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UNITED STATES GEOLOGICAL SURVEY

Trace elements investigations report

TEI-239

THE DETERMINATION OF SMALL AMOUNTS OF RARE EARTHS IN PHOSPHATE ROCKS

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June 1952

DEPARTMENT OF THE INTERIOR
March 3, 1849

Prepared by the Geological Survey for the
UNITED STATES ATOMIC ENERGY COMMISSION
Technical Information Service, Oak Ridge, Tennessee

18689

ABSTRACT

Rare earths and thorium in phosphate rock samples are determined by a combined chemical and spectrographic method. After the removal of iron by the extraction of the chloride with ether, the rare earths and thorium are concentrated by double oxalate precipitation, using calcium as a carrier. The rare earths are freed from calcium by an ammonium hydroxide precipitation with a fixed amount of aluminum as a carrier. The aluminum also serves as an internal standard in the final spectrographic analysis. The method will determine from 0.02 mg to 2 mg of each rare earth with an error no greater than 10 percent.

CHEMISTRY

AEC, Oak Ridge, Tenn.-W25314

THE DETERMINATION OF SMALL AMOUNTS OF RARE EARTHS IN PHOSPHATE ROCKS*

By Claude L. Waring and Henry Mela, Jr.

INTRODUCTION

The analysis of phosphate rock samples, from the Bone Valley formation of Florida and from the Phosphoria formation of the northwestern United States, containing rare-earth elements has resulted in the development of a combined chemical and spectrographic procedure. This procedure has been applied to the determination of Ce, Y, Pr, Gd, Nd, Sm, La, Dy, Eu, Yb, and Th. The remaining rare earths were not tested because of the lack of materials, but the fact that all rare-earth groups are represented in the above list indicates that the method may be applicable to all of them.

Few individual separations of the rare earths have been made by strictly chemical means because of the similarity of their chemical properties. Fractional crystallization and ion-exchange methods have been used for the separation, but these methods are not useful for quantitative analytical purposes.

The rare-earth elements emit complex spectra when excited in the arc. The full intensity of the light emitted by the arc produces an intense continuous background on the spectrum plate making analysis very difficult. The conditions established in this work attained the objective of a sensitivity of 0.001 percent for all of the rare-earth elements studied.

The principal lines of the rare-earth elements were not selected for the determinations because many of them fall in that part of the spectrum where molecular banding and continuum interfere. Instead of these principal lines, other lines of desired sensitivity were selected in the ultra-violet portion of the spectrum where interferences are insignificant.

This work was done on behalf of the Division of Raw Materials of the Atomic Energy Commission.

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

PREVIOUS RELATED STUDIES

Most of the rare-earth methods described in the literature are concerned with the rare-earth elements in rare-earth minerals. McCarty, Scribner, Lawrenz, and Hopkins (1938) present such a method using zirconium as the internal standard. They suggest that better results can be expected if a rare-earth line of the major component is used as the internal standard. Fassel (1949) applies this suggestion to determine yttrium and gadolinium in rare-earth mixtures. A standard deviation of ± 2.5 percent is reported. The use of one rare earth as an internal standard for the others is described by DeAzcona (1941) and Fassel and Wilhelm (1948).

Moeller and Brantley (1949) made spectrophotometric studies of salt solutions of the rare earths but were limited by the equipment used. Sahama and Vahatalo (1939) describe a chemical method for concentrating the rare earths, mostly from silicate rocks. The final analysis was completed by X-ray spectrographic methods. DeRubies and Doetsch (1935) apply an arcing enrichment procedure for low amounts of rare earths in lead minerals. The undesirable elements are first volatilized to leave the rare-earth concentrates. These concentrates are arced under more strenuous conditions. It is doubtful that this procedure can be applied to samples containing such elements as Ca, Mg, Fe, Si, and Al because these elements tend to linger in the crater.

EXPERIMENTAL DATA-CHEMICAL

The preparation of standards

The rare-earth elements that are accessible in the laboratory in salt or oxide form are Ce, Gd, La, Nd, Pr, Sm, Y, Dy, Eu, Yb and Th. They comprise members of the La group, Y group, and the Er group.

To prepare the standard solutions, each rare earth is weighed on a microbalance, dissolved in water or acid, and made to 25 ml in volume. An aliquot is taken to dryness and ignited at 1000 C. The oxides are tested for purity by spectrographic procedures. The purity of these oxides is acceptable. The solutions are then diluted to make 1 ml $\Bumpeq$ 0.005 g, 1 ml $\Bumpeq$ 0.0005 g, and 1 ml $\Bumpeq$ 0.00005 g of the oxide.

Aluminum oxide was selected to be the chemical carrier and also to serve as the experimental internal standard for the spectrographic analysis. The excitation potential and ionization potential of aluminum are fairly close to those of the rare earths. However, the ideal internal standard should have vaporization characteristics close to that of the unknown element. In this respect aluminum does not meet the desired qualifications, but the results of the tests indicate that aluminum can be used successfully as an internal standard.

To determine if rare-earth mixtures will produce spectrographic working curves similar to those of single rare-earth standards, composite standards were prepared and arced. Points obtained from the composite standards fall in approximately the same location on the curve as those obtained from similar percentages in the single rare-earth standards. $Al(NO_3)_2 \cdot 9H_2O$ is dissolved in water and nitric acid and made to volume so that 1 ml $\Bumpeq$ 0.005 g of Al_2O_3. An aliquot is evaporated, ignited to 1000 C, and tested spectrographically for purity.

These solutions are used to prepare the spectrographic standards. Each rare-earth solution is pipetted into a porcelain crucible and aluminum nitrate solution added to give the ratios of Al_2O_3 to rare-earth oxides shown in table 1. The solutions are evaporated to dryness on a steam bath, ignited at 1000 C, gently ground in an agate mortar, and submitted for spectrographic study.

Table 1.--Ratios of rare-earth and aluminum oxides used in preparing solutions for spectrographic standards

Rare-earth oxide (g)	Aluminum oxide (g)
0.00002	0.01
0.00004	0.01
0.00008	0.01
0.00014	0.01
0.0002	0.01
0.0004	0.01
0.0008	0.01
0.0014	0.01
0.002	0.01

Tests were conducted to determine the rare-earth recovery of precipitates from calcium phosphate solutions that simulate phosphate rock samples. The preparation of these precipitates follows.

A solution of calcium phosphate is prepared, and aliquots equivalent to a rock sample taken. Each rare earth in three concentrations is added to three of the calcium phosphate aliquots. The solutions are made to about 400 ml, and 2 g of $(NH_4)_2C_2O_4$ in solution are added. The pH is then adjusted to 3, using a pH meter and adding silicon-free NH_4OH. This acidity was selected because previous experiments indicated that an increase in the basicity toward a definite blue of bromphenol blue causes iron to precipitate.

After digestion for one hour on the steam bath and several hours of cooling, the samples are filtered through no. 2 Whatman paper, washed with 0.1 percent $(NH_4)_2C_2O_4$ solution, and gently ignited until the paper is completely charred. Then the samples are heated to approximately 1000 C in a muffle furnace, cooled, a few milliliters of water added, and 5 ml of HNO_3 (1 + 1). The solutions are transferred to 600-ml beakers, and the oxalate again precipitated, filtered, ignited, and dissolved in the manner previously described. The solutions are then transferred to 150-ml beakers, made to approximately 50 ml, and 10 ml of the aluminum solution added (10 mg Al_2O_3). The hydroxides are precipitated with silicon-free NH_4OH using 2 ml in excess per 100 ml of solution after the phenolphthalein end point. Filter pulp is added, and the samples are allowed to remain on the steam bath until the precipitates coagulate, then filtered through no. 40 Whatman paper. After gentle charring of the paper and ignition at 1000 C, the samples are ready for spectrographic study. Table 2 shows the rare-earth additions and recoveries.

Treatment of phosphate rock samples

A phosphate rock from the Florida land-pebble field and a western phosphate from the Phosphoria formation were selected for the initial rock tests. The samples were dissolved in 10 ml HNO_3 (1 + 1), 3 ml $HClO_4$, and 5 ml HF, heated to copious fumes of $HClO_4$, to break up all fluorides. They were cooled, taken up in HNO_3 and water, made to 400 ml, and the procedure as given above for the simulated samples was completed. Inspection of the spectra showed that a sufficient amount of iron had precipitated with the rare earths to interfere with the lines selected. Accordingly an additional step was introduced in the chemical procedure to remove iron at the start by extraction of the chloride with ether.

Table 2.--Rare-earth recoveries from calcium phosphate solutions

Oxides	Percent added	Percent recovered
Ce	0.1	0.09
	0.01	0.012
	0.001	0.0011
Y	0.1	0.09
	0.01	0.012
	0.001	0.0008
Pr	0.07	0.077
	0.01	0.009
	0.001	0.001
Gd	0.07	0.08
	0.01	0.012
	0.001	0.0007
Nd	0.07	0.06
	0.01	0.011
	0.001	0.001
Sm	0.07	0.056
	0.01	0.01
	0.001	0.0009
La	0.07	0.072
	0.01	0.011
	0.001	0.0008
Th	0.07	0.062
	0.01	0.011
	0.001	0.0014
Dy	0.08	0.09
	0.001	0.0013
Eu	0.07	0.06
	0.01	0.01
	0.001	0.001
Yb	0.07	0.07
	0.01	0.009
	0.001	0.0007

Another set of samples were treated as above, to the copious fumes of $HClO_4$, cooled, taken up in 20 ml of HCl (1 + 1), a few drops of 30 percent H_2O_2 added to keep titanium in solution, then transferred to 125-ml separatory funnels. Two ether extractions were made using 20-ml portions of ether. The aqueous layers were drawn into 600-ml beakers, and any ether present was volatilized on the steam bath. Volumes were then made to 400 ml, and the procedure carried out as stated previously.

The results of spectrographic analyses applied to these samples are shown in table 3. When rerun tests were conducted, with additional amounts of rare earths introduced, the results were as shown in table 4.

EXPERIMENTAL DATA-SPECTROGRAPHIC

In testing to determine the optimum exposure conditions, moving-plate technique showed complete consumption of the sample in 90 seconds. The accepted transmission was found to be 25 percent. This transmission keeps the intensity of the spectra of the easily excited rare-earth elements within workable limits and simultaneously permits detection of the most difficultly excited rare earths.

The previously prepared standards were exposed under the proper conditions and two sets of working curves were drawn, one based on straight transmission, and one on log intensity ratios.

The samples and suitable standards were placed in different electrode cups (positive) and arced for a period of 90 seconds, the gap held constant at 6 mm by manual adjustments.

Table 3.--The rare-earth content of two phosphate rock samples

Rare-earth oxides	Phosphate rock from Florida land-pebble field (percent)	Western phosphate (Phosphoria formation) (percent)
Ce	0.01	0.001
Y	0.0025	0.005
Sm	0.001	0.0025
Gd	Not detected	Not detected
Pr	Not detected	Not detected
La	0.005	0.015
Nd	0.001	0.0025
Th	Not detected	Not detected
Eu	< 0.001	0.001
Yb	0.001	0.001
Dy	0.001	0.001

Table 4.--The rare-earth element recovery from phosphate rock samples (percentage)

Oxides	Ce	Y	Gd	Pr	La	Nd	Th	Eu	Yb	Dy	Sm
Florida phosphate original and additions	0.006	0.012	0.0025	0.0025	0.015	0.006	0.005	0.005	0.006	0.005	0.006
Recovery	0.005	0.011	0.002	0.0025	0.013	0.005	0.005	0.005	0.005	0.005	0.005
Florida phosphate original and additions	0.011	0.025	0.007	0.007	0.025	0.011	0.015	0.01	0.011	0.009	0.011
Recovery	0.0095	0.023	0.006	0.006	0.023	0.02	0.013	0.013	0.010	0.008	0.010
Western phosphate original and additions	0.006	0.015	0.0025	0.0025	0.02	0.012	0.005	0.006	0.007	0.006	0.012
Recovery	0.005	0.013	0.002	0.002	0.018	0.010	0.004	0.005	0.005	0.004	0.011
Western phosphate original and additions	0.011	0.025	0.007	0.007	0.025	0.025	0.015	0.011	0.011	0.009	0.025
Recovery	0.009	0.023	0.006	0.006	0.024	0.023	0.014	0.010	0.010	0.008	0.023

The following multisource conditions and photographic procedures were used:

Capacitance	60 microfarads
Inductance	400 microhenries
Resistance	15 ohms
Initiator	high
Phase	0
Strike	strike position
Amperes	12 (± 0.5)
Spectrograph	21-ft. Wadsworth mounted grating
Emulsion	SA-1
Photographic development	4 minutes at 18° C ± 0.5° C, D-19
Slit	25 microns
Volts	300
Intensity control	25 percent

After processing the plates, the transmission values of the rare earth and aluminum internal standard (3059.997 A) were read by applying either a recording or non-recording densitometer.

Emulsion calibration

A two-step method was used in calibrating the emulsion. A similar method has been described by Harvey (1950). This method was developed with the expectation of eliminating or reducing stroboscopic effects, intermittency effects on the response of the photographic emulsion. The method does not require highly critical adjustments of optics. The gamma may be checked on any production plate, if the iron content of the samples is greater than 0.1 percent.

Calculations

Standard practices were used in making the final calculations. The working or percentage curves were prepared by two methods, straight transmission and log intensity ratios. At least one composite standard was arced on each plate. Relative intensities of the lines produced by the standard samples were used to set the index for the unknown sample calculations. The lines used are shown in table 5.

DISCUSSION

The data on the rare-earth content of phosphates from the Florida land-pebble field and from the northwestern United States are presented in figure 1, but these data should not be considered as representative of the rare-earth content of the two fields.

The mutual abundance relationships of even- and odd-numbered elements was found to be as follows:

$Ce = Nd = Sm = Dy = Yb$ (Even atomic numbers)

$La > Y > Eu > Pr$ (Odd atomic numbers)

With the exception of La, the rule of Oddo and Harkins stating that rare earths with odd atomic numbers are less abundant than the even numbered ones, is true for the two phosphate rock samples.

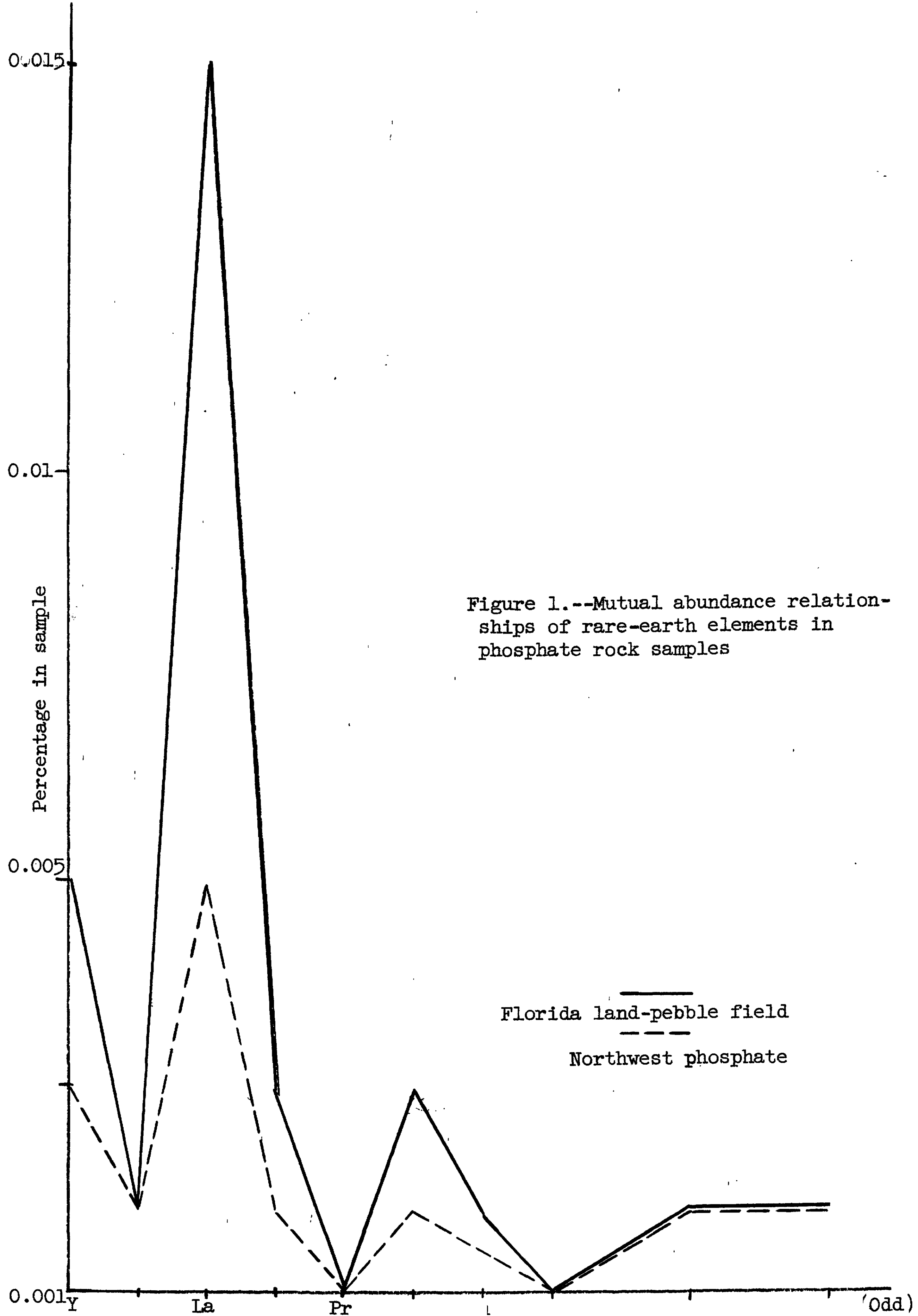

Figure 1.--Mutual abundance relationships of rare-earth elements in phosphate rock samples

Table 5.--Arc lines used in the quantitative tests 1,2/

Element	Wavelength (in A)	Element	Wavelength (in A)
Ce	4222.599 3256.682	Th	2870.413 2837.299
Dy	3251.260 3232.652	Y	3195.615 3179.418
Eu	3280.682 3/ 2906.676	Yb	3261.509 3031.110 2859.800
Gd	3046.480 3034.059	Al	3059.997
La	3245.120 3215.813		(internal standard line)
Nd	4247.367 3275.218		
Pr	4241.019 4225.327 3245.462		
Sm	3262.263 3306.372		

1/ Gatterer, A., and Junkes, J., Spektren der Seltenen Erden, Specola Vaticana, Citta del Vaticano, 1945.

2/ Harrison, G. R., M. I. T. Wavelength Tables, John Wiley and Sons, Inc., New York, N. Y., 1948.

3/ Not listed in Gatterer and Junkes tables.

DETAILED PROCEDURES

1. Weigh out 2.000 g, transfer to a 70-ml platinum dish, and heat to destroy organic matter.

2. Add 10 ml of HNO_3 (1 + 1), 3 ml of $HClO_4$, and 5 ml of HF, take down to $HClO_4$ on the steam bath, then to copious fumes of $HClO_4$ on a hot plate (drive off as much $HClO_4$ as possible).

3. Cool and take up in 20 ml of HCl (1 + 1), add a little H_2O_2, boil gently (covered). If the sample has been decomposed and a hydrolytic precipitate remains filter the sample and wash the precipitate with (1 + 1) HCl and discard the material remaining in the filter paper. Transfer the clear solution to a separatory funnel, washing the beaker with (1 + 1) HCl.

4. Make two ether extractions using 20-40 ml portions each time, and drain the aqueous layer into a 600-ml beaker. Place beaker on steam bath and volatilize the ether. Evaporate the solution to about 20 ml.

5. Add several drops of 30 percent H_2O_2 to keep Ti in solution, make to about 400 ml, add a solution containing approximately 2 g of $(NH_4)_2C_2O_4$, and adjust the pH to 3 on a pH meter with NH_4OH.

6. Place beaker on steam bath for 1 hour, cool for 4 hours, and filter on an 11-cm no. 42 Whatman paper. Wash with a cool 0.1 percent $(NH_4)_2C_2O_4$ solution.

7. Gently ignite in a porcelain crucible till filter paper is charred, then in a muffle furnace at 900-1000 C for 15-20 minutes.

8. Carefully moisten the oxide after it has cooled with several milliliters of H_2O, then add about 5 ml of HNO_3 (1 + 1). If complete solution is not obtained, add several drops of H_2O_2 and warm gently after transferring from the crucible to a 600-ml beaker.

9. Repeat steps 5, 6, 7, and 8. Transfer the solution to a 150-ml beaker.

10. Heat if necessary to dissolve all the oxide, make to approximately 50 ml, add 10 mg of Al_2O_3 from a buret, several drops of phenolphthalein, then NH_4OH free from silica until the end-point. Now add 2 ml NH_4OH in excess, and place on steam bath till precipitate coagulates.

11. Add a little paper pulp, filter thru a 9-cm no. 40 Whatman paper, and wash with a 2 percent NH_4NO_3 solution.

12. Place in a small previously ignited and weighed porcelain crucible, gently char paper, then ignite in a muffle furnace at 1000 C for 15-20 minutes.

13. Cool in a dessicator, weigh, gently grind and mix with a pestle and reserve for spectrographic analysis.

14. Weigh 10 mg of sample, mix with 2 parts of graphite, place all material in number eight [1] pure graphite electrode. Upper electrode 1/4 inch is pure graphite cut to hemispherical 0.06-inch radius.

15. Arc the sample, under the following conditions: transmission 25 percent, time 90 seconds, voltage 300, amperes 12, slit 25 microns.

16. Develop the plate 4 minutes, 18° C, D-19 developer. Fix, wash, and dry the plate.

17. Place the plate in densitometer, read lines (table 5).

18. Calculate, using standard curves.

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[1] Number 8 pure graphite electrode (1/4 inch) outside diameter cut to 0.22 inch, inside diameter 0.19 inch, depth of crater 0.24 inch, depth of shoulder 0.24 inch.

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