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DETERMINATION OF IRON CONTAMINATION OF USED LUBRICATING OIL
FOR USE IN MEASURING RATES OF WEAR IN AIRCRAFT ENGINES

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RESTRICTED BULLETIN

DETERMINATION OF IRON CONTAMINATION OF USED LUBRICATING OIL
FOR USE IN MEASURING RATES OF WEAR IN AIRCRAFT ENGINES

By Adelbert O. Tischler

SUMMARY

Object.— To develop suitable methods of determining the iron contamination of used lubricating oil in order to study wear rates of piston rings and cylinder barrels of aircraft engines.

Scope.— Two methods of separating the iron from the used lubricating oil are presented. In one procedure the oil is burned and the residual ash containing the iron is dissolved in acid; in the other, the iron is extracted from the oil with acid. Methods are described for determining the amount of iron present in the resulting solutions using o-phenanthroline to form a colored complex with the iron.

Summary of results.— The results obtained in the analyses of lubricating oil for iron contamination using the procedures described are as follows:

1. The iron concentrations of oil samples containing from 0.0001 to 0.010 percent by weight of iron can be determined.
2. With the ashing procedure, the average difference between the results of duplicate analyses of 40 representative samples of used lubricating oil was less than 5 percent.
3. The use of porcelain crucibles for ashing resulted in a loss of iron. This loss was avoided when silica crucibles were used.

4. Extraction of lubricating-oil samples with dilute hydrochloric acid for 4 hours yielded a recovery of 98 percent of the iron in the oil.

5. With calibration, any photoelectric or visual-type colorimeter will be found suitable for measurement of the color intensities of the iron o-phenanthroline solutions. Comparison of results obtained for the same solutions with a spectrophotometer and a colorimeter showed an average difference of less than 3 percent.

INTRODUCTION

Analysis of lubricating-oil samples for metallic contaminants as a method of determining rates of wear of internal-combustion engines offers a number of advantages over methods that involve mechanical measurements of the engine parts. Samples of the lubricating oil are withdrawn from the engine at periodic intervals and analyzed by sensitive chemical methods. The metallic concentrations, plotted against engine running time, yield a curve of progressive metal contamination from which the rate of wear at any time during the run can be calculated. The rate of wear can be established in considerably less engine running time than would be required to produce a significant change in weight or dimensions of engine parts and without the necessity of dismantling or stopping the engine. In application of this method, the wear or corrosion of a particular engine part or combination of parts can be measured only if the wear of other engine parts does not appreciably contribute to the concentration of the metal contaminant in the oil.

Among the metallic contaminants in oil, iron is of particular interest in the study of wear rates. When aluminum pistons are used in the engine, the iron in the oil is principally due to abrasion of the cylinder walls and the piston rings. Because most of the abraded iron is washed into the crankcase by the lubricant, periodic analyses of the iron contamination of the oil will indicate the rate of wear of the cylinder barrel and the piston rings.

Procedures for analyzing iron in lubricating oil can be resolved into two steps: (1) the separation of the iron from the organic matter and (2) the determination of

the amount of iron separated. Everett and Stewart (reference 1) burned samples of oil in silica crucibles, dissolved the residue containing iron oxide in hydrochloric acid, formed ferric thiocyanate, and determined the iron content colorimetrically. In reference 2, the thiocyanate method of estimating iron was also used, but the iron was obtained in solution by extracting the oil with dilute hydrochloric acid. These investigators found that the intensity of the ferric thiocyanate color was dependent upon the pH of the solution and that the color faded within a few minutes.

The method of determining iron with o-phenanthroline does not have the objectionable features of the thiocyanate method. Fortune and Mellon (reference 3) have shown that, when ferrous iron is combined with o-phenanthroline, the intensity of the color produced is determined solely by the amount of iron present when there is an excess of the o-phenanthroline reagent. The color does not fade and is not affected in the pH range from 2.0 to 9.0. Other metals, including aluminum, chromium, copper, and lead, which are generally found in used lubricating oil, do not interfere with the iron determination.

The use of either of these colorimetric methods for the determination of small amounts of iron in lubricating oil requires the development of a suitable method of obtaining the iron in an aqueous solution. The separation of the iron from the oil may be accomplished by one of the following methods: (1) burning the oil sample and dissolving the residual ash containing the iron in acid (ashing); (2) extracting the iron from the oil with acid; and (3) consuming the organic matter with chemical oxidizing agents (wet ashing).

This report describes procedures for ashing and acid extracting the oils, for analyzing the solutions, and for determining the accuracy of these methods. The third procedure, which requires sulfuric and perchloric acids for consuming the organic matter of the oil samples, was not used because a large volume of acid is required for a small oil sample and because noxious fumes are formed when the excess acid is eliminated.

The work was performed at the Aircraft Engine Research Laboratory of the National Advisory Committee for Aeronautics at Cleveland, Ohio, during December 1943 and January 1944.

APPARATUS

The extractors used for acid extraction of the oil samples were those commonly used for the determination of lead in gasoline and are described in reference 4.

The color intensities of the solutions of ferrous o-phenanthroline were measured on either of two instruments. For most of the work, a Beckman quartz spectrophotometer was used. The details of construction and operation of this instrument are described in reference 5. The extinction, or the optical density, of an unknown solution was read directly on the instrument dial in the range from 0.0 to 2.0.

The other instrument used was a colorimeter. In this instrument the light transmissions of the unknown and of a standard solution of the colored complex are visually matched by varying the length of the light path through one of the solutions.

METHODS

Two methods, ashing and acid extracting, for separating the iron from the lubricating oil were studied.

Ashing.— Care was taken to mix thoroughly all used lubricating-oil samples because a small amount of black sediment was observed to have separated from the oil after it had stood a few days. The inside of the bottle was scrubbed with a rubber-tipped glass stirring rod and the sludge was again mixed with the oil by vigorous stirring. Two standard-size portions (10 ± 0.05 grams) of each lubricating-oil sample were weighed on a small torsion balance and placed in 50-milliliter crucibles. The samples were analyzed in duplicate.

The oil was burned by heating over a Bunsen flame in a hood. After the oil became sufficiently hot to ignite, the burner was adjusted in such a way that the oil burned quietly without boiling. When the oil had been burned, the carbonaceous residue was ignited by the hot flame of a Meker-type burner until no carbon remained in the crucible. Tilting the crucible to provide better access of air to the residue hastened the combustion of the carbon. The entire burning procedure required approximately 1 hour.

The metal residue in the crucibles was taken up with 30 milliliters of 6 N hydrochloric acid. In order to hasten the dissolution of the metals, the crucibles were kept warm on a hot plate for about an hour. About 15 milliliters of acid were usually lost by evaporation. The solutions were then transferred quantitatively to 100-milliliter volumetric flasks. About 30 milliliters of distilled water were used to wash the solution from the crucible into the flask.

Acid extraction.— After thorough mixing, standard-size samples (10 ± 0.05 grams) of used lubricating oil were weighed into a small beaker. The oil was transferred quantitatively into the extractors, and about 100 milliliters of filtered lead-free gasoline were used to wash the oil from each beaker into the extraction apparatus. Fifty milliliters of 6 N hydrochloric acid were run into the extractor. Heat was applied and the current to the electrical heating elements was adjusted by means of rheostats to just avoid maintaining a continuous stream of condensate. Some difficulty was encountered with the reflux flooding the condenser in surges, and, in the case of some oils, with foaming of the oil layer; but these factors apparently did not affect the results obtained. The extraction proceeded for 2 hours. After the 2-hour extraction period, the liquids were allowed to cool somewhat and the acid layer was drained off directly into a 250-milliliter volumetric flask. Fifty milliliters of distilled water were added to the extractor, the solutions were again heated to boiling for 5 minutes, and, after they had cooled, the water layer was drained into the volumetric flask. The purpose of the water treatment was to wash extraction liquids that remained in the extractor into the flask.

Determination of iron in the aqueous solutions.— To the acid solutions obtained from either of the foregoing procedures were added 2 milliliters of a 10-percent hydroxylamine-hydrochloride solution and from 5 to 15 milliliters of a 0.1-percent solution of o-phenanthroline in water. The hydroxylamine reduced the iron to the ferrous state. Six milliliters of o-phenanthroline reagent were required for each 0.005 percent by weight of iron in a 10-gram oil sample. Sufficient 6 N ammonium hydroxide to develop the orange-red color of the ferrous o-phenanthroline complex was added, and the solutions were buffered with 20 milliliters of a 10-percent sodium-acetate solution. The amount of base used was so adjusted that, after the solutions were cooled and were diluted to the mark on the flask with distilled water, the final pH of the solution was between 4.0 and 8.0.

A correction for the amount of iron present in the reagents was obtained by preparing a blank solution containing the same amounts of each of the reagents as used for the samples.

The color intensities of the sample solutions were measured with either the spectrophotometer or the colorimeter. The wave-length scale of the spectrophotometer was set at 506 millimicrons (the peak of the absorption band of ferrous o-phenanthroline), and the slit width was set at 0.05 millimeter. Four matched Corex cells having a light path of 1.00 centimeter through the solution were used. From the extinction of each solution measured with the spectrophotometer, the amount of iron present in the oil sample was calculated from the formula:

$$W = \frac{0.000515 (E_s - E_b) V}{\text{weight of oil sample}}$$

where

W weight percentage of iron in the oil sample

E_s extinction of the sample solution as measured with the spectrophotometer

E_b extinction of blank sample

V volume of volumetric flask used, milliliters

0.000515 experimentally determined constant relating extinction and iron concentration of a solution for the spectrophotometer (The extinction was found to be a linear function of the iron concentration of the solution.)

When the colorimeter was used, the iron concentrations of the samples were determined by comparison of the color intensities of the unknown sample solutions with those of prepared samples containing known amounts of iron. The unknown iron concentrations were calculated from the formula.

$$C = \frac{C_1 d_1}{d}$$

where

- C concentration of iron in unknown sample solution
- C₁ concentration of iron in prepared solution
- d₁ length of light path through standard solution with light fields matched
- d length of light path through unknown solution

Three values of the ratio d_1/d were obtained, varying d between readings, and averaged before calculating C. A correction for the blank solution, determined in a similar manner, was applied before the amount of iron in the original oil sample was calculated.

RESULTS AND DISCUSSION

Analyses of prepared oil samples.— Repeated analyses of lubricating oil present difficulty in checking the accuracy of the methods, inasmuch as any error consistently introduced during the procedure would not be apparent in the results of the repeat runs. In order to test the accuracy of the ashing procedure, a series of four oil samples containing amounts of iron from 0.000268 to 0.00828 percent by weight were therefore prepared by dissolving a paint drier containing iron in mineral oil. The exact iron concentration of the paint drier was not known. An oil solution containing approximately 0.1 percent by weight of iron was first prepared, and the other solutions were made from it by diluting a weighed portion of the 0.1-percent solution with a weighed amount of mineral oil.

The results of analyses of the prepared oil samples using both the ashing and the extraction procedures are given in table 1. Two of the prepared oil samples (2 and 3) were analyzed by the acid-extraction procedure. Duplicate analyses checked satisfactorily, and further acid extraction of the same samples showed that all the iron was recovered in the first 2-hour extraction. The ratio of the experimental concentrations for samples 2 and 3 agreed with the ratio calculated on the basis of the dilution weighings. The average of the analyses of sample 2 was taken as correct and the concentrations of iron in the other samples were calculated from the dilution ratios.

Comparison of silica and porcelain crucibles for ashing procedure.— It was observed that when porcelain crucibles were used about five or more times for these analyses, the disagreement of duplicate analyses was considerably greater than when new crucibles were used. This fact was presumably due to absorption of the iron by the glaze of the porcelain crucibles at the temperatures reached in burning the carbonaceous residues. The analyses of the synthetic oil samples were therefore made using both silica and porcelain crucibles. The analyses with silica crucibles showed an average deviation of less than 3 percent from the calculated iron concentrations; high as well as low percentages were obtained. As may be seen from table 1, the porcelain-crucible results averaged about 6 percent less than the results obtained with acid extraction. This loss makes the use of porcelain crucibles undesirable for this procedure.

Analyses of used lubricating-oil samples.— The ashing method has been used to analyze numerous oil specimens in this laboratory. The average difference between the results of duplicate analyses with silica crucibles of 40 oil samples, chosen as representative, was less than 5 percent. The iron concentrations of these samples ranged from 0.001 to 0.010 percent by weight. The percentage deviation of duplicate analyses is plotted in figure 1 against the average of two determinations for each sample.

In order to illustrate the nature of the results obtained from this type of analysis, a typical set of analyses of lubricating-oil samples taken from an engine oil sump is plotted against hours of engine operation in figure 2. The analyses were made in duplicate by the ashing technique using silica crucibles and the iron content of the solutions was measured with the spectrophotometer.

Acid extraction of the iron from used lubricating-oil samples was found to be more difficult than the extraction of prepared mineral-oil samples. Two-hour acid extractions of used lubricating oil gave a recovery of the iron in the oil of 90 to 97 percent, based on results obtained by the ashing procedure. Second and third 2-hour extractions of the same samples showed the presence of iron but, in all cases, the iron present in the third extract was less than 2 percent of the total iron extracted.

The use of gasoline to lower the viscosity of the oil layer appears to result in faster extraction of the iron

from the oil than when it is not used. Extractions of undiluted oil samples gave relatively poor results and left a yellow color in the acid layer that was not due to iron.

Photometry and colorimetry.— Repeated measurements of the extinctions of a number of solutions with the spectrophotometer showed that the values were consistently reproducible within 1 percent when the measured extinction was between 0.10 and 2.0. The percentage error in measuring the extinctions of solutions containing very small amounts of iron increased as the extinction of the solutions approached zero. Solutions that had extinctions greater than 2.0 required dilution before the extinctions could be accurately measured. Although a spectrophotometer was used for most of this study, a photoelectric colorimeter should be capable of equally accurate results if a calibration curve for the amount of iron in the solutions is prepared.

The errors introduced by using a visual-type colorimeter to estimate the iron concentrations were also studied. A series of 30 solutions was analyzed with both the spectrophotometer and the colorimeter. The results are plotted in figure 3. The analyses obtained by the two methods showed an average deviation of less than 3 percent.

Evaluation of oil-analysis methods.— Analysis of lubricating-oil samples using the ashing technique described requires less apparatus and can be carried out in somewhat less time than the acid-extraction procedure for a single determination. If a battery of extractors could be set up, the extraction method would require less man-hours per sample, inasmuch as this equipment requires little attention during the extraction.

In the acid-extraction procedure, the use of smaller extractors, smaller samples, and, correspondingly, less of reagents would save materials, because only a few milliliters of solution are required for measuring the color intensity. Preliminary tests with an extractor of about one-third the dimensions of the lead-extraction apparatus have given satisfactory results.

Permissible concentration range.— Although the limiting measurable concentration of iron with a 1.00-centimeter spectrophotometer cell was 0.01 percent by weight in a 10-gram oil sample, much larger quantities in an unknown

sample could be determined by diluting the aqueous sample solution. The range of measurable iron concentrations could also be considerably extended by use of larger or smaller oil-sample portions or by use of longer or shorter cells in the photometric instrument.

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TABLE 1.- ANALYSES OF MINERAL-OIL SAMPLES CONTAINING
KNOWN RATIOS OF IRON CONCENTRATION

Sample →	1	2	3	4
Ratio of iron concentration of samples to iron concentration of sample 2	0.327	1.00	3.58	10.1
Calculated iron concentrations, ^a percent by weight × 10 ⁴	2.68	8.20	29.3	82.8
Acid extraction				
Iron concentration, percent by weight × 10 ⁴	-----	8.29	29.0	-----
Mean value		<u>8.11</u> b8.20	<u>29.0</u> 29.0	
Observed ratio of iron concentrations	-----	1.00	3.54	-----
Ashing (silica crucibles)				
Iron concentration, percent by weight × 10 ⁴	2.65	8.21	29.3	81.0
	2.81	8.54	29.0	84.3
	2.58	-----	28.7	79.4
	<u>2.88</u>	-----	<u>29.9</u>	<u>80.7</u>
Mean value	2.73	8.37	29.2	81.4
Observed ratio of iron concentrations	0.333	1.02	3.56	9.93
Ashing (porcelain crucibles)				
Iron concentrations, percent by weight × 10 ⁴	2.52	7.65	26.6	83.0
	2.40	7.88	27.4	81.4
	2.70	7.62	25.3	76.3
	2.59	7.00	28.6	84.3
	2.47	7.50	25.5	81.0
	<u>2.42</u>	<u>7.80</u>	<u>27.0</u>	-----
Mean value	2.52	7.58	26.7	81.2
Observed ratio of iron concentrations	0.307	0.924	3.26	9.90

^aComputed on the basis of 8.20 × 10⁴ percent iron in sample 2 (acid-extraction analysis) and the known ratios of iron concentrations in the four samples.

^bThis quantity taken as unity in computing observed ratios of iron concentrations.

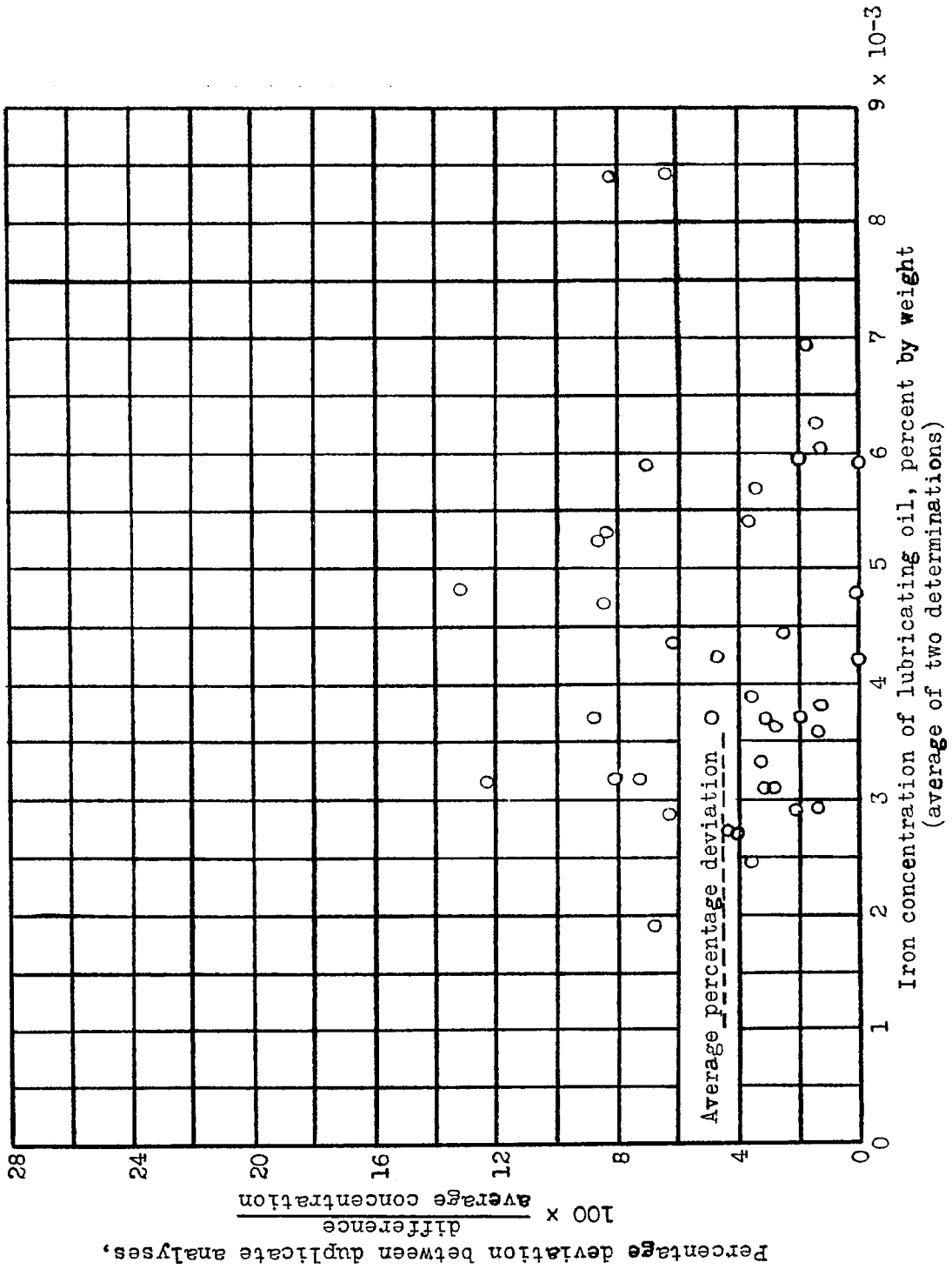


Figure 1.- Deviation between duplicate iron analyses of lubricating-oil samples analyzed by ashing procedure.

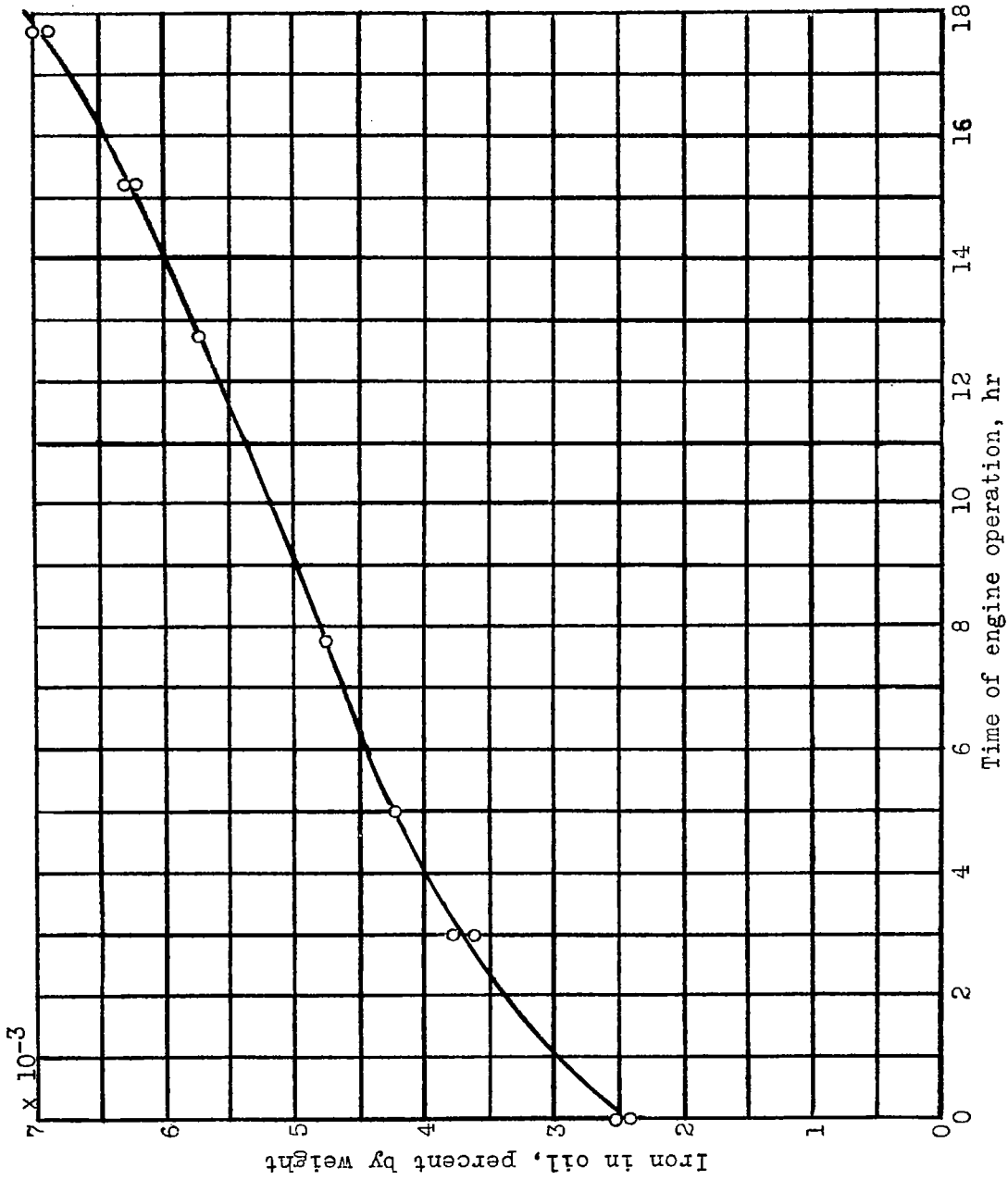


Figure 2.- Example of progressive contamination of lubricating oil with iron during engine operation. (Oil samples analyzed by ashing procedure.)

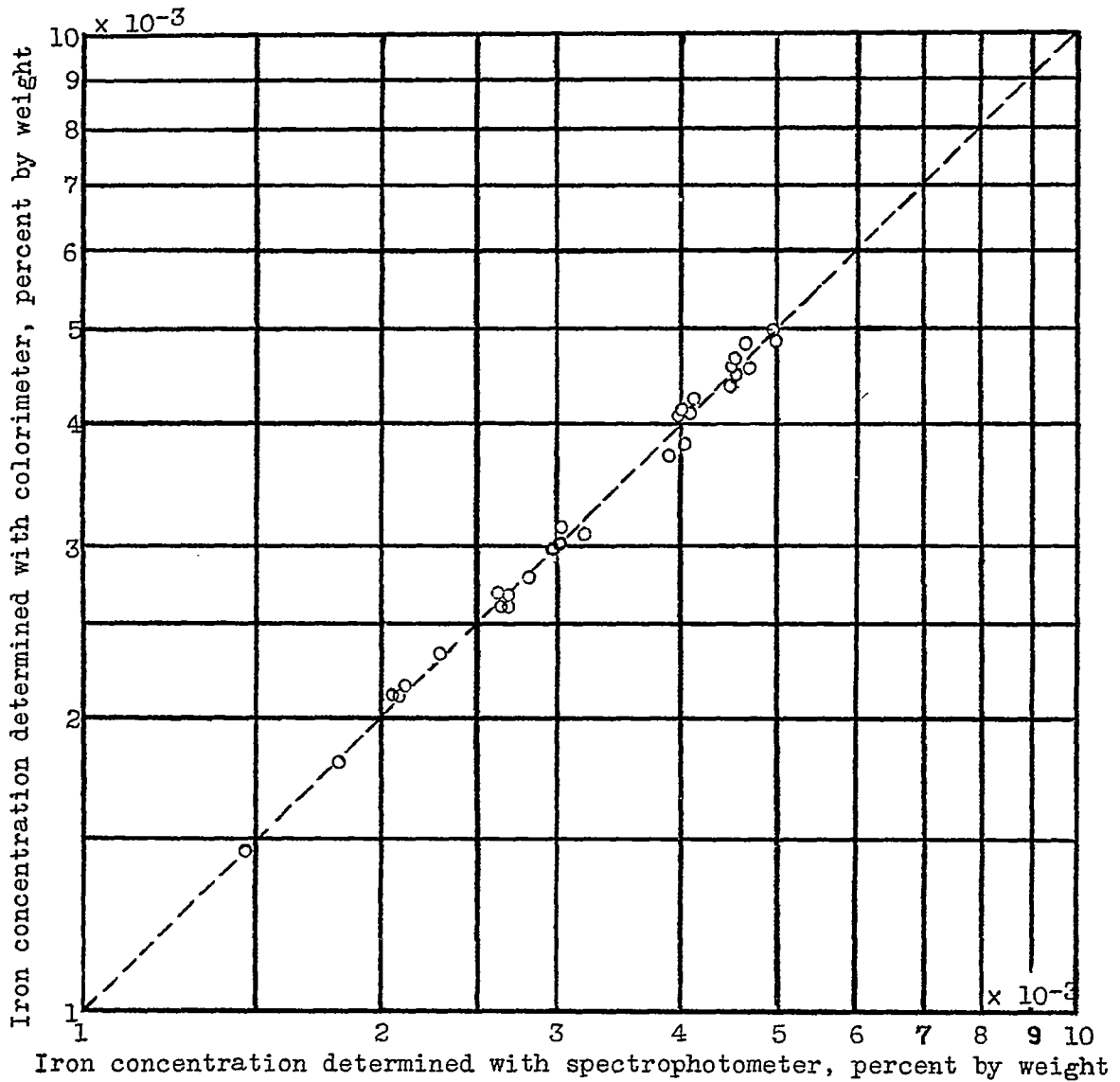


Figure 3.- Comparison of spectrophotometric and colorimetric determination of iron in aqueous solutions prepared from used lubricating-oil samples.

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An investigation was made to develop a means of determining iron contamination of used lubricating oil in aircraft engines in order to study wear rates of piston rings and cylinder walls. One method for the separation of the iron from the used oil was by burning and dissolving the residual ash containing the iron in an acid. Another method used was by extraction of the iron from the oil with acid. The amount of iron in the resulting solutions was determined by using o-phenanthroline to form a colored complex with the iron. Results of tests utilizing both methods are given.

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