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MASTER

DETERMINATION OF CERIC OXIDE IN LEAD
BY X-RAY FLUORESCENCE

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ABSTRACT

The analysis of CeO_2 in Pb is accomplished by X-ray fluorescence. Three techniques are described for various concentration ranges.

INTRODUCTION

A material containing Pb powder and CeO_2 was prepared in the ceramics laboratory for research purposes. A rapid analytical method was needed for verification of the material content.

The method developed and reported here has two significant features. First, by varying the sample preparation procedure, X-ray fluorescence was used to determine CeO_2 over a concentration range from ppm to major constituent level. Second, an excellent separation of Pb from Ce was accomplished using anion exchange from an aqueous hydrobromic acid medium.

Stewart and Elion (1) reported on the investigation of the adsorption of the elements by ion exchange resins from HBr-organic solvent media. They reported that, "Elements in pure aqueous hydrobromic acid media do not show a behavior deviating appreciably from that observed in hydrochloric acid systems under comparable conditions."

This has been found not true in the case of Pb. The data in Table I indicate that the adsorption behavior of Pb from HBr media is decidedly different from that in comparable HCl media.

Microgram quantities of Ce (limit of detection is $\sim 1 \mu\text{g}$) are adsorbed on ion exchange paper prior to analysis by X-ray fluorescence. The technique of concentrating trace elements on ion exchange paper, and subsequently analyzing the paper by X-ray fluorescence, was pioneered by Campbell and his co-workers (2).

The sample material received for analysis was prepared from pure Pb and CeO_2 , so possible interferences were not investigated. A study to establish interferences would be advisable before using the method on a multicomponent system.

SUMMARY

Three techniques are described for determining CeO_2 in Pb by X-ray fluorescence. The techniques are applicable to the concentration of CeO_2 ranging from ppm to major constituent levels. Ion exchange in a bromide medium is used to separate

Pb from micro amounts of Ce. Microgram amounts of Ce are concentrated on ion exchange paper for analysis. Higher concentrations of Ce are analyzed in solution. Samples containing >five percent CeO_2 are analyzed without separating from Pb. The relative standard deviations are 6 percent, 2.4 percent, and 1.1 percent, respectively, for the micro, macro, and high level techniques.

EXPERIMENTAL

Reagents

1. Conc. HCl - reagent grade
2. Conc. HNO_3 - reagent grade
3. Conc. HBr - reagent grade
4. 2N HBr - dilute conc. HBr with H_2O
5. pH2 solution - dilute conc. HCl with H_2O
6. Dowex^R 1x4, Br^- form - convert Cl^- form to Br^- form with HBr
7. Cation exchange paper - SA2 grade, Na^+ form
8. Cerium stock solution - 10 g/l (as CeO_2) prepared from CeO_2
9. Lead stock solution - 100 g/l (as Pb) prepared from Pb Metal.

Apparatus

1. Filtering device for ion exchange disc (Figure 1)
2. Philips Norelco 100 kv spectrograph
 - a. Tube Tungsten
 - b. Power 90 kv, 20 ma
 - c. Crystal LiF
 - d. Detector Scintillation, 875 v
 - e. Goniometer $10.17^\circ \text{Ce}_{\text{K}\alpha 1}$, 11.50° Background
 - f. Counting Mode Fixed Time - 100 sec.

Standards

Standard solutions were prepared from dilutions of the stock solutions listed above.

A. Micro Technique

1. A set of standard 1 in. discs was prepared by adsorbing 0, 10, 25, 75, and 100 μg of Ce (as CeO_2) on individual cation exchange papers.

FIGURE 1

Filtering Device for Ion Exchange Disc

2. A standard curve was prepared by irradiating each disc using the parameters listed above and plotting

$$[\text{Ce}] \text{ vs } \frac{I_{\text{Ce}_{K\alpha 1}}}{I_{\text{Background}}}$$

B. Macro Technique

1. A standard curve was prepared by irradiating a set of standard solutions containing 0, 0.25, 0.50, 1.0, and 2.0 mg Ce/ml (as CeO_2) using the parameters listed above. Plot

$$[\text{Ce}] \text{ vs } \frac{I_{\text{Ce}_{K\alpha 1}}}{I_{\text{Background}}}$$

C. High Level Technique

1. A standard curve was prepared by irradiating a set of standard solutions containing both Pb and Ce. The concentrations of these two elements in each standard was varied such that the $[\text{CeO}_2] + [\text{Pb}] = 100$ percent. Plot on log-log paper.

$$[\text{Ce}] \text{ vs } \frac{I_{\text{Ce}_{K\alpha 1}}}{I_{\text{Background}}}$$

Distribution Coefficients

Preliminary experiments indicated that Ce was not adsorbed by Dowex 1 from HBr media, and that Pb was adsorbed. Optimum conditions for Pb adsorption were established by determining the distribution coefficients for Pb in various concentrations of HBr.

Eight solutions were prepared so that five ml contained 100 mg of Pb. The HBr concentration of these solutions varied from 2 N to 8.8 N. Five ml of each solution were placed in separate vials along with one g of Dowex 1x4 (Br^- form). After equilibrium (48 hrs) the liquid phase was analyzed for its Pb content. The distribution coefficient was calculated from these data using the formula:

$$D_{\text{Pb}} = \frac{\text{grams Pb}_{\text{resin phase}} (\text{ml solution})}{\text{grams Pb}_{\text{sol'n phase}} (\text{grams resin})}$$

Table I compares the D_{Pb} 's which the author determined for the Br^- system with the D_{Pb} 's which Kraus (3) determined for the Cl^- system. This comparison was made to discount the general statement that the Br^- system offered no advantage over the Cl^- system.

TABLE I
Distribution Coefficients for Pb
in HBr and HCl Systems

<u>Normality</u> <u>HBr</u>	<u>D_{Pb} (HBr system)</u>	<u>Normality</u> <u>HCl</u>	<u>D_{Pb} (HCl system)^a</u>
2.0	2495	2.0	15
3.0	995		
4.0	370	4.0	7
5.0	141		
6.0	56	6.0	1
7.0	27		
8.0	11	8.0	<1
8.8	3		

^a Values listed for the HCl system were taken from a chart prepared by Kraus and Nelson which appears in ASTM Publication Number 195.

Separation Procedure

The sample (0.1 to 1 g) was dissolved by heating in concentrated HBr (20 ml/g spl). After dissolution was complete, H_2O was added until Pb just began to precipitate. The final HBr concentration was approximately 2 N. The bromide form of Dowex 1x4 resin was added (10g resin/g of sample) to the solution which was then warmed and mixed for 30 minutes. The liquid phase was filtered through a column containing two ml of fresh Dowex 1x4 (Br^- form). The resin was washed with 2 N HBr to assure complete recovery of the cerium.

In experiments starting with 500 mg of Pb, an average of 1.3 mg of Pb was found in the effluent after the separation process. This indicated that a separation factor of 300 to 400 can be expected using this procedure.

Micro Technique

An aliquot containing 10 to 100 μg of Ce was taken from the effluent obtained in the separation procedure. This aliquot was evaporated to remove the acid present. The residue was taken up by heating with 40 ml of dilute HCl (pH2). The resulting solution was passed through a 1 in. disc of cation exchange paper five times using the filtering device shown in Figure 1. The disc was then mounted on a pipe cap, dried with an infrared lamp, covered with mylar film (0.25 mil), and inserted in the X-ray unit for analysis.

Table II indicates the precision obtained using this technique on six separate cuts from one sample. An idea of the accuracy of the technique can be realized by comparing the results listed with the prepared value of the sample which was 1.29 percent CeO_2 .

TABLE II

Micro Technique Results on a Sample of
Pb-CeO₂ Having a Prepared Value of 1.29% CeO₂

<u>Sample Cut</u>	<u>%CeO₂</u>
1	1.30
2	1.17
3	1.26
4	1.19
5	1.29
6	1.37
Mean	1.26
Std. Dev.	± 0.07
R.S.D.	5.9%

Eighteen additional samples were analyzed by this technique. These samples were prepared to contain from 1.10 to 1.50 percent CeO_2 . All 18 results fell within the specified range.

Macro Technique

An aliquot containing 2 to 20 mg of Ce was taken from the effluent obtained in the separation procedure. Excess HNO_3 was added to convert Br^- to Br_2 . The Br_2 was removed by boiling. It is advisable to trap the Br_2 being expelled from the solution since Br_2 is extremely toxic and corrosive. The solution was evaporated to a small volume, and then transferred to a ten ml volumetric flask. A portion of the solution from the volumetric was transferred to a pipe cap, covered with two layers of 0.25 mil mylar film, and inserted into the X-ray unit for analysis.

Table III indicates the results obtained using this technique on six cuts from the same sample and is used to establish the precision of the micro technique.

TABLE III

Macro Technique Results on a Sample of
Pb-CeO₂ Having a Prepared Value of 1.29% CeO₂

<u>Sample Cut</u>	<u>%CeO₂</u>
1	1.32
2	1.23
3	1.32
4	1.28
5	1.30
6	1.31
Mean	1.29
Std. Dev.	± 0.03
R.S.D.	2.4%

High Level Technique

If more than five percent CeO_2 is present, it was found not necessary to separate Ce from Pb. The sample was dissolved in concentrated HBr, Br^- converted to Br_2 with HNO_3 , and the solution heated to expel Br_2 . The resulting solution was transferred to a volumetric flask and a portion from the flask was transferred to a pipe cap. It was then covered with two layers of 0.25 mil mylar film and inserted into the X-ray unit for analysis.

Table IV indicates the precision obtained using this technique on six synthetic sample solutions. Each solution was prepared to contain 70 mg of Pb and 30 mg of CeO_2 in 10 ml of solution.

TABLE IV

High Level Technique Results on Synthetic Sample Solutions that Contained 70 Parts Pb and 30 Parts CeO_2

<u>Sample Solution</u>	<u>%CeO_2</u>
1	29.0
2	30.0
3	29.5
4	29.4
5	29.5
6	29.5
Mean	29.5
Std. Dev.	± 0.3163
R.S.D.	1.07%

CONCLUSION

The data in this report indicate that X-ray fluorescence is an excellent analytical tool for determining Ce in Pb over concentrations ranging from ppm to major constituent levels.

The effectiveness of this instrument to make determinations over such a wide range is of course not limited to Ce. It is applicable to most of the elements ($>Ca$) if a suitable separation procedure is developed to isolate the element prior to adsorption on ion exchange paper.

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