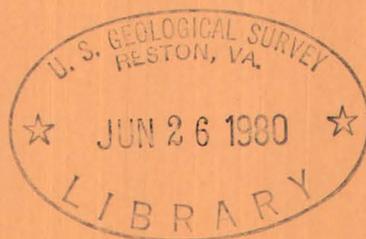


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# A dithizone method for the determination of lead in monazite

By R. A. Powell and C. A. Kinser



*Trace Elements Investigations Report 630*

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

Chemistry

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UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

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R. A. Powell and C. A. Kinser

June 1956

Trace Elements Investigations Report 630

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 64

## CONTENTS

	Page
Abstract .....	4
Introduction .....	4
Experimental .....	5
Sample treatment .....	5
Control of sample and reagent concentration .....	6
Method .....	8
Apparatus, reagents, and standard solutions .....	8
Procedure .....	11
Preparation of sample solution .....	11
Isolation of lead .....	12
Absorbance measurement .....	13
Preparation of standard curve .....	13
Calculation of results .....	15
Results .....	15
Conclusions .....	15
Acknowledgments .....	17
Literature cited .....	17

## ILLUSTRATION

Figure 1. Typical lead dithizonate curve at 520 m $\mu$ .....	14
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## TABLE

Table 1. Comparison of lead in monazite determined by the dithizone method and by the mass spectrometer .....	16
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## A DITHIZONE METHOD FOR THE DETERMINATION OF LEAD IN MONAZITE

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## ABSTRACT

In determining lead in monazite  $[(\text{Ce}, \text{La}, \text{Th})\text{PO}_4]$ --to be used as the basis for geologic age measurements--it was necessary to eliminate interferences due to the presence of phosphates of thorium and the rare-earth metals.

The method, in which monazite samples are attacked with hot concentrated sulfuric acid, taken up with dilute nitric acid, lead extracted as the dithizonate and then determined spectrophotometrically at 520  $\mu$ , was successfully applied to a series of monazite samples. Rapid determinations were made with good reproducibility.

## INTRODUCTION

Early in the work on the determination of lead in monazite it was thought that the thorium-rare earth phosphates were causing interferences. Sandell (8) reported that dithizone extraction fails in the presence of much calcium or magnesium and phosphates because the phosphates of these metals are only slightly soluble in ammoniacal citrate solution and carry down lead strongly. Thorium and rare earth phosphates behave similarly.

To minimize or eliminate the interferences in the analysis of monazites and other related materials, it became necessary to study various methods of sample attack, lead separation, and reagent concentrations.

The method developed as a result of this investigation is based on established spectrophotometric methods (8,2,1,5,3) for the determination

of lead but has been altered at several points which were found to be critical when working with samples containing thorium and rare earth phosphates. With this procedure, lead determinations can be made rapidly on a routine basis. The method has given excellent reproducibility in the laboratory, and its accuracy was proved by check analysis with two other laboratories using mass-spectrographic techniques.

### EXPERIMENTAL

The established method upon which the following experimental work is based consists of: dissolution of the sample; addition of citrate to prevent precipitation of metal hydroxides, cyanide to complex other metals,  $\text{H}_2\text{SO}_3$  to reduce iron, and  $\text{NH}_4\text{OH}$  to adjust pH to 9.2; extraction of lead into a  $\text{CHCl}_3$  solution of dithizone; stripping of the lead into a dilute  $\text{HNO}_3$  solution; re-extraction of the lead into a standard dithizone solution; and measurement of the optical density of the extract at 520  $\mu$  against water as a reference.

#### Sample treatment

Several methods of sample treatment were investigated in an effort to select the one best suited to effect solution prior to the lead determination.

Sintering the sample with sodium peroxide (9,7) seemed promising, but its use was discontinued because of erratic lead analyses obtained after this initial treatment. Later work indicated that the erratic results might have been caused by the difficulty of removing all of the excess peroxide before the lead determination.

Fusion with  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{S}_2\text{O}_7$ , or a (3+1) mixture of  $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$  failed to give complete decomposition of monazites.

Samples seemed to be completely decomposed when the  $\text{Na}_2\text{CO}_3$ - $\text{Na}_2\text{B}_4\text{O}_7$  ratio was changed to 1+3, but lead results were variable. When  $\text{Na}_2\text{B}_4\text{O}_7$  alone was used as the flux, clear melts were obtained which were exceedingly difficult to dissolve.

Treatment with  $\text{H}_2\text{SO}_4$  was the most successful method (4) investigated for the attack of monazites. By this means decomposition of samples was completed within 1 hour, and the use of platinumware, a source of lead contamination, was eliminated. Spectrographic analysis of typical platinumware in this laboratory showed the presence of lead in the 0.0X percent range.

After the initial treatment with  $\text{H}_2\text{SO}_4$  and the subsequent addition of dilute  $\text{HNO}_3$ , a trace of residue was usually apparent but was found to be insignificant and could generally be ignored. Only one monazite sample (labeled impure) gave an appreciable residue. Spectrographic analysis of this residue showed the major constituent to be silicon but also disclosed the presence of lead. This residue was easily decomposed by HF and  $\text{HNO}_3$ .

#### Control of sample and reagent concentration

Coprecipitation of lead with insoluble thorium and rare earth phosphates probably accounts for most of the error when the established dithizone method for lead is applied to monazite or related samples.

Cloudiness or precipitation was observed occasionally in sample solutions after adjustment of pH to approximately 9.2. This phenomenon sometimes appeared immediately, and at other times was delayed until after

the extraction had been completed. As this precipitation seemed to be associated with larger samples, a series of experiments was undertaken to establish the relationship between sample size and time and amount of precipitation and lead recovery.

For the sake of convenience and sample conservation, a synthetic monazite solution containing the equivalent of 5 mg of a typical monazite per milliliter in  $\text{HNO}_3$  (1+1) was prepared from cerium and thorium nitrates and disodium monophosphate.

Preliminary experiments showed that when the established dithizone method that had been used successfully on other kinds of samples was applied to 1-ml aliquots of the synthetic monazite solution, to which were added known amounts of lead, recoveries were consistently 3.5 percent low. A twofold increase in the sodium citrate overcame this difficulty and complete recoveries were then obtained. This change was incorporated in the method, described later.

A series of solutions was prepared containing increasing amounts of the synthetic monazite solution and a constant amount of lead. Sodium citrate, KCN,  $\text{H}_2\text{SO}_4$ , and  $\text{NH}_4\text{OH}$  were added to each solution, bringing the pH to 9.2 as required by the established procedure. The solutions were then allowed to stand undisturbed for 1 hour. Those solutions which contained 5 to 10 mg of monazite were only slightly cloudy at the end of this time. Those containing 15 to 25 mg precipitated slightly in the same length of time. Solutions containing 30 to 50 mg appeared to precipitate completely within a few minutes.

Another series of solutions was prepared exactly as before but the solutions were extracted immediately after the addition of reagents. Complete recovery of lead was obtained from solutions containing 5 to 25 mg

of monazite, whereas recoveries ranged from 89 to 45 percent on solutions containing from 30 to 50 mg of monazite.

Extractions were made on a similar series of solutions which had been allowed to stand for varying lengths of time. After standing 15 minutes, only those solutions containing 5 to 20 mg of monazite gave complete lead recoveries. Those containing 25 to 50 mg of monazite gave from 74 percent to less than 10 percent lead recoveries. After standing for 1 hour, only the solutions containing 5 to 10 mg of monazite gave complete lead recoveries.

Additional tests have shown that complete recoveries of lead can be made on samples as large as 50 mg if proportional increases of all reagents and final volumes are made and the lead extracted immediately.

## METHOD

### Apparatus, reagents, and standard solutions

All glassware should be cleaned routinely with  $\text{HNO}_3$  (1+1) and rinsed with distilled water.

Transfer pipettes should be used exclusively to eliminate the possibility of lead contamination from the enamel markings on measuring pipettes (6).

Only analytical reagent-grade chemicals should be used and even these should be tested before use to insure a low lead blank.

$\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_3$ , and  $\text{CHCl}_3$ .--In this investigation these reagents required no additional purification. The  $\text{H}_2\text{SO}_4$  can be purified, if necessary, by distillation from all-glass apparatus.  $\text{H}_2\text{SO}_3$  can be prepared free of lead by dissolving cylinder  $\text{SO}_2$  in chilled redistilled water. Chloroform

can be purified or recovered by the procedure described by Bambach and Burkey (2).

HNO<sub>3</sub>, HCl, HF, and NH<sub>4</sub>OH.---As these reagents usually contain more lead than can be tolerated, they are purified as follows: Distill HNO<sub>3</sub> from a borosilicate glass still; dilute HCl with an equal volume of redistilled water and distill from a borosilicate glass still; distill HF from a platinum still into chilled redistilled water; and distill NH<sub>4</sub>OH from a borosilicate glass still into chilled redistilled water.

Distilled water.---Redistill the distilled water from a borosilicate glass still.

Sodium citrate solution.---Dissolve 500 g of sodium citrate in water and add sufficient NH<sub>4</sub>OH to bring the pH to 9.2. Dilute the solution to 1 liter with redistilled water and remove traces of lead by shaking with successive small portions of dithizone solution (50 mg purified dithizone per liter) until the dithizone retains its original green color. Shake with a small portion of CHCl<sub>3</sub> to remove dithizone that remains in the solution.

KCN solution.---The KCN used in this investigation required no purification. When necessary, lead can be removed from KCN as described by Bambach and Burkey (2). Prepare a solution, with double distilled water, containing 100 g of KCN in 1 liter of solution.

Ammoniacal KCN solution.---To 100 ml of the above KCN solution add 325 ml of redistilled water and 75 ml of distilled NH<sub>4</sub>OH (15N).

m-Cresol purple indicator solution.---Dissolve 100 mg of m-cresol purple in 5.2 ml of 0.05N NaOH, dilute to 100 ml with redistilled water and filter through a medium porosity filter paper.

Dithizone.--Dithizone solutions deteriorate quickly when exposed to heat or direct sunlight (8). It is recommended that ruby glass bottles be used for storage and that the solutions be kept in a cool dark place, preferably under refrigeration, when not in use. If these precautions are taken and purified dithizone is used, the solution can be used for at least one month with no apparent deterioration. Unpurified dithizone was unsatisfactory even for the purification of reagents.

Dithizone can be purified as follows: Dissolve 0.5 g of dithizone in 50 ml of  $\text{CHCl}_3$  and filter the solution through a coarse fritted glass crucible to remove any insoluble material. Extract the dithizone from the  $\text{CHCl}_3$  by shaking the solution with four successive 50- to 75-ml portions of distilled  $\text{NH}_4\text{OH}$  (1+99). Discard the  $\text{CHCl}_3$  phase. Pass the combined aqueous extracts through a small plug of cotton to absorb droplets of  $\text{CHCl}_3$  and collect the solution in a separatory funnel. Make the ammoniacal solution slightly acid with distilled  $\text{HCl}$  (1+1) to precipitate the dithizone and extract with two or three 15- to 20-ml portions of  $\text{CHCl}_3$ . Shake the combined  $\text{CHCl}_3$  extracts twice with an equal volume of redistilled water. Deliver the  $\text{CHCl}_3$  solution into a small glass dish, preferably silica, and evaporate the  $\text{CHCl}_3$  at  $50^\circ\text{C}$ . Dry the purified product in a desiccator.

Concentrated dithizone solution.--Dissolve 18 mg of purified dithizone in 1 liter of purified  $\text{CHCl}_3$ .

Standard dithizone solution.--Dissolve 8 mg of purified dithizone in 1 liter of purified  $\text{CHCl}_3$ .

Stock standard lead solution.--Dissolve 160.0 mg of  $\text{Pb}(\text{NO}_3)_2$ , previously dried at  $100\text{--}110^\circ\text{C}$ , in 300 ml  $\text{HNO}_3$  (1+2) in a 1-liter volumetric

flask, dilute to exactly 1 liter with distilled  $H_2O$ , and mix well. One milliliter of this solution contains 100 micrograms of lead.

Working standard lead solution.---Transfer 5.00 ml of stock standard lead solution into a 500-ml volumetric flask, dilute to exactly 500 ml with redistilled  $H_2O$  and mix well. One milliliter of this solution contains 1 microgram of lead. This dilute solution should not be kept for more than a day or two.

### Procedure

#### Preparation of sample solution

Weigh a sample of monazite (usually about 50 mg) containing approximately 150 micrograms of lead, transfer to a 100-ml round bottom flask, add 3 ml of  $H_2SO_4$  and heat for 1 hour at  $150^{\circ}$  to  $200^{\circ}$  C. Place a short-stemmed funnel in the neck of the flask to reduce loss of acid during the heating. Allow the solution to cool, add 30 ml of  $HNO_3$  (1+2), and boil the solution to remove oxides of nitrogen. Add 20 ml of hot redistilled  $H_2O$  and digest on the steam bath for 15 minutes. If no appreciable residue remains, transfer the solution quantitatively to a 100-ml volumetric flask. Dilute almost to 100 ml with hot redistilled water and cool to room temperature. Dilute to 100 ml and mix well.

If appreciable residue remains after the  $H_2SO_4$  and  $HNO_3$  treatments and the addition of water, filter the hot solution through a medium porosity filter paper into a 100-ml volumetric flask and wash the paper with hot  $HNO_3$  (1+99). Place the paper in a small platinum crucible, saturate the paper and residue with  $H_2SO_4$  and ignite at  $500^{\circ}$  C until the paper is completely ashed. Allow the crucible to cool, treat the residue with HF

and  $\text{HNO}_3$ , and evaporate to dryness. Repeat the process of adding  $\text{HNO}_3$  and evaporating to dryness several times to remove HF. Dissolve the residue in a small amount of hot  $\text{HNO}_3$  (1+9) and add this solution to the main part of the sample solution in the volumetric flask. Dilute almost to 100 ml with hot redistilled water and cool to room temperature. Dilute to 100 ml and mix well.

#### Isolation of lead

Transfer a 10.00-ml aliquot of the sample solution into a 125-ml separatory funnel and add 5 ml of  $\text{H}_2\text{SO}_4$  (6 percent), 5 ml of the sodium citrate solution, and a few drops of m-cresol purple indicator solution. Add  $\text{NH}_4\text{OH}$  dropwise until the solution turns purple, then add an additional 4.5 ml of  $\text{NH}_4\text{OH}$  and 2.5 ml of the KCN solution. Add 10 ml of concentrated dithizone solution to the sample solution which is approximately pH 9.2 and shake the separatory funnel for 1 minute. Drain the dithizone extract into a 60-ml separatory funnel. Add 10 ml more of the concentrated dithizone solution to the aqueous phase and shake the separatory funnel again for 30 seconds. Drain this dithizone extract into the separatory funnel that contains the first dithizone extract. Add 10 ml of  $\text{CHCl}_3$  to the aqueous phase and shake the separatory funnel again for 5 seconds. Drain the  $\text{CHCl}_3$  layer into the funnel that contains the combined dithizone extracts and discard the aqueous phase. Add 25 ml of  $\text{HNO}_3$  (1+99) to the combined dithizone extracts and shake the funnel for 30 seconds to strip the lead from the  $\text{CHCl}_3$  phase. Discard the  $\text{CHCl}_3$  phase. Add 25 ml of  $\text{CHCl}_3$  to the aqueous phase and shake again for 5 seconds. Discard the  $\text{CHCl}_3$  layer and add 5 ml of ammoniacal KCN to the aqueous phase, which again brings the pH of the solution to approximately 9.2. Add exactly

15 ml of the standard dithizone solution to the aqueous phase and shake the separatory funnel for 2 minutes for the final extraction of lead. Allow the liquid to stand for 2 minutes for complete separation of phases. Insert a small roll of filter paper into the stem of the funnel. Draw off and discard the first 2 or 3 ml of the  $\text{CHCl}_3$  layer. Deliver the remainder of this layer into a glass-stoppered test tube. The roll of filter paper absorbs suspended droplets of  $\text{H}_2\text{O}$  as the  $\text{CHCl}_3$  passes through the stem of the funnel.

Note: Bismuth was below the limits of spectrographic detection in the monazite samples analyzed in this investigation. If bismuth is present in significant amounts, it should be separated from the lead by stripping the lead from the dithizone- $\text{CHCl}_3$  with a pH 3.4 buffer (2) instead of the  $\text{HNO}_3$  (1+99).

#### Absorbance measurement

Transfer the dithizone extract from the test tube into a corex absorption cell having a 1-cm light path and measure the absorbance against redistilled water as a reference solution in a matched corex cell. Optimum wavelength for the measurement is 520  $\text{m}\mu$ . A Beckman Model B spectrophotometer was used in the work reported here.

#### Preparation of standard curve

Prepare a standard curve from data obtained by carrying reagent blanks and a series of lead standards containing 5 to 20 micrograms of lead through the entire procedure except the preliminary heat treatment described in sample preparation. It should be noted that the blank of 0.13 absorbance unit shown in the typical standard curve (fig. 1) is due mostly to the

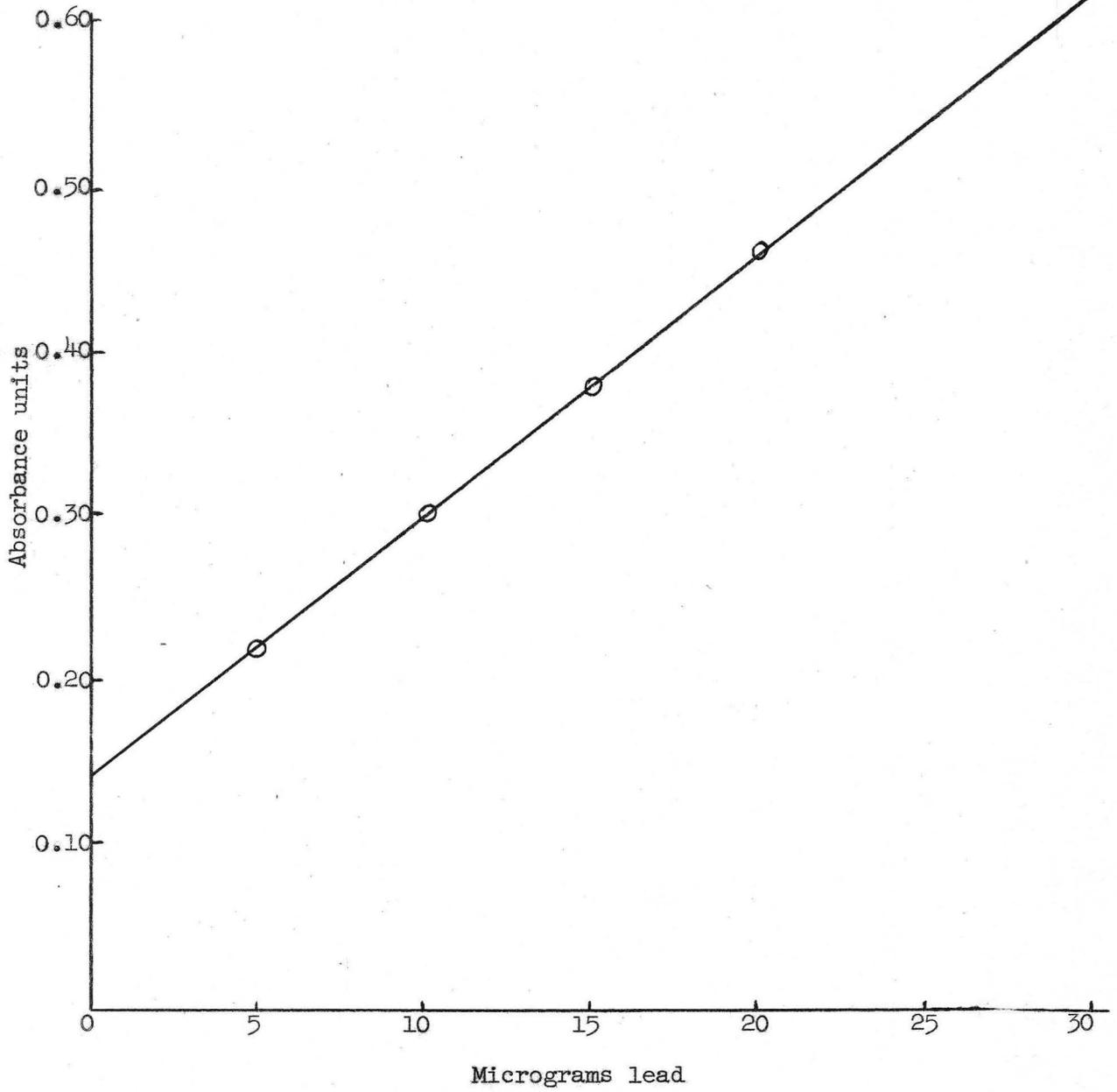


Figure 1.--Typical lead dithizonate curve at 520 m $\mu$ .

absorbance of the unreacted dithizone which is always present when the mixed-color method is used.

#### Calculation of results

The average slope of the standard curves was 0.0160 absorbance unit per microgram of lead. This figure was so highly reproducible that the frequent preparation of a standard curve was not necessary. Instead, only reagent blanks were run daily and the lead concentration was computed by the formula:

$$\frac{\text{Absorbance of unknown} - \text{absorbance of blank}}{0.0160} = \text{micrograms of lead.}$$

Absorbance readings can be converted to micrograms of lead directly from the standard curve or calculated by the formula.

#### RESULTS

Table 1 shows the analysis of 9 monazites from various localities in the United States. Their lead content ranged from 0.04 to 0.6 percent. Also included in the table are lead determinations on 6 of the samples by the mass-spectrographic isotope-dilution technique.

#### CONCLUSIONS

Previous difficulties in the determination of lead in monazites have led to the development of a procedure that eliminates the interferences present in this type of material.

Dithizone extractions should be made immediately after addition of reagents and adjustment of pH to about 9.2. The amount of sample in the aliquot taken for lead extraction must be less than 20 mg to prevent the

Table 1.--Comparison of lead in monazite determined by the dithizone method and by the mass spectrometer.

Sample no.	Percent lead	
	Dithizone method	Mass spectrometer
Standard no. 1 .....	0.35 <sub>8</sub>	0.37 <sub>2</sub>
	0.35 <sub>3</sub>	
45 MT 266 .....	0.18 <sub>3</sub>	0.19 <sub>3</sub>
	0.18 <sub>3</sub>	
	0.18 <sub>4</sub>	
	0.18 <sub>6</sub>	
SQ 81 .....	0.17 <sub>8</sub>	0.17 <sub>3</sub>
	0.17 <sub>4</sub>	
	0.17 <sub>6</sub>	
	0.17 <sub>7</sub>	
49 OT 22L .....	0.12 <sub>4</sub>	--
	0.12 <sub>5</sub>	
	0.12 <sub>6</sub>	
44 MT 121 .....	0.040	--
	0.040	
49 MT 15 .....	0.084	--
	0.086	
	0.083	
	0.086	
52 MT 8 .....	0.10 <sub>9</sub>	0.10 <sub>7</sub>
	0.10 <sub>7</sub>	
GS/436/55 .....	0.61 <sub>7</sub>	0.68 <sub>1</sub>
	0.62 <sub>1</sub>	
GS/451/55 .....	0.52 <sub>4</sub>	0.54 <sub>0</sub>
	0.51 <sub>4</sub>	

loss of lead by coprecipitation with thorium-rare earth phosphates. If the procedure is modified by increasing all solution volumes and reagents proportionately, samples as large as 50 mg can be used.

The method described for initial sample attack was successfully applied to all pure monazite samples. One impure monazite gave an appreciable residue, following this treatment, which was easily decomposed by HF and HNO<sub>3</sub>. The presence of lead in this residue indicates the desirability of recovering lead from the residue obtained after the acid attack.

Good reproducibility has been obtained consistently, and the accuracy has been verified by independent checks using mass-spectrographic methods.

#### ACKNOWLEDGMENTS

The authors wish to thank their colleagues at the Geological Survey, Carmen M. Cialella and Lorin R. Stieff for the mass-spectrographic analyses included in table 1, and Joseph Haffty, Katherine V. Hazel, and Claude L. Waring for the spectrographic analyses referred to in the text. This work is part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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