

A Simple EDTA Titration Method for the Determination of Lead in Monazite

by

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모나자이트 중의 납 정량을 위한 신속한 EDTA 적정법

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ABSTRACT

In this paper a simple and rapid method is described for the determination of lead in monazite. A monazite sample was dissolved with hot concentrated sulfuric acid and diluted to 200 ml with distilled water. Lead is quantitatively separated by coprecipitating with strontium. Lead-strontium sulfate is dissolved in 3N NaOH solution. An excess Zn-EDTA is added. The remaining zinc ion is titrated with standard 0.01 M EDTA solution using xylenol orange as indicator at pH 5 in the presence of KCN and acetyl acetone as masking agents.

요 약

모나자이트 중의 납함량을 신속하고 간편하게 결정하는 방법을 기술하였다. 즉 모나자이트 시료를 황산에 녹여 200ml 가 되었을 때 회석하였다. 스트론튬으로 납을 정량적으로 분리한 후 3N 수산화나트륨에 녹였다. 여분의 Zn-EDTA 를 가한 다음 남은 아연 이온을 0.01M EDTA 표준용액으로 적정하였으며 이때 가리움제(masking agent)로서 시안화칼륨 및 아세틸 아세톤을 가하였고 pH 5 에서 자이렌올 오렌지(Xylenol orange) 를 지시약으로 사용하였다.

1. INTRODUCTION

The determination of small amount of lead in geologic sample like monazite has received some attentions in recent years as the basis for geologic age measurements.

Among analytical methods for lead in monazite dithizone method was reported. However, in this method⁽¹⁾ all reagents should be repurified for the micro content of lead impurity.

Goldin⁽²⁾ and Reynolds⁽³⁾ found that barium is quantitatively coprecipitated when a large quantity of lead is precipitated as sulfate because barium sulfate

is much less soluble than lead sulfate. It was thought from this finding^(4,5) and also from the solubility product principle that strontium would coprecipitate lead quantitatively as the solubility product of lead sulfate, 1.00×10^{-6} , is much less than that of strontium sulfate, 3.81×10^{-7} . Therefore strontium was added as precipitant for lead.

The method developed as result of this investigation is based on several established methods^(2,3) for the determination of lead, but has been altered several points.

With this procedure lead determination can be made rapidly on a routine basis. The method has given excellent reproducibility in the laboratory and its accuracy was proved by checking with synthetic monazite and EDTA titration after ion exchange separation⁽⁶⁾.

2. EXPERIMENTAL

(2-1) Reagents and apparatus

Analytical grade chemicals were employed whenever possible. Lead nitrate, barium chloride, and strontium chloride were dissolved in dist. water and diluted to finite volumes respectively. Thorium, cerium, lanthanum, samarium, iron, aluminium, zirconium and phosphorus were taken as solid oxide form. The filtration of precipitate was carried out with a centrifuge tube of 100 ml capacity.

(2-2) Effects of alkaline earth elements

A synthetic mixture (Table 1) of lead and alkaline earths was checked for the quantitative coprecipitation of lead with strontium and also for the influence of these metals on titration.

TABLE 1. Results of Lead Determination in the Presence of Alkaline Earth Elements

Taken (mg)	Found (mg)
Pb : 5.00	Pb : 4.98 ± 0.02
Alkaline earth elements taken	
Ca : 30	
Sr : 50	
Ba : 10	

(1) The sample solution of the synthetic mixture of Table 1 is diluted to 100 ml with distilled water. 3 ml of concentrated sulfuric acid are added as precipitant for the precipitation of strontium and lead.

(2) The solution is warmed, stirred and centrifuged.

(3) Precipitate is dissolved in 10 ml of 3N NaOH solution and washed with 0.1N NaOH solution three times. Lead and strontium are completely dissolved by this step.

(4) An Excess Zn-EDTA solution is added, warmed, stirred and the filtrate was diluted to 50 ml with distilled water.

(5) pH is adjusted to about 3 with 6N HCl solution, 3 ml of 6N ammonia acetate are added, and finally pH is adjusted to 5 with hexamine.

(6) The remaining zinc is titrated with 0.01N standard EDTA solution with xylenol orange as the indicator.

(2-3) Effects of thorium, rare earth elements, iron, and aluminium.

A synthetic monazite sample (Table 2) was checked for the interference of thorium, rare earths, iron and aluminium on the titration.

TABLE 2. Results of Lead Determination in the Synthetic Monazite.

Taken: mg	Found: mg
Pb; 5.00	Pb; 5.00 ± 0.01
Other elements taken	
ThO ₂ : 60	Ce ₂ O ₃ : 250
La ₂ O ₃ : 150	Sm ₂ O ₃ : 150
Fe ₂ O ₃ : 10	Al ₂ O ₃ : 20
ZrO ₂ : 5	P ₂ O ₅ : 300

(1) 5.00 mg of aqueous lead solution are accurately pipetted into a 30 ml platinum crucible and dried under a infra-red lamp. Other elements of table 2 are then weighed into the crucible as oxides.

(2) 7 ml of concentrated sulfuric acid are added and digested for 3 hours on a hot plate.

(3) After cooling, the sample is transferred to 400 ml beaker with jet of distilled water, diluted to 200 ml and warmed for 10 min. with stirring.

(4) 50 mg of strontium are added, stirred and centrifuged.

(5) Precipitate is dissolved in 10 ml of 3N NaOH solution and washed with 0.1 N NaOH solution three times. Lead and strontium is satisfactorily dissolved in this step, while other elements are precipitated as hydroxide.

(6) The steps (4) and (5) of (2-2) are followed.

(7) Finally zinc is titrated with 0.01N standard EDTA solution with xylenol orange as the indicator in the presence of KCN and acetyl acetone as masking agents⁽⁶⁾.

(2-4) Experimental procedure with monazite.

Among the several methods reported the sulfuric acid method^(4,7) seems most suitable for the opening of monazite.

(1) 1 g of monazite sample, in the form of finely ground powder, is weighed in 30 ml capacity platinum crucible.

(2) The steps (2)---(7) of (2-3) were followed.

(2-5) Separation of lead by ion exchange resin.

Separation of lead⁽⁸⁾ by anion exchange resin was carried out before EDTA titration in order to check the possible interference of other elements which may be followed in the coprecipitation with strontium and also in the dissolution of lead sulfate with 3N NaOH solution. This procedure are as follows.

TA solution at pH of 5 with xylenol orange as the indicator.

In the present study, it was confirmed that lead is selectively and quantitatively separated with above elution procedure⁽⁸⁾. Both results of lead content, i. e. one that was obtained from direct titration(2-4), i. e., 0.445±0.005% of PbO and the another obtained after anion exchange separation (2-5), i. e., 0.447 ±0.005% of PbO agreed well within the experimental errors.

3. DISCUSSION AND CONCLUSION

Table 3 presents the calculated conditional stability constants of the several metal ions with EDTA at pH 5.

The presence of the following cations Cu²⁺, Hg²⁺, and Fe³⁺, with higher stability constants than Pb²⁺, would cause higher results on this titration, but the contents of these metals are negligibly small in monazite⁽⁹⁾. Other elements with high conditional stability constants, i. e., Th⁴⁺ (16.75), V³⁺ (19.55), and Zr⁴⁺ (12.95) did not make any differences because these elements are either completely separated out or are negligibly small in contents.

The present study provides the quantitative copreci-

TABLE 3. Conditional Stability Constants, K_{H} of Some Cations, with EDTA at pH of 5

Cations	Sr ²⁺	Mg ²⁺	Ca ²⁺	Ba ²⁺	Zn ²⁺	Pb ²⁺	Cu ²⁺	Mg ²⁺	Fe ³⁺
Log K_{H}	2.18	2.24	4.25	1.31	9.81	11.85	12.34	15.35	18.65

(1) The monazite sample solution in 3N NaOH solution of experiments of (2-4) is made in 1N hydrobromic acid and loaded on a column of Dowex 1 ×4 resin (50--100 mesh in particle, 10 cm in length, 2 cm in diameter).

(2) The column is eluted with 250 ml of 0.1N HBr, lead is then eluted with 400 ml of 0.30N HNO₃ + 0.025 N HBr solution.

(3) Flow rate is adjusted in 5.0 ml per min.

(4) The elute is taken to dryness with HNO₃ to remove bromine.

(5) Lead is then titrated with 0.01N standard ED

titration of lead with strontium as shown Table 1 and 2. The agreement between the results, one that was obtained from direct titration(2-4) and the another obtained after anion exchange separation(2-5) indicates that the present method is not affected by the presence of other ions on titration. These results indicate that lead in monazite is easily separated by coprecipitation with strontium and by dissolving lead sulfate with 3N sodium hydroxide solution for the indirect EDTA titration with xylenol orange as indicator at pH of 5 in the presence of KCN and acetyl acetone as masking agents.

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