Spectrophotometric Determination of Traces of Lead in Igneous Rocks

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GEOLOGICAL SURVEY BULLETIN 1084-F

Spectrophotometric Determination of Traces of Lead in Igneous Rocks

By C. E. THOMPSON *and* H. M. NAKAGAWA

CONTRIBUTIONS TO GEOCHEMISTRY

GEOLOGICAL SURVEY BULLETIN 1084-F

A quantitative method for the determination of traces of lead in rocks high in iron and zinc

U. S. DEPARTMENT OF THE INTERIOR
March 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1960

UNITED STATES DEPARTMENT OF THE INTERIOR

FRED A. SEATON, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington 25, D.C.

CONTENTS

Page
Abstract 151
Introduction 151
Apparatus and reagents 152
Procedure 153
  Digestion of rocks 153
  Extraction and estimation 154
Principal interferences 155
  Iron 155
  Large amounts of zinc 158
  Calcium and magnesium phosphates and aluminum hydroxide 159
  Other interferences 160
Results 161
Recovery of added lead 162
Reproducibility 162
Summary 163
Literature cited 164

ILLUSTRATIONS

FIGURE 22. Transmission curves of ferric dithizonate and the oxidation product of dithizone 156
23. Transmission curves of various concentrations of ferric dithizonate 157
24. Transmission curves of lead and lead plus iron obtained without using the ethyl acetate extraction 158
25. Transmission curves of iron and lead plus iron obtained by the use of the ethyl acetate extraction 159
26. Transmission curves of zinc dithizonate obtained before and after the ethyl acetate extraction 160
27. Transmission curve of lead plus zinc and iron obtained by use of the ethyl acetate extraction 161

TABLES

TABLE 1. Comparison of transmittance obtained for standard lead solution by the dithizone procedure and by the proposed ethyl acetate procedure 162
2. Recovery of added lead 162
3. Comparison of lead values obtained for different weights of same sample 163
4. Replicate determinations of lead 163

SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF LEAD IN IGNEOUS ROCKS[1]

By C. E. Thompson and H. M. Nakagawa

ABSTRACT

A method for the reliable determination of traces of lead has been developed to overcome the inadequacy of existing dithizone methods for the determination of lead in mafic igneous rocks that contain relatively large amounts of iron, zinc, and certain alkaline earths. In this method, interferences from these elements are overcome without using special equipment or time-consuming separation techniques.

Ferric dithizonate has been extracted from alkaline solutions and observed to exhibit a maximum absorbance at 435 millimicrons. This dithizonate of iron has prevented accurate determinations in our laboratory of lead in mafic igneous rocks containing 10 percent or more iron.

A simple extraction of iron and zinc thiocyanates from an acid solution with ethyl acetate separates the iron and zinc from the lead, eliminating any possible interference from these elements. The precipitation of calcium or magnesium phosphate and of aluminum hydroxide that otherwise would occur at the optimum pH for the dithizone extraction of lead is prevented by using a sample solution that contains 20 percent ammonium citrate. The method permits the determination of 1 part per million of lead in igneous rocks.

INTRODUCTION

U. S. Geological Survey analytical studies for geochemical exploration require a reliable method for the determination of traces of lead in mafic igneous rocks. Diphenylthiocarbazone has probably been the most successful reagent for these determinations of trace amounts of lead. Many methods using diphenylthiocarbazone (dithizone) for various types of materials, including biological material, water, soils, and rocks, have been described in the literature. Among them are those of Cholak and others (1948, p. 671) for biological material, Snyder (1947, p. 684) for solutions containing lead, Sandell (1937, p. 464; 1950, p. 388) for silicate rocks, Maynes and McBryde

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[1] Presented at the Pittsburgh Conference, American Chemical Society, Mar. 5, 1958.

(1957, p. 1259) for samples containing bismuth and thallium, and Holmes (1945) for soils.

There are several disadvantages in the use of dithizone procedures for the determination of traces of lead in igneous rocks: (1) the interference of iron, especially in samples containing relatively large amounts of iron; (2) the difficulty in determining lead in samples that have a large amount of zinc compared with the amount of lead in the sample; and (3) the precipitation of calcium or magnesium phosphate or aluminum hydroxide, causing the occlusion and loss of lead. The method that had been used in our laboratory was essentially the monocolor method for silicate rocks described by Sandell (1950, p. 404); it was found to be inadequate for samples that are high in iron, zinc, aluminum, calcium, and magnesium. The methods now employed for separating lead from these and other elements are time consuming and often require special equipment. The method presented here requires no special equipment and eliminates the interferences mentioned above without time-consuming techniques; this method allows a greater number of determinations to be made per day.

The iron and zinc are removed by a simple extraction technique. The aluminum hydroxide and the calcium and magnesium phosphates are prevented from precipitating by complexing the aluminum, calcium, and magnesium with much larger amounts of citrate than those used previously for the analysis of lead in silicate rocks.

APPARATUS AND REAGENTS

The transmittance curves in figures 22 through 27 were obtained by using a Beckman Model DK–2 recording spectrophotometer. The transmittance readings for tables 1 through 4 were obtained by using a Beckman Model B spectrophotometer.

Hydrochloric acid: The acid is purified by distilling a 1 to 1 mixture of hydrochloric acid and demineralized water in an all-pyrex still. The part at constant boiling point is collected for use. Dilute acid is prepared from the constant boiling distillate.

Nitric acid: The acid is purified by distilling in a pyrex still. The resulting distillate is about 68 percent nitric acid. Dilute acid is prepared from the distilled acid.

Perchloric acid: Use 78 percent reagent grade.

Hydrofluoric acid: The acid used must contain less than 0.02 ppm (parts per million) lead. Satisfactory acid can be made by passing anhydrous hydrogen fluoride into demineralized water.

Ammonium hydroxide, 4 *N:* This is prepared by passing anhydrous ammonia gas into demineralized water.

Carbon tetrachloride: Technical or reagent grade is purified by distilling in the presence of pebble lime. Used carbon tetrachloride may be purified by washing it with dilute ammonium hydroxide, allowing it to stand several days in contact with carbon black, and finally distilling it in the presence of pebble lime.

Dithizone reagent, approximately 0.01 percent: Dissolve 0.25 grams of diphenylthiocarbazone in 1 liter of carbon tetrachloride, using a 4-liter separatory funnel as a container. Shake the funnel frequently during a 15-minute period, then add 2 liters of 0.02 *N* ammonium hydroxide. Extract the dithizone into the aqueous phase by vigorous shaking. Discard the carbon tetrachloride phase, and extract the ammoniacal solution of dithizone with 50 ml portions of carbon tetrachloride until the carbon tetrachloride is light green. Discard the carbon tetrachloride phase after each extraction. After the final extraction, add 500 ml of carbon tetrachloride and 50 ml of purified 1 *N* hydrochloric acid; shake the solution to transfer the dithizone into the carbon tetrachloride. Dilute the carbon tetrachloride containing the dithizone to 2 liters with carbon tetrachloride, and store in a pyrex bottle that has been covered or painted white, and keep it cool.

Ammonium citrate, 50 percent: Dissolve 500 g of ammonium citrate in 1 liter of water, using a large separatory funnel as a container. Add concentrated ammonium hydroxide until the solution has a pH of 7. Purify the solution by repeated extractions with dithizone reagent until the carbon tetrachloride is pure green. Then remove the excess dithizone by repeated extractions with purified carbon tetrachloride.

Ammonium thiocyanate solution: Dissolve 50 g of ammonium thiocyanate in 100 ml H_2O. Add ammonium hydroxide until the pH is approximately 7.5, and purify the same way the ammonium citrate solution was purified.

Ethyl acetate, reagent grade: Purify the ethyl acetate by passing through a 10- by 0.5-inch mixed bed resin column containing IR–120 and IR–400.

Potassium cyanide solution: Dissolve 25 g of reagent-grade potassium cyanide in 1 liter of demineralized water. This solution must not contain any detectable acid.

Thymol blue: Dissolve 0.1 g of the sodium salt in 20 ml of 0.01 *N* sodium hydroxide and dilute to 250 ml with demineralized water.

Lead standard solution, 0.01 percent: Dissolve 0.016 g of dried lead nitrate, $Pb(NO_3)_2$, in 100 ml of demineralized water containing 1 ml of concentrated nitric acid.

PROCEDURE

DIGESTION OF ROCKS

Weigh the sample (usually 0.5 g) and transfer it to a 50-ml platinum dish. Moisten the sample with a few drops of water. Add 2 ml of constant-boiling nitric acid, 2 ml of concentrated perchloric acid, and about 15 ml of hydrofluoric acid. Place the dish on a hot plate, and evaporate the contents slowly to dryness. Repeat the addition of nitric, perchloric, and hydrofluoric acids, and again evaporate to dryness. Repeat process with 5 ml of constant boiling nitric acid and 5 ml of concentrated perchloric acid and evaporate to dryness. Add 15 to 20 ml of 1.5 *N* nitric acid, and warm the dish and contents to dissolve the residue. Except for atypical samples, the sample will be completely in solution. The residue which remained after the digestion of the unusual samples comprised magnetite, spinel, or tourmaline. The amount of lead in this residue was generally negligible. The residue should be put into solution by a method suitable to the composition of the residue. A pyrosulfate or carbonate fusion is usually adequate. Transfer the contents of the dish to a 50-ml volumetric flask; wash the platinum dish with about 5 ml of 1.5 *N* nitric acid, and add this nitric acid to the 50-ml volumetric flask. Dilute the sample solution to 50 ml with 1.5 *N* nitric acid. At this stage, the sample solution can be stored for a week without any adsorbance of lead on the glass.

EXTRACTION AND ESTIMATION

1. Place a suitable aliquot of the sample solution into a 125-ml separatory funnel. Add 1. 5 *N* nitric acid until the volume is 25 ml. Then add 5 ml of the ammonium thiocyanate solution, and shake the separatory funnel.

2. Add 25 ml of ethyl acetate, and shake the funnel vigorously for about 10 seconds. Drain the aqueous phase into a clean 125-ml separatory funnel, and wash the ethyl acetate with 2 ml of 1.5 *N* nitric acid. Add this acid wash to the aqueous phase. Repeat the ethyl acetate extraction of the aqueous phase until the final ethyl acetate phase is colorless. Four extractions are usually sufficient. This step must be completed without hesitation, because a vigorous reaction occurs between the nitric acid and ethyl acetate if the separatory funnel is allowed to stand. Only four samples can be extracted conveniently at one time.

3. Add 15 ml of the ammonium citrate solution to the aliquot and acid washes. Adjust the pH to 8.5 with 4 *N* ammonium hydroxide, using thymol blue as the indicator. Add 10 ml of 0.01 percent dithizone solution in carbon tetrachloride, and shake the separatory funnel for 3 minutes.

4. Drain the carbon tetrachloride phase into another separatory funnel. Again extract the ammoniacal sample solution with 10 ml of dilute dithizone (10 ml of 0.01 percent dithizone diluted to 75 ml with carbon tetrachloride). Combine the second carbon tetrachloride extract with the first, and discard the aqueous phase.
5. Add 50 ml of 0.02 *N* hydrochloric acid to the combined carbon tetrachloride extracts, and shake the separatory funnel for 3 minutes. Drain and discard the carbon tetrachloride phase. Wash the dilute acid with 5 ml of carbon tetrachloride, then discard the carbon tetrachloride.
6. Add 5 ml of a 10 percent ammonium citrate solution, 10 ml of 0.005 percent dithizone solution in carbon tetrachloride, and 10 ml of 2.5 percent potassium cyanide solution to the dilute acid. Shake the funnel for 3 minutes.
7. Drain the carbon tetrachloride phase into another separatory funnel containing 10 ml of 0.25 percent potassium cyanide solution, and shake the funnel for 30 seconds.
8. Drain the carbon tetrachloride through a clean cotton plug into a colorimeter tube, and read the transmittance at 520 mμ.
9. The amount of lead which gives this transmittance is read from a standard curve.

PRINCIPAL INTERFERENCES

Iron, zinc, and certain alkaline earths are the principal elements among those elements that interfere in the analysis of igneous rocks for traces of lead when the dithizone procedures described in the literature are used.

IRON

In the final step of the usual procedure, an interference was observed in which many samples emitted a yellow color in the carbon tetrachloride instead of the pink color of the lead dithizonate. These samples usually displayed a brown color and a precipitate in the first step of the procedure; the authors thought that this brown color and the precipitate were due to iron hydroxide. To test this conclusion, a solution of ferric nitrate was carried through the lead procedure. The brown color and precipitate were obtained, and the yellow color was also observed in the final dithizone extraction.

Sandell (1950, p. 92) states that ferric iron does not react with dithizone, but oxidizes it, especially in the presence of cyanide. The yellow color that we obtained seemed to be the color of oxidized dithizone; however, there should be no iron present nor any other reason for the dithizone to oxidize in the final step. A transmittance

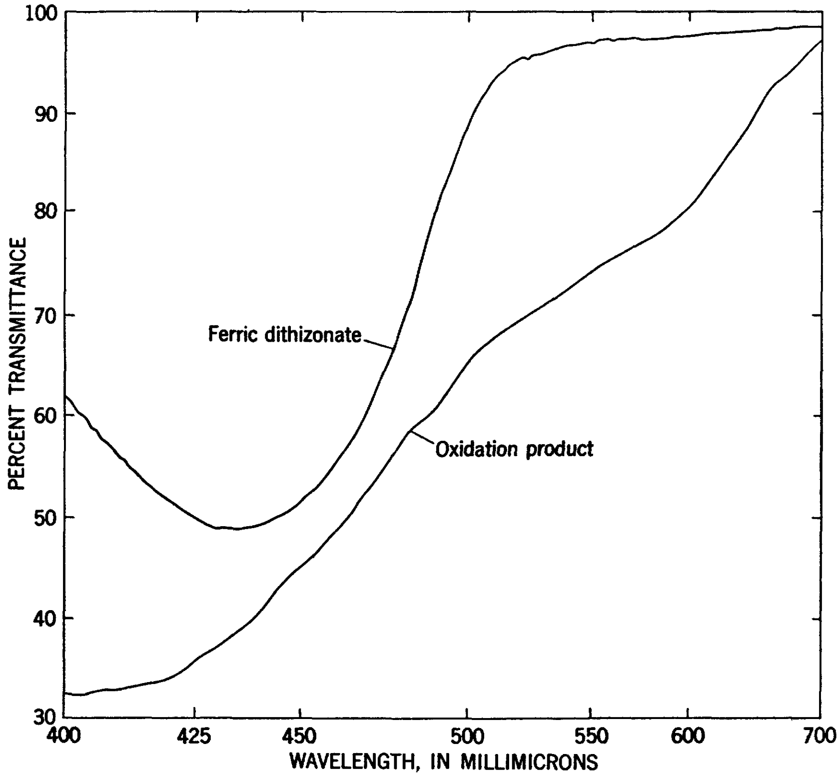

FIGURE 22.—Transmission curves of ferric dithizonate and the oxidation product of dithizone.

curve for the yellow color differed from that for the oxidation product of dithizone. In figure 22 the transmission curves for the oxidation product of dithizone and for this yellow color are shown. The oxidation product has no maximum absorbance in the range from 400 to 700 mμ, whereas the yellow color has a maximum absorbance of 425 mμ.

Dawson (1952, p. 618) reported that ferrous and ferric iron react with dithizone in an organic solvent to give a yellow compound, and he believes that this compound is formed mainly when ferric iron reacts with dithizone in basic mediums. To verify the iron-dithizone reaction, various amounts of ferric nitrate were carried through the lead procedure. The transmittance curves obtained for the colors are shown in figure 23. Maximum absorbance is at 435 mμ. A solution containing an excessive amount of ferric iron at a PH of 8.5 can be extracted a number of times with dithizone, and each extraction will give the same absorption curve and the same percent transmittance at 435 mμ. A solution containing 5,000 μg of iron was extracted with five 10-ml portions of 0.01 percent dithizone, and each extraction gave

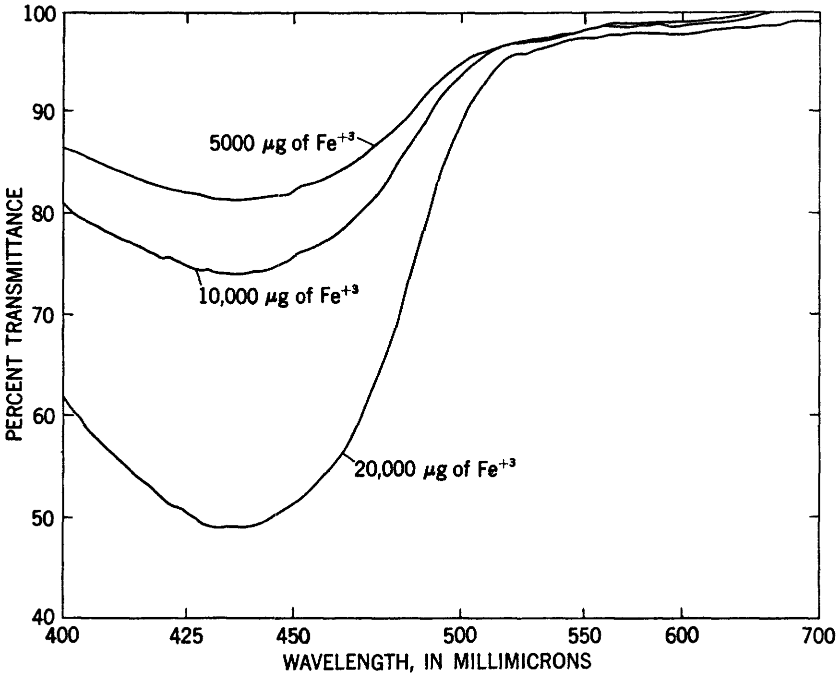

FIGURE 23.—Transmission curves of various concentrations of ferric dithizonate.

a transmittance of 19 percent. Where the citrate is present, the iron is bound as a citrate complex, so that only a very small portion of the iron is free to react with the dithizone; this free iron is governed by the equilibrium of the iron citrate complex in the basic medium. The absorption curves shown in figure 23 are not due to the amount of iron present but to the free ferric ions present when the last dithizone extraction is made. Our experiments thus indicate that the yellow color is due to a ferric dithizonate.

To estimate the extent of interference of iron with the determination of traces of lead, 10 μg of lead in the presence of 20 mg of iron were carried through the procedure without using the ethyl acetate extraction; less than half of the lead was recovered. The transmittance curves for 10 μg of lead in the presence of iron and for 10 μg of lead with no iron present are shown in figure 24. The ferric nitrate used contained a small amount of lead. These curves show that iron forms a dithizonate which is yellow and which interferes with the determination of traces of lead.

Hamence (1932, p. 622) states that iron can be removed from an acid solution by extracting iron thiocyanate with amyl alcohol and ether at 12°C; West and Carlton (1952, p. 406) extracted iron thiocyanate from a 5 percent hydrochloric acid solution with methyl-iso-

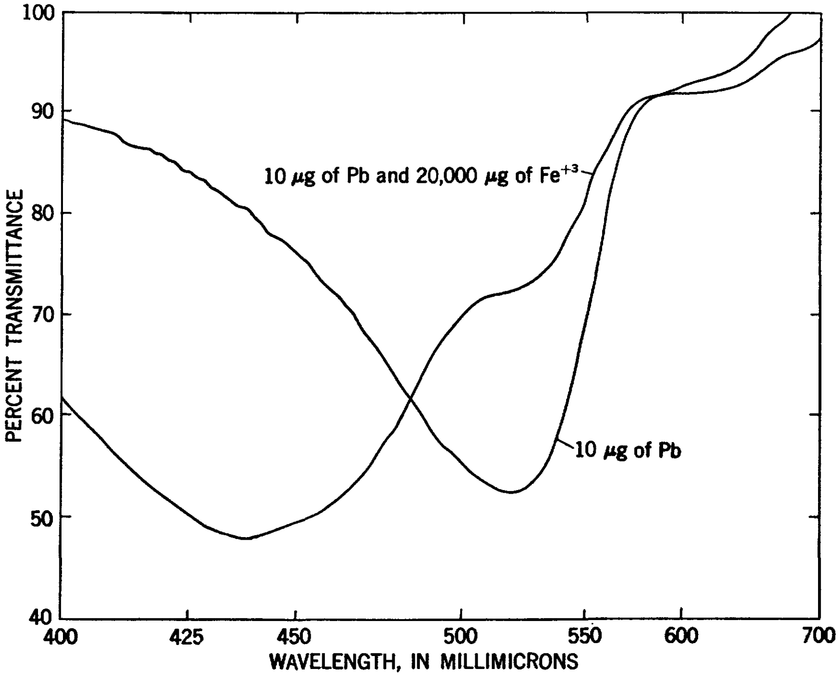

Figure 24.—Transmission curves of lead and lead plus iron obtained without using the ethyl acetate extraction.

propyl ketone. We tested several solvents and determined that ethyl acetate was most convenient to use for the extraction of iron thiocyanate from 1.5 *N* nitric acid. Figure 25 shows the results of the ethyl acetate extraction for iron alone and for lead in the presence of iron. Therefore, the interference of iron can be eliminated without any loss of lead by the simple ethyl acetate extraction of iron thiocyanate from a nitric acid solution.

LARGE AMOUNTS OF ZINC

We have found that lead values are usually high for samples containing a large amount of zinc in comparison with the amount of lead. Thus the removal of zinc from such samples prior to the lead determination is necessary. The use of cyanide to complex the zinc in the first extraction of lead was unsatisfactory because the dithizone oxidized more frequently, and the lead was not completely extracted. Zinc forms a thiocyanate complex which is also extracted by ethyl acetate. The removal of zinc by the ethyl acetate extraction was tested by comparing the absorption curve obtained from a zinc dithizonate solution in carbon tetrachloride with an absorption curve obtained after a solution containing 10 μg of zinc had been extracted by ethyl acetate and the aqueous layer then had been shaken with a carbon tet-

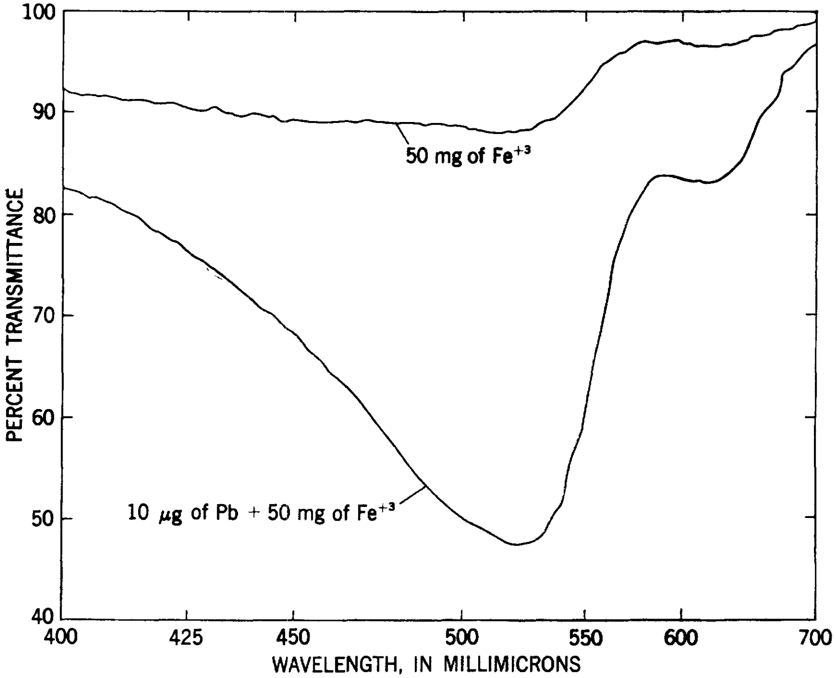

FIGURE 25.—Transmission curves of iron and lead plus iron obtained by use of the ethyl acetate extraction.

rachloride solution of dithizone. The two curves, shown in figure 26, indicate that all the zinc was removed by the ethyl acetate extraction.

Figure 27 shows the curve for 10 μg of lead taken through the proposed procedure in the presence of large amounts of iron and zinc. This curve illustrates that, by adding only the ethyl acetate extraction step to the procedure, traces of lead in igneous rocks can be determined even though large amounts of iron and zinc are present.

CALCIUM AND MAGNESIUM PHOSPHATES AND ALUMINUM HYDROXIDE

During the analysis of igneous rocks for lead using the usual procedure sometimes a white precipitate appeared in the initial stages after adding ammonium hydroxide to adjust the pH of the solution to 8.5. A similar precipitate resulted when a solution of calcium and phosphoric acid was carried through the procedure. Ten μg of lead were added to a solution containing calcium and phosphoric acid; the lead was then extracted and estimated by using the usual procedure, and only 2.3 μg of lead were recovered. Sandell (1950, p. 389) states that "* * * the dithizone extraction of lead fails in the presence of large amounts of calcium (or magnesium) and phosphorus. The

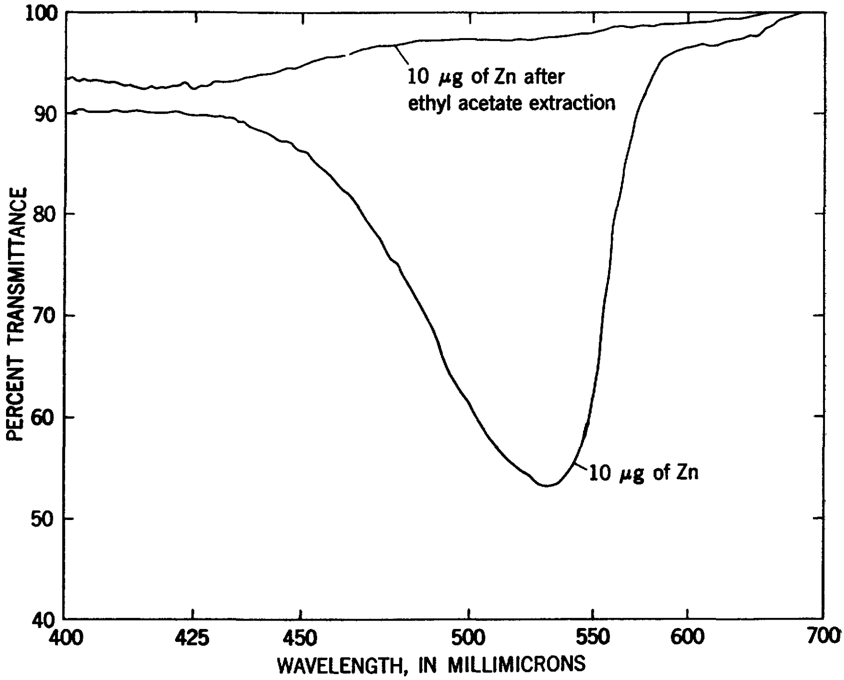

FIGURE 26.—Transmission curves of zinc dithizonate obtained before and after the ethyl acetate extraction.

phosphates of these metals are only slightly soluble in ammoniacal citrate solution, and carry down lead strongly."

When similar solutions were carried through the proposed procedure, the large amount of ammonium citrate present prevented the precipitation of calcium phosphate, and the 10 μg of lead were recovered. Similar results were obtained with magnesium phosphate and aluminum hydroxide. A sample solution containing 20 percent ammonium citrate prevented the precipitation of these phosphates and hydroxides in the same samples in which precipitation had originally occurred.

OTHER INTERFERENCES

A number of other cations were tested for interference by the usual procedure. Ten μg of lead were carried through the procedure in the presence of 1,000 μg each of molybdenum, tungsten, vanadium, uranium, tin, and mercury, and a mixture of all these elements. None of the elements reacted with dithizone, and the 10 μg of lead were recovered. Ten μg of lead were carried through the procedure in the presence of 10,000 μg of manganese; there was no interference from the manganese.

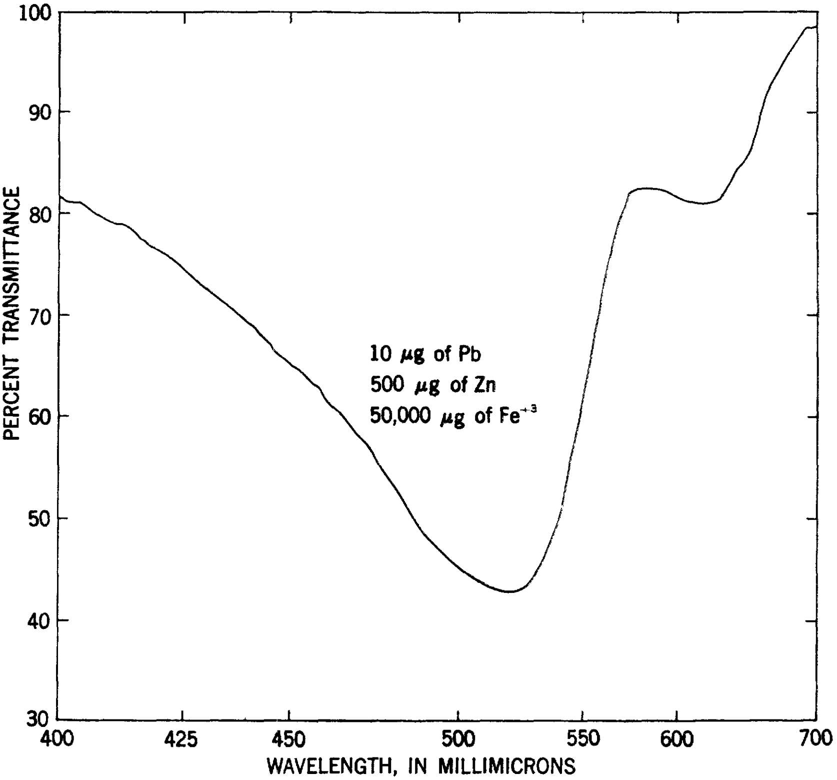

FIGURE 27.—Transmission curve of lead plus zinc and iron obtained by use of the ethyl acetate extraction.

Bismuth and thallium are reported to react with dithizone in a basic cyanide solution (Sandell, 1950, p. 92). Bismuth forms a thiocyanate complex which is yellow; however, it is not extracted by the ethyl acetate from the 1.5 *N* nitric acid. One hundred micrograms of either bismuth or thallium did not interfere with the determination of 10 μg of lead. Copper reacts with dithizone to form a dithizonate which is not decomposed by the dilute hydrochloric acid and which, therefore, remains in the organic layer that is discarded. Copper also forms a thiocyanate and is extracted to some extent by the ethyl acetate.

RESULTS

The reliability of the proposed procedure was checked by comparing the transmittance obtained from standard lead solutions, containing no interfering elements, by the method which had been used in the U.S. Geological Survey geochemical exploration laboratory with the transmittance obtained by the proposed procedure. Virtually no difference between the two curves resulted for these standard lead solutions by plotting the concentration against the transmittance. The data for the old procedure given in table 1 are an average of three determinations, whereas those of the proposed procedure are a single determination, which illustrates the excellent reliability of the proposed procedure. The results obtained by the experiments show that no lead is lost during the ethyl acetate extraction.

TABLE 1.—*Comparison of transmittance obtained for standard lead solutions by the dithizone procedure and by the proposed ethyl acetate procedure*

Lead present (micrograms)	Percent transmittance	
	Dithizone procedure	Proposed procedure
0	95. 5	95
1.0	89	87
2.0	85	83. 5
5.0	68. 5	68
10.0	48. 5	48. 5
20.0	25	26
30.0	13	12

RECOVERY OF ADDED LEAD

To determine the loss of lead during the digestion and estimation procedure, known amounts of lead were added to a standard sample containing less than 10 ppm of lead. The sample used was the standard diabase W-1, which was analyzed several times, and an average value of 8 ppm lead was obtained. Lead was added to 1 g samples of W-1 in the amounts of 10, 30, 70, and 150 μg and carried through the digestion and extraction process. The recovery of the added lead was complete within the variation of the instruments used. The values obtained for the five analyses are listed in table 2.

TABLE 2.—*Recovery of added lead*

Sample	Lead (micrograms)			
	Present	Added	Found	Recovered
1	8	0	8. 5	0. 5
2	8	10	18	10
3	8	30	37. 5	29. 5
4	8	70	78	70
5	8	150	157. 5	149. 5

REPRODUCIBILITY

One method of checking reproducibility in gravimetric analyses is to determine the desired constituent in various weights of sample and to compare the results. This method was adopted for use in the proposed procedure; the reproducibility was determined by taking various weights of a sample of quartz that contained less than 5 ppm lead, and analyzing each sample separately, using all the sample that was weighed. The concentrations of lead in the quartz for each weight and for the total weights were calculated.

The results obtained are given in table 3. The difference between the value obtained by using a 1 g sample and the value obtained for the total number of grams was 1.1 percent.

TABLE 3.—*Comparison of lead values obtained for different weights of same sample*

Grams of sample	Lead	
	Micrograms found	ppm
1	3. 5	3. 5
2	7. 3	3. 65
3	10. 0	3. 33
[1] 6	[1] 20. 8	[2] 3. 46

[1] Total

[2] Weighted average.

To evaluate in another manner the reproducibility of the method, 1-gram samples were weighed from five separate splits of five samples and taken through the procedure. These five samples were examples of some of the igneous rocks which produced the different types of interferences during the procedure that we had been using previously. There is good agreement between each value and the average of all the values. The results obtained are given in table 4.

TABLE 4.—*Replicate determinations of lead*

Sample	Lead (ppm)					Average of replicates
1	20. 6	20.	20	20	19. 4	20
2	16. 5	16. 5	17	17	17	16. 8
3	14. 5	14. 5	14. 5	15	14	14. 5
4	8	7. 4	8. 5	7. 8	8	8. 0
5	3. 5	3. 6	3. 7	3. 6	3. 4	3. 5

SUMMARY

As U.S. Geological Survey chemists frequently must determine traces of lead in igneous rocks high in iron, zinc, and certain alkali earths, a method has been developed which eliminates the interference caused by these elements. The data presented here indicate that the iron does not interfere in the determination of lead by oxidizing the dithizone but by actually forming a ferric dithizonate. The iron and zinc are removed by a simple extraction, and the calcium and magnesium are complexed and kept in solution by using a large amount of citrate. By using the proposed procedure, which has only one additional step and which only slightly decreases the number of determinations that can be completed in 1 day, reliable lead values with a sensitivity of 1 ppm are obtained on those samples where interferences occurred by the method used previously.

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