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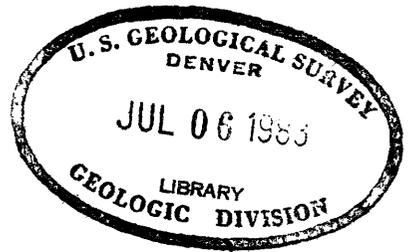
UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

THE FLUORIMETRIC DETERMINATION OF ALUMINUM IN PHOSPHATE ROCK
WITH 8-HYDROXYQUINOLINE

by

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CONTENTS

	Page
Abstract	1
Introduction	1
Apparatus and reagents	3
Experiments and discussion	4
Effect of other ions	8
The determination of aluminum in phosphate rock	10
Procedure	10
Results	11
References	13

ILLUSTRATIONS

	Following page
Figure 1. Effect of 8-hydroxyquinoline concentration	7
2. Effect of pH on fluorescence intensity	7
3. Effect of extraction time on fluorescence intensity of aluminum quinolate	7
4. Effect of different amounts of same buffer	7
5. Working curve	7

TABLES

	Page
Table 1. Effect of time and order of addition of reagents on the fluorescence intensity of chloroform solution of aluminum hydroxyquinolate	6
2. Tests of the effect of various ions	9
3. Results of analysis of phosphate rock	12

THE FLUORIMETRIC DETERMINATION OF ALUMINUM IN PHOSPHATE ROCK
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ABSTRACT

A method is described whereby aluminum in phosphate rock is determined by the fluorescence of aluminum hydroxyquinolate in chloroform solution. The procedure is designed to determine from 0.01 to 3 percent Al_2O_3 with a 0.1-mg sample of rock. The accuracy is better than 5 percent. No element, in the percentages commonly occurring in phosphate rock, interferes in the procedure.

INTRODUCTION

In connection with certain geochemical investigations, the U. S. Geological Survey had occasion to analyze several thousand phosphate rock samples for aluminum. For this project a rapid, simple, and reasonably accurate method of analysis was necessary.

The accurate determination of aluminum in phosphate rock by gravimetric procedure is difficult, rather tedious, and lengthy. For example in the method of Hoffman and Lundell (1938), aluminum is separated from most of the calcium, magnesium, and phosphorus by several precipitations of the phosphate from acetate-acetic acid solutions, and

from iron by several precipitations with sodium hydroxide and sodium carbonate. The aluminum is finally determined as the phosphate of aluminum. It is to be expected that some loss of aluminum will occur in the sodium hydroxide precipitation (especially if iron is high) and that more or less chromium and vanadium and possibly some rare earths will contaminate the final aluminum phosphate precipitate. Chromium and vanadium are common in the western phosphates, and the rare earths have been reported in many phosphate rocks.

Colorimetric methods for determining aluminum are based on the formation of strongly colored lakes with either aluminum, alizarin S, eriochromcyanin, or hematoxylin. These methods usually call for preliminary separation of aluminum from interfering ions, especially iron. Barton (1948) used alizarin S for the determination of aluminum in phosphate rock, and showed that in measurements at wavelength of 370 m μ there was practically no interference from iron. He gave no data on the effects of other common constituents of phosphate rocks.

8-Hydroxyquinoline (oxine) is commonly used for the gravimetric determination of macro amounts of aluminum, and it has also been used for the colorimetric determination of aluminum. Goto (1940) has described the detection of aluminum, zinc, calcium, cadmium, magnesium, beryllium, and zirconium by means of the fluorescence of their hydroxyquinolates. Tulio (1949) used the fluorescence of aluminum quinolate in chloroform solution for the estimation of aluminum in beer. His procedure calls for the extraction of the aluminum from slightly alkaline solutions with a chloroform solution of 8-hydroxyquinoline.

Sandell (1941) used the fluorescence of gallium hydroxyquinolate for the detection and determination of gallium, and Merritt (1944) determined zinc fluorimetrically with the same reagent. Other elements mentioned in the literature as giving fluorescent quinolates under certain condition are lithium, scandium, and indium.

The method presented in this paper is based on a study of the fluorescence of aluminum hydroxyquinolate in chloroform solution. No elements interfere in the concentrations usually occurring in phosphate rock. The procedure is designed to determine 0.01 to 3.0 percent Al_2O_3 in 0.1-mg samples of rock. The data given in table 2 indicate that the method should also be applicable to silicate and carbonate rocks.

APPARATUS AND REAGENTS

Fluorimeter: The fluorimeter, designed by Mary H. Fletcher, U. S. Geological Survey, is essentially the same as the one previously described (Fletcher, 1946) except for the measuring unit. This consists of the Photovolt Electronic Photometer Model 512 with C search unit. The B-H₄ high-pressure mercury lamp, operated from a Sela constant-voltage transformer No. 30,852 for H₄-type lamps, supplies the ultraviolet light source. The lamp is cooled by a dark-room ventilating fan. Primary filter, Corning No. 5874; secondary filter, Corning No. 3385. Diaphragm opening 0.8 inch. Square glass cells of 30-ml capacity.

8-Hydroxyquinoline (oxine) solution: Dissolve 1.5 g of 8-hydroxy-quinoline in 2M acetic acid. 1 ml equals 0.015 g.

Standard aluminum solution: Prepare a solution of concentration 1 γ (microgram) Al_2O_3 per ml from purified potassium alum.

Buffer: Mix equal volumes of 2M acetic acid (12 g CH_3COOH per 100 ml of solution) and 2M ammonium acetate (15.4 g $NH_4C_2H_3O_2$ per 100 ml of solution).

Distilled water: If blank is high, redistill from all-glass apparatus.

Chloroform: Technical chloroform, distilled from all-glass apparatus, was as good as redistilled C. P. chloroform.

Fluorescein solution A: Dissolve 0.05 g of fluorescein in 200 ml (1 + 1) alcohol and make up to 2 liters.

Fluorescein solution B: Take 3 ml of solution A, add 3 ml of alcohol, and make up to 1 liter.

EXPERIMENTS AND DISCUSSION

Experiments were made to study the following factors that affect the fluorescence of the oxine complex of aluminum: (1) order of addition of reagents, (2) pH, (3) concentration of 8-hydroxyquinoline, (4) time, and (5) concentration of buffer.

Preliminary work consistently showed that when the aluminum-oxine complex is extracted with chloroform from solutions containing no phosphate, the intensity of fluorescence of the chloroform solution is independent of the order of addition of reagents or time of standing of the test solution before extraction.

However, when phosphate is present, the order of addition of reagents and the time of standing before extracting with chloroform affect the intensity of fluorescence. The phosphate ion complexes aluminum, but 8-hydroxyquinoline forms a more stable complex with aluminum. The aluminum quinolate is formed immediately if the solution containing aluminum and phosphate is added to the 8-hydroxyquinoline. If the order of addition is reversed (i.e., the 8-hydroxyquinoline is added to the aluminum phosphate solution), the system reaches the same equilibrium in about 20 minutes. In the former case equilibrium is established immediately because the ratio of concentration of quinoline to aluminum phosphate is relatively higher than in the latter case. The faster procedure of adding test solution to 8-hydroxyquinoline solution and extracting immediately was adopted.

With this procedure the intensity of fluorescence of the chloroform solution of aluminum quinolate is independent of the time the test solution stands before extracting the aluminum quinolate. The chloroform solution obtained is stable and the intensity of its fluorescence is constant for at least 4 hours.

Table 1 shows the effect of time and order of addition of reagents. The aluminum phosphate solution was slightly acid and 2 ml (containing 2% Al_2O_3 and 50% P_2O_5) was always used. The other reagents were water (17 ml), 8-hydroxyquinoline solution (1 ml), 1M acetic acid - 1M ammonium acetate buffer (2 ml), and chloroform for extraction (30 ml). Additional data obtained in the absence of phosphate are not included in table 1 because the fluorescence intensity obtained was independent of time or order of addition of reagents. On the basis of these tests,

the standard order of addition selected is as follows: oxine, aluminum solution, buffer, water, immediate extraction with chloroform.

Table I.—Effect of time and order of addition of reagents on the fluorescence intensity of chloroform solution of aluminum hydroxyquinolate. (Test solutions contain 2% Al_2O_3 and 5% P_2O_5 , and order of addition is from left to right.)

Procedure	Meter readings	
	Immediate extraction	Extraction after 20 minutes
Order of addition:		
1. AlPO_4 , water, oxine, buffer	58	73
2. AlPO_4 , oxine, buffer, water	62	(72 (72(a))
3. AlPO_4 , oxine, water, buffer	61	72
4. Oxine, AlPO_4 , buffer, water	73	(72 (73(a))
5. Oxine, AlPO_4 , water, buffer	71	72
6. Al^{+++} (no phosphate), oxine, water, buffer	72	

(a) Water added after 20 minutes, before extraction.

Figure 1 shows the variation in fluorescence of 2% of Al_2O_3 with different concentrations of oxine. It is seen that 0.5 ml of 8-hydroxyquinoline gives the greatest sensitivity. The fluorescence of aluminum quinolate is particularly sensitive to change of oxine concentration when the amount of quinolate is less than 0.5 ml. Because other elements consume oxine, we preferred to standardize on 1 ml of oxine.

Figure 2 illustrates graphically the relationship between the fluorescence intensity of 2% Al_2O_3 and the pH of the solution before extraction with chloroform. Different pH's were obtained by varying the proportions of 1M ammonium acetate and 1M acetic acid in the 2 ml of buffer solution. The optimum pH is clearly 5.4. Because more elements react either with phosphate or with 8-hydroxyquinoline at higher pH's, we standardized on a pH of 4.6.

The data on the fluorescence of aluminum quinolate obtained with different shaking periods are shown in figure 3. The solutions were shaken with chloroform for the prescribed period (4 shakes per second), the chloroform layer was then withdrawn, and the fluorescence measured. It is seen that, for periods between 5 and 25 seconds, essentially the same fluorescence is obtained. We standardized on a 10-second shaking period.

Figure 4 shows the effect of varying amounts of buffer solution on the fluorescence intensity of aluminum quinolate.

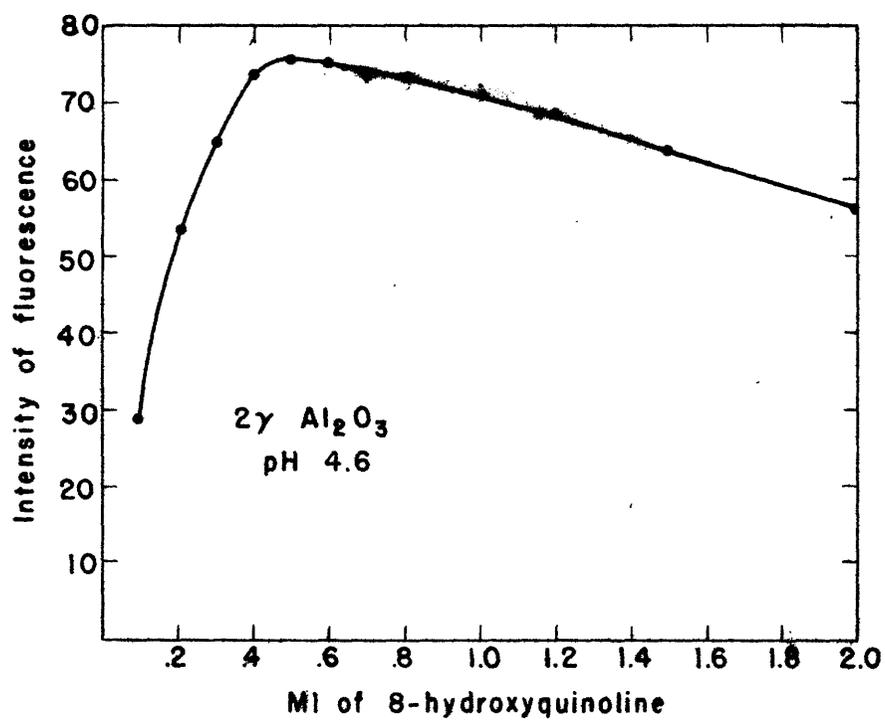


Figure 1. Effect of 8-hydroxyquinoline concentration.

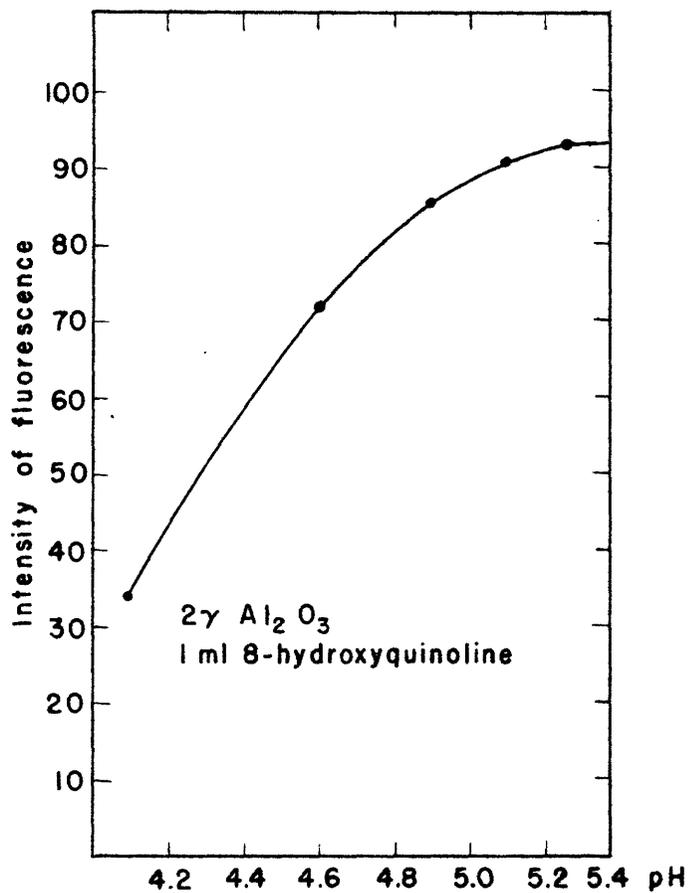


Figure 2. Effect of pH on fluorescence intensity.

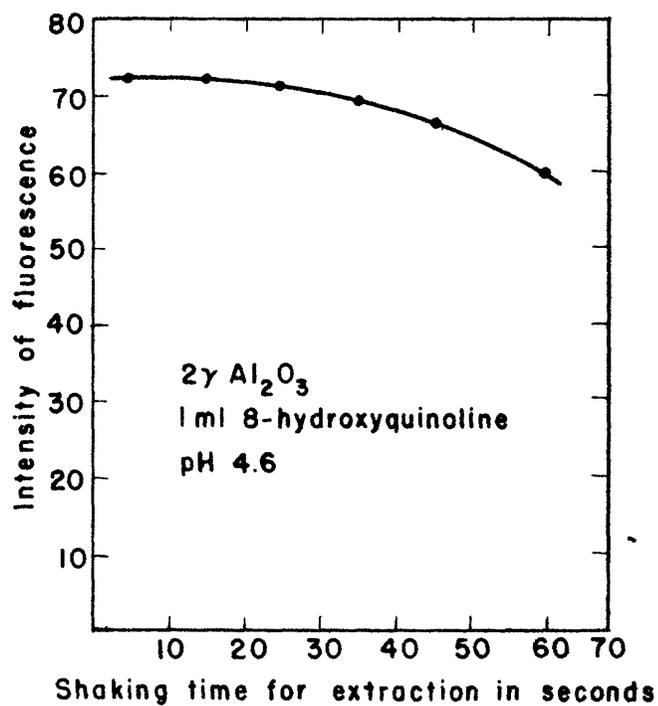


Figure 3. Effect of extraction time on fluorescence intensity of aluminum quinolate.

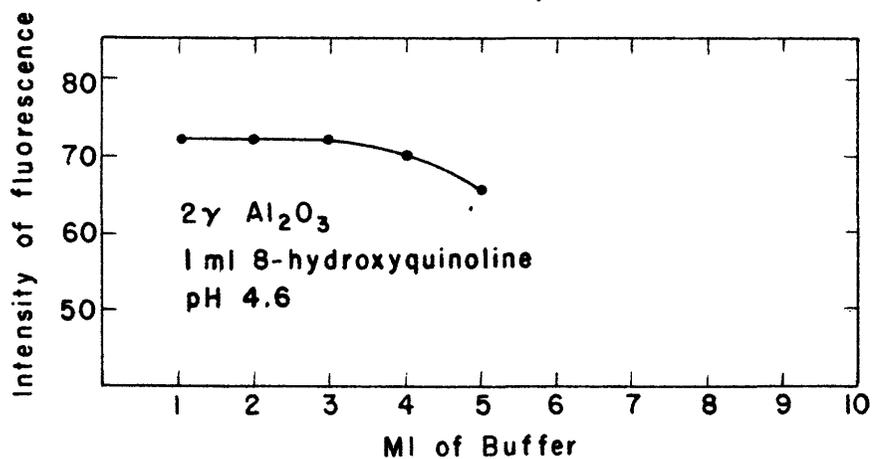


Figure 4. Effect of different amounts of same buffer.

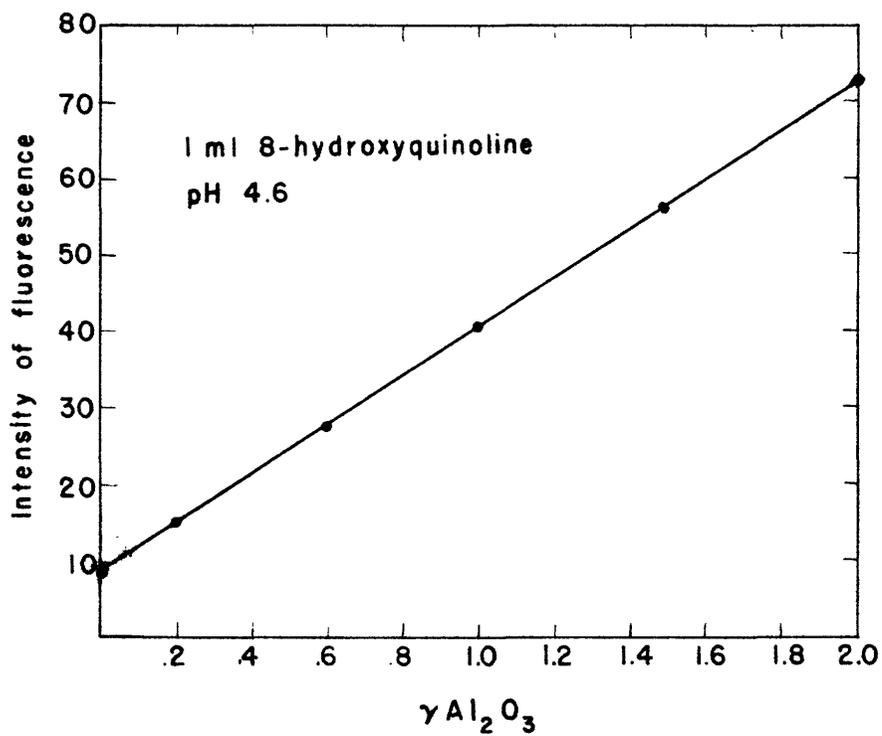


Figure 5. Working curve

The working curve of figure 5 is the result of plotting the fluorescence intensity of aluminum quinolate against micrograms of Al_2O_3 . The order of addition of reagents is the standard order: 8-hydroxyquinoline (1 ml), Al_2O_3 (varying amounts in 2 ml), buffer (2 ml), water (17 ml), 10 seconds extraction with 30 ml of chloroform. The photometer was set to read 72 for 2% Al_2O_3 . The same curve was obtained in the presence of 50% P_2O_5 .

EFFECT OF OTHER IONS

Tests were made on the elements occurring in phosphate rock to determine possible interferences. In general the amounts tested were considerably in excess of what would normally be present in phosphate rock. Fluorine was found to interfere seriously, but it is removed in the preparation of the solution for analysis. Large quantities of zirconia give a positive error. In phosphate rocks no interference should be expected from zirconium because not only is it present in small amounts but it precipitates out of solution as phosphate.

Table 2 gives the results obtained in testing the effect of various ions. In the analysis of phosphate rock 0.1 mg (100%) of sample is always used, therefore the quantity (%) of the element represents the percentage.

Table 2.—Tests of the effect of various ions.
(Instrument set to read 72 for 2% Al₂O₃, blank reading 10)

Material added as soluble ion to test solution	Meter readings	
	No Al ₂ O ₃ present	2% Al ₂ O ₃ present
2% MnO	9	74
1% Y ₂ O ₃	9	70
1% La ₂ O ₃	9	70
1% Ce ₂ O ₃	10	71
1% Nd ₂ O ₃	10	71
2% ThO ₂	10	73
1% TiO ₂	10	72
0.4% ZrO ₂	10	74
50% ZrO ₂	--	97
2% Cr ₂ O ₃	9	73
2% V ₂ O ₅	10	72
5% Fe ₂ O ₃	10	74
10% Fe ₂ O ₃	10	71
50% P ₂ O ₅	9	72
4% F	--	54
36% K ₂ O	10	74
67% Na ₂ O	10	72
20% Li ₂ O	10	72
60% CaO	10	73
50% MgO	10	73

THE DETERMINATION OF ALUMINUM IN PHOSPHATE ROCK

Procedure

1. Weigh 0.1000 gram of sample, ground to pass 80 mesh, into a 50-ml beaker.
2. Add 5 ml $\text{HNO}_3(1 + 1)$ and 3 ml of perchloric acid.
3. Evaporate the solution to fumes of perchloric acid and fume for several minutes. Cool.
4. Add 5 ml $\text{HNO}_3(1 + 1)$ and 20 ml of water. Digest on steam bath for several minutes to dissolve soluble salts.
5. Filter on a small No. 40 Whatman filter paper and wash with water. Reserve filtrate in 100-ml beaker. Ignite residue in a platinum crucible.
6. Fuse the residue with a minimum amount of sodium carbonate. Cool the melt.
7. Pour a slight excess of $\text{HNO}_3(1 + 1)$ into the crucible to dissolve the cake. Transfer this solution to the beaker containing the main solution.
8. Add 2 ml of perchloric acid and evaporate to fumes of HClO_4 . Fume until about 1 ml of HClO_4 remains. Cool.
9. Add 30 ml of water and digest the solution on the steam bath to dissolve soluble salts.
10. Filter off the silica and wash with water. Reject residue.
11. Make up the solution to 1 liter in a volumetric flask and mix.

12. Take a 1-ml aliquot (if a higher dilution is used, aliquots up to 15 ml containing 0.1 mg of sample may be used) and transfer it to a 60-ml separatory funnel containing 1 ml of 8-hydroxyquinoline and mix.
13. Add 2 ml of buffer solution, mix, and then add 17 ml of water.
14. Add 30 ml of CHCl_3 and shake the vessel for 10 seconds (a total of about 38 shakes).
15. Withdraw chloroform layer and measure the fluorescence with the photometer.
16. Determine the amount of aluminum from the working curve (fig. 5).
The photometer may be set to read 72 against a chloroform solution of aluminum quinolate ($2\gamma\text{Al}_2\text{O}_3$) or alternately against fluorescein solution B. If the fluorescein solution is used, it should be checked daily against the standard chloroform solution of aluminum quinolate.

Results

Two samples of phosphate rock from the National Bureau of Standards were tested. One was "spiked" with a known amount of aluminum. Four western phosphates were also run, and one of these was "spiked" with extra aluminum. The western phosphates were previously analyzed by the following procedure.* The acid solution of the sample was treated with cupferron, and the cupferrates of iron, titanium, etc., were extracted

* This unpublished procedure was developed by the late Norman Davidson of the U. S. Geological Survey.

with ethyl acetate. The water layer was treated with 8-hydroxyquinoline, and the aluminum precipitated at a pH of 5.2. The aluminum quinolate was filtered off, dissolved in acid, and reprecipitated with oxine. The precipitate was again filtered and ignited to Al_2O_3 under cover of oxalic acid. The results obtained (table 3) show good recovery and good agreement with the results of fluorimetric determination.

Table 3.--Results of analysis of phosphate rock

Sample number and source	Percent Al_2O_3 fluorimetrically	Percent Al_2O_3 gravimetrically
N.B.S. Standard		
120	0.81	0.80 Av.
120	0.82	
120	0.80	
120	0.81	
120, "spiked" to give 1.50% Al_2O_3	1.52	
120, "spiked" to give 2.00% Al_2O_3	2.07	2.02 Av.
120, "spiked" to give 2.50% Al_2O_3	2.56	
56a	2.00	
56a	2.02	
56a	2.04	
56a	2.03	
Western phosphates		
1 (a)	6.4	6.5
2 (b)	2.3	2.2
3 (c)	2.6	2.6
4 (d)	1.8	1.7
4, "spiked" to give 2.2% Al_2O_3	2.2	
4, "spiked" to give 2.6% Al_2O_3	2.6	

- (a) sample contained 5.8% Fe_2O_3
 (b) sample contained 2.9% Fe_2O_3
 (c) sample contained 3.2% Fe_2O_3
 (d) sample contained 3.8% Fe_2O_3

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