 3, the amounts of tetraethyl lead and dilead hexaethyl can readily be calculated.

Method 5. TRIETHYL LEAD SALTS, WITH OR WITHOUT TETRAETHYL LEAD PRESENT

The triethyl lead salts are extracted with aqueous ammonia in which they are more soluble than in organic solvents.

Procedure. Dilute about 5 cc. of the concentrated preparation with 20 cc. of petroleum ether, and shake it with two successive portions of 20 cc. of a concentrated aqueous ammonia solution. Boil most of the ammonia off gently, acidify the remaining solution with nitric acid, boil down to about 3 cc., and analyze for lead as per Method 2 (a) or 2 (b).

Method 6. TETRAETHYL LEAD AND TRIETHYL LEAD SALTS

Extract the preparation with ammonia as per Method 5 to obtain the triethyl lead compounds. Treat the residue as per Method 1 to obtain the tetraethyl lead.

DISCUSSION

ACCURACY

According to the experience of the authors, Method 1 is as accurate as ordinary analytical methods in inorganic chemistry--i.e., 0.3 to 0.1 percent depending on the skill and care applied. In Method 2 the accuracy depends somewhat on the concentration of lead present, and on the nature of the solvent. (Gasolines containing large amounts of unsaturated compounds tend to give a tarry precipitate, which cannot always be transferred quantitatively.) However, the accuracy of routine analysis is better than 1 per cent for quantities of 0.75 to 3.0 cc. of tetraethyl lead per gallon of gasoline (0.02 to 0.08 per cent by volume, 0.04 to 0.16 per cent by weight), which seems to be sufficient for all practical purposes.

Method 3 appears to be good to at least 0.3 per cent when pure preparations are handled and when the procedure is followed accurately. The accuracy of Method 4 is somewhat uncertain, because no alkyl compound of the type $RbgNg$ has ever been isolated in the pure state. Comparison with other properties (density, stability) seems to indicate that the method is quite reliable.

Method 5 and 6 will give results accurate to within 1 to 2 per cent on the triethyl lead salts. The accuracy appears to be limited more by the instability of the compounds involved than by any shortcomings of the method.

APPLICABILITY

As stated in the introduction, the methods have been developed primarily for the analysis of tetraethyl lead and accompanying impurities. The aryl lead compounds are much more stable than the alkyl compounds, and the methods given here would have to be modified somewhat to apply in their case (8).

Methods 1 and 2 have been applied successfully to several alkyl lead compounds beside ethyl. Methods 3 and 4 would probably also be applicable in their case, but the authors have had no experience with them.

Methods 5 and 6 will determine with certainty the presence of as little as 1 per cent of a triethyl lead salt in tetraethyl lead.

Methods 1 and 2 appear to be applicable to practically all organic solvents, with the exception of those that would react too violently or too completely with bromine. Methods 3 and 4 are obviously applicable only in the absence of substances which react with iodine in the conditions specified. The conditions of concentrations and the amount of reagent are of such importance from the standpoint of accuracy that the method would probably not be applicable to dilute solutions in the presence of unknown substances.

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