Colorimetric Determination of Red Lead (Minium)

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Many unsuccessful attempts have been made to determine red lead in mixed paint pigments. Results are difficult to duplicate in the analysis of commercial red lead by recognized methods. These analyses can now be made quickly and accurately by a simple colorimetric procedure.

THE Diehl-Topf, Figg, Schaeffer, and other methods for analysis of red lead are to a great extent applicable to unmixed red lead but not to mixed pigments containing red lead. These methods depend on the liberation of iodine by red lead or on the reduction of red lead by hydrogen peroxide, oxalic acid, arsenious oxide, etc., and thus can be used only in the absence of substances other than oxides of lead that liberate iodine or reduce peroxides under the conditions of the analysis. In the iodometric methods, light causes the liberation of iodine in excess of the anticipated amount when analysis of mixed pigments is attempted. This effect is seemingly increased when lead chromate pigment is present. In attempting to analyze mixed pigment the necessary filtration is an additional source of error.

Red lead, mixed or unmixed, has been successfully determined by a simple colorimetric procedure in which the decomposition of lead tetraacetate by sufficient water to reduce the acidity of the final solution to 0.2 N or less, results in a clear yellow to red colloidal suspension of insoluble lead dioxide. The following equations describe the reaction:

$$\begin{split} Pb_3O_4 &+ 4CH_3COOH = Pb(CH_3COO)_4 + 2PbO + 2H_2O \\ Pb(CH_3COO)_4 &+ 2H_2O = PbO_2 + 4CH_3COOH \end{split}$$

ANALYTICAL PROCEDURE

The analytical procedure varies slightly, depending on whether red lead under analysis is isolated or mixed with other pigments. Both methods are given, since the establishing of color standards is identical with the analysis of the isolated red lead.

For Red Lead (Unmixed). The red lead powder is dried for several hours at 125° C. under full vacuum and 0.5 gram is weighed to 4th decimal accuracy into a predried 125-ml. glassstoppered flask. Exactly 20 ml. of fresh, glacial acetic acid are added from a precision buret, and the flask is quickly stoppered and swirled at room temperature for a few minutes until the lumps are finely divided. A small strip of paper is inserted at one side of the stopper and the flask is placed in a water bath at 60° C. and swirled every few minutes until red lead has completely dissolved. Vigorous shaking of the tightly stoppered flask may be necessary to effect solution. When cooled, the solution should be clear. If a slight cloudiness or dark coloration appears, conditions or materials have not been anhydrous.

This red lead solution is transferred to a microburet and an exact aliquot of not less than 0.25 ml. and not more than 3.0 ml. is drawn off into a 600-ml. beaker. Without delay, 5 ml. of absolute alcohol for each 0.25 ml. of aliquot are added from a graduate and the mixture is quickly swirled for 2 or 3 seconds. About 225 ml. of cool distilled water are quickly added from a graduate with immediate and rapid stirring. Color will develop at once. If any appreciable color appears when the alcohol is added, water is present in either the alcohol or the acetic acid and erroneous results will be obtained. The solution is next transferred to a 250ml. volumetric flask, brought to volume with water, and compared to colored standards containing known amounts of red lead, developed by the same procedure. The color comparison should be made immediately and the use of Fisher electrophotometer with green light filter is recommended. A graph developed in this way is a straight line if the logarithmic scale of the instrument is used. This graph should be prepared by following the procedure through with exactly 0.5 gram of red lead of known high purity, 99% or higher, and developing colored standards by drawing off a series of aliquots ranging from 0.25 to 3.0 ml.

For Mixed Pigments Containing Red Lead. The pigment is extracted from the wet paint by the usual centrifuge method, except that anhydrous ethyl ether (technical) is used as the extraction solvent.

The finely ground and sifted pigment (100-mesh sieve) is dried

for several hours at 125° C. under full vacuum and a sample containing not less than 0.2 gram of red lead is weighed into a predried 50-ml. centrifuge tube having a constricted neck. Exactly 20 ml. of glacial acetic acid are added from a precision buret. The tube is quickly stoppered with a rubber stopper and shaken for a few minutes at room temperature, then placed in a water bath at 60° C. The stopper is loosened momentarily to release pressure and the tube is vigorously shaken every few minutes. It is removed from the bath after 15 minutes, then centrifuged until the solution is clear and can be drawn off. The clear liquid is transferred to a microburet by means of a pipet and exactly 1 ml. is drawn off into a 600-ml. beaker. Then 20 ml. of absolute ethyl alcohol are added quickly from a graduate, the mixture is swirled for 1 second, and 200 ml. of distilled water are added immediately with constant and rapid stirring. Speed of addition of alcohol and water, respectively, is very important at this point. Alcohol prevents cloudiness which may appear when small amounts of red lead are present.

The colored solution is then transferred to a 250-ml. volumetric flask, diluted to volume with water, and compared on the electrophotometer at once. Fading will begin in 10 or 15 minutes and is accelerated by a delay in adding water to the aliquot following addition of alcohol. If the color formed is faint a larger aliquot may be used from the buret, provided 5 ml. of alcohol are added for each 0.25 ml. of aliquot used. Per cent of red lead is calculated from a graph prepared from standards as outlined above.

ACCURACY METHOD

A pigment mixture duplicating the minimum requirements of U. S. Army specification 3-181, O. D. enamel, was prepared from pigments predried at 125° C. under vacuum. This mixture contained precisely 17% red lead by weight. Baker's analyzed c.p. powder, analyzing 99.9% red lead was used. The approximate composition of the mixture was as follows: lead chromate 35%, red lead 17%, zinc oxide 8%, extenders and tinting pigments (magnesium silicate, carbon, etc.) 40%. Triplicate samples weighing exactly 2, 3, and 4 grams were

Triplicate samples weighing exactly 2, 3, and 4 grams were taken and the analysis proceeded according to the method given for mixed pigments. Results are as charted.

Weight of Sample Grams	Aliquot Used Ml .	Colorimetric Readings	Red Lead %
$\frac{2}{2}$	1 1	7.6, 7.6, 7.5 7.4, 7.4, 7.4	$\substack{17.25\\16.75}$
2 3	2	16.2, 16.1, 16.2 11.8, 11.8, 11.7	$17.0 \\ 17.0 \\ 16.87$
3 4	1 2 1	11.7, 11.8, 11.7 24.9, 24.9, 25.0 16.2, 16.2, 16.3	$10.87 \\ 17.0 \\ 17.05$
$\overline{4}$	$\hat{1}$	16.0, 16.2, 16.2 33.5, 33.6, 33.6	17.0 17.05

It is notable that accuracy increases as the red lead content of the aliquot taken approaches 50 mg. Results are reproducible to 0.05% when the aliquot contains 30 to 60 mg. of Pb₃O₄.

DISCUSSION

This method is specific, since red lead is the only compound used as a paint pigment that is completely soluble in glacial acetic acid and develops color when diluted under the conditions given. Litharge is soluble under the conditions but remains in solution when diluted. Lead dioxide is insoluble in glacial acetic acid. To attempt to separate red lead from mixed pigments with glacial acetic acid and determine the total lead in the extraction would require correction for any litharge present. In the analysis of extracted pigments, some loss of red lead must be anticipated, since it is a highly reactive pigment and readily forms lead soaps with fatty acids of the vehicle. The unreacted red lead in the pigment would vary with the type of pigment and vehicle.