

TRACE CONCENTRATIONS OF LEAD IN GASOLINE OR PETROLEUM NAPHTHAS

UOP Method 350-82

SCOPE

This method is for rapidly determining trace concentrations (10 to 400 ppb) of lead in gasolines and petroleum naphthas. The method is not applicable to higher boiling range materials. The method is specifically applicable to alkyl lead compounds, for example, TEL and TML. Application to other lead compounds has not been investigated.

OUTLINE OF METHOD

The sample is brominated and the lead present is extracted with a dilute nitric acid solution. The total lead present is measured colorimetrically after conversion to lead dithizonate.

APPARATUS

Balance, capable of weighing 0.1 mg

Balance, top loading, capable of weighing 0.01 g

Bottle, Pyrex, glass stoppered, 4-L capacity, available from Sargent-Welch Scientific Co., Cat. No. S-8465-A, or equivalent

Bottle, round, amber glass, glass stoppered, 500-mL capacity, available from Sargent-Welch Scientific Co., Cat. No. S-8355-E, or equivalent

Bottle, round, borosilicate glass, glass stoppered, one-liter capacity, available from Sargent-Welch Scientific Co., Cat. No. S-8335-F, or equivalent

Color comparator tubes, Hellige Inc., Cat. No. 600T13, standard tubes of 13-mm viewing depth, or equivalent

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Cylinders, graduated, 100-, 50-, and 25-mL

Funnel, separatory, 250-mL

Lead dithizonate disk, Hellige Inc., Cat. No. 620S-10, or equivalent. This disk is calibrated in units of 0, 1, 2, 3, 4, 6, 8, 10, 15 and 20.

Visual color comparator, Hellige Inc., Cat. No. 605 AHT, or equivalent

Pipet, volumetric transfer, 2- and 10-mL

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications exist, unless otherwise specified. References to water mean distilled or deionized water.

Reagent grade chemicals usually are free of lead. However, if the reagent blank as determined under *PROCEDURE* should exceed the equivalent of 20 ppb of lead, it is necessary to delead the buffer solution.

Ammonium hydroxide, concentrated

Bromine solution. Dilute 454 g (1 lb) of bromine (avoid contact with the skin or inhaling the fumes, see Note 1) to 500 mL with carbon tetrachloride (see Note 2).

Buffer solution. Dissolve 25 ± 0.1 g of ammonium citrate, 10 ± 0.1 g of potassium cyanide (protect hands from accidental contact, see Note 3) and 75 ± 0.1 g of anhydrous sodium sulfite in 400 mL of water. Dilute to 2 L with concentrated ammonium hydroxide (see Notes 4 and 5).

Chloroform, 99.5% minimum purity. Use chloroform dispensed directly from its container.

Cyclohexene, 99% minimum purity, available from Aldrich Chemical Co., Cat. No. 12543-1, or equivalent

Dithizone solution. Dissolve 120 ± 5 mg of dithizone in 500 mL of chloroform. Store the solution in an amber bottle in a refrigerator.

Naphtha, delead. This is required only for dilution of samples of higher lead content. Naphtha may be delead by shaking with dilute nitric acid and checking the extracts with dithizone and the buffering solution, repeating the treatment until the dithizone color remains unchanged.

Nitric acid (1:99). Dilute one volume of concentrated nitric acid with 99 volumes of water.

Nitric acid (1:1). Dilute one volume of concentrated nitric acid with one volume of water.

Petroleum jelly, "Vaseline"

Sodium thiosulfate

Thymol blue, indicator solution

PREPARATION OF APPARATUS

Delead a one-liter borosilicate glass bottle and stopper by rinsing with hot nitric acid (1:1) followed by water. Thoroughly rinse with water so that no traces of acid remain. Test for lead by adding 5 mL of buffer solution, 50 mL of water and 10 mL of dithizone solution. Shake for 30 seconds and observe the color. The absence of a red color ensures lead-free glassware. Discard the test solution and rinse the bottle with lead-free water. Collect all gasoline and naphtha samples in lead-free bottles.

Delead all separatory funnels, color comparison tubes and any other glassware used, by the method outlined for sample bottles in the preceding paragraph.

PROCEDURE

Bring the sample to a temperature of about 15 C and then measure a volume of the sample equivalent to 45 g with a 100-mL graduated cylinder. In practice it is sufficiently accurate to use 60 mL and assume a specific gravity of 0.75. Transfer the material into the 250-mL separatory funnel and add 10 mL of cyclohexene to heat the sample by reaction with the bromine. The addition of cyclohexene is not required for cracked gasolines since they contain sufficient olefins to increase the temperature to about 50 C. Use "Vaseline" to lubricate the stopper and stopcock of the separatory funnel. Mix the contents well. Slowly, and with extreme care, add the bromine solution (see Note 1) until the color of excess bromine persists for at least 5 minutes. Allow the mixture to stand for 4 additional minutes.

Add 30 mL of chloroform (see Note 2) and 100 mL of dilute (1:99) nitric acid to the separatory funnel. Immediately shake the funnel for one minute. Allow the contents to settle and discard the lower (organic) layer. *Do not allow* the layers to remain in contact with each other for over 2-3 minutes.

Wash the acid solution containing the lead with 25 mL of chloroform for 20-30 seconds and discard the washings. Add 50 mL of the buffer solution (See Note 3) and 5 mL of chloroform; shake for 20-30 seconds. Allow the chloroform layer to separate completely from the aqueous phase and discard this and all droplets of chloroform. Swirl to dislodge the droplets. (An aspirator bulb can be used to dislodge the chloroform droplets by using the exhaust end, forcing air into the surface of the liquid, and then swirling.) When all chloroform is removed add 2 mL of dithizone solution to the funnel and shake vigorously for 30 seconds. Allow the chloroform-lead dithizonate solution to settle. Draw off the colored solution into a color comparison tube.

Run a reagent blank by following the same procedure with these exceptions: use 30 mL of chloroform in place of the sample and omit the addition of chloroform in the extraction with the dilute nitric acid. Use this blank (it should be "water white") as a background for the glass standards. Now compare the dithizone extract of the unknown by matching its color with a corresponding color of the standard in the Hellige comparator. By estimating the color to one-half unit, a lower limit of detection of 10 ppb of lead is realized.

In the event the dithizone extract of the sample is darker than the highest standard (400 ppb), a somewhat less accurate determination of the lead content of the naphtha may be made by diluting a suitable volume of the sample (usually 25-100 mL) to 500 mL, with a delead naphtha, and repeating the determination as outlined in the *PROCEDURE*. When dilutions are made, it is sufficiently accurate to assume the specific gravity of the sample to be 0.75.

When lead concentrations of 10 ppb or less are sought, use a larger sample size, in all cases keeping the volume of the chloroform used to at least one-half the volume of the sample in order to ensure easy phase separation. It is advisable to limit the mass of sample used to not more than 135 g (approximately 180 mL).

When lead concentrations of 20 ppb and below are sought, the use of reagents having correspondingly low lead contents is mandatory.

CALCULATIONS

Calculate the lead concentration as follows:

$$\text{Lead, mass-ppb} = 20 A$$

where:

A = color comparator reading

If a mass of sample other than 45 g is used, calculate the lead content as follows:

$$\text{Lead, mass-ppb} = \frac{900 A}{W}$$

where:

A = color comparator reading

W = mass of sample used for the determination, g

When the lead concentration is high and the sample has been diluted with lead-free naphtha, calculate the lead content as follows:

$$\text{Lead, mass-ppb} = \frac{20 A V_2}{V_1}$$

where:

A = color comparator reading

V₁ = volume of sample used for dilution, mL

V₂ = final volume to which sample is diluted, mL

NOTES

1. The bromine solution is capable of causing severe burns if allowed to contact the skin. In the event this happens, wash the area with a concentrated solution of sodium thiosulfate until the bromine coloration disappears. Rinse in running water to remove the mildly poisonous thiosulfate. Bromine fumes *must not* be inhaled.

2. The fumes of both carbon tetrachloride and chloroform are toxic if inhaled.

3. The buffer solution contains potassium cyanide. Handle it with care. Do not make it acidic or dispose of it with an acidic solution. Use rubber gloves when handling solid potassium cyanide.

4. It may be necessary in rare instances to delead the buffer solution. Use the following procedure: To the reagents dissolved in 400 mL of water add ammonium hydroxide until alkaline to thymol blue. Transfer to a separatory funnel and shake with 25-mL portions of dithizone solution. Discard the dithizone solutions and

repeat shaking with fresh portions until the dithizone color remains unchanged. Wash the aqueous solution through a previously wetted, fluted filter to remove the chloroform (Note 2). Dilute the delead solution to 2 L with concentrated ammonium hydroxide.

5. The stored buffer solution can become less basic through the loss of ammonium hydroxide. This can result in a green color formation instead of red when the dithizone is added. If this occurs, it is necessary to prepare fresh buffer solution.

PRECISION

Based on 6 replicate determinations the estimated standard deviation (esd) for lead at the 35 ppb level was calculated to be 5.0 ppb.

Duplicate results by the same operator should not differ by more than 18 ppb (95% probability) at the stated level.

TIME FOR ANALYSIS

The elapsed time for one analysis is 0.83 hour. The labor requirement is also 0.83 hour.

REFERENCE

Griffing, M. E., Rozek, A., Snyder, L. J., and Henderson, S. R., *Anal. Chem.* **29**, 190-195 (1957)

SUGGESTED SUPPLIERS

Aldrich Chemical Co., 940 W. St. Paul Avenue, Milwaukee, WI 53233
Hellige Inc., 877 Stewart Avenue, Garden City, Long Island, NY 11530
Sargent-Welch Scientific Co., 7300 N. Linder Avenue, Skokie, IL 60077