July, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 1899—1902 (1985)* 1899

Differential Pulse Polarographic Determination of Lead Using Coprecipitation with Hafnium Hydroxide

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(Received January 28, 1985)

A differential-pulse polarographic determination of trace amounts of lead using coprecipitation with hafnium hydroxide has been studied. Hafnium hydroxide is effective as a collector of lead and makes 2.5 to at least 1250 μg of lead coprecipitate quantitatively from 100—500 cm^3 of sample solution. The formed precipitate is easily dissolved with hydrochloric acid and the presence of hafnium does not affect to the polarogram of lead. The effects of twenty-three diverse ions such as aluminium, zinc, cadmium, chromium(III), manganese(II), cobalt, and nickel were examined, and it was found that the presence of tin(IV), copper, and iron(III) interfered with the determination, even in small amounts. The recommended procedure for the determination is as follows. To a sample solution containing lead, 5 mg of hafnium is added and the pH is adjusted to about 10 with 1:1 aqueous ammonia. Then, the precipitate is filtered with a glass filter and dissolved with 2 cm^3 of concd hydrochloric acid. After the solution is diluted to 25 cm^3 with distilled water and deaerated with pure nitrogen for 5 min, lead is determined by the current peak height at −0.41 V.

The methods for the determination of trace amounts of lead by a combined coprecipitation-polarography have frequently been studied, and several coprecipitants such as hydroxides of beryllium,(1) aluminium,(2,3) iron(III),(4,5) thorium,(6) and zirconium,(7) or carbonates of calcium(8) and strontium(9) or sulfides of nickel,(10) copper,(11) and zinc(12) or barium chromate(13) have been proposed for a concentration of trace amounts of lead. The majority of these coprecipitants except hydroxides of zirconium and thorium, however, have more or less their individual disadvantages: It is difficult to dissolve the precipitates, the recovery of lead is not so good or the polarogram of lead is affected by the presence of the coprecipitants. This time, we have investigated a new collector of lead, and have found that hafnium hydroxide is excellent. That is, hafnium hydroxide can not only quantitatively collect lead as well as zirconium hydroxide,(7) but it can also quantitatively coprecipitate lead from a wider pH range than zirconium. Furthermore, it dissolves easier than zirconium hydroxide. In this work, we have also tried to filter the precipitate by means of suction with a glass filter and have obtained good results; shortening of the filtration time without the loss of the precipitate and simplifying the filtration procedure. This paper describes the fundamental conditions for the collection of trace amounts of lead by coprecipitation with hafnium hydroxide and a differential pulse polarographic determination of lead.

Experimental

Apparatus. A Yanagimoto model p-1000 polarograph was used for the differential-pulse polarographic measurements. It was operated in a three-electrode configuration with a dropping-mercury electrode, a saturated calomel reference electrode and a platinum counter electrode. A Hitachi-Horiba model M-5 glass electrode pH meter was used for the pH measurements.

All measurements were carried out at 25.0±0.1 °C and the solutions were deaerated with pure nitrogen for 5 min before the polarographic analysis. Voltage scans were made from −0.25 to −0.65 V at a rate of 10 $mV\,s^{-1}$, a modulation amplitude of 100 mV and a drop time of 1 second.

Reagents. *Standard Lead Solution*: A solution containing about 1 $mg\,cm^{-3}$ of lead was prepared by dissolving guaranteed reagent-grade lead nitrate in a small amount of nitric acid and diluting with distilled water. The solution was standardized by the complexometric titration using Xylenol Orange as an indicator. This solution was diluted as required.

Hafnium Solution: A solution containing about 5 mg of hafnium was prepared by dissolving hafnium chloride (Nakarai Chemicals Co.) in 2 $mol\,dm^{-3}$ hydrochloric acid. The solution was standardized by the complexometric back titration with a standard solution of thorium using Xylenol Orange as an indicator.

1:1 aqueous ammonia and 1 $mol\,dm^{-3}$ hydrochloric acid were used for pH adjustments.

All the other reagents used were of guaranteed reagent grade.

Recommended Procedure. To a sample solution (100—500 cm^3) containing 2.5—1250 μg of lead, 5 mg of hafnium is added and the pH is adjusted to about 10 with 1:1 aqueous ammonia. Then, this solution is allowed to stand for more than 10 min. The precipitate is filtered by suction using a 3G4 glass filter, washed with aqueous ammonia of pH 10, and dissolved with 2 cm^3 of concd hydrochloric acid (with two 1 cm^3 portions of concd hydrochloric acid in about 5 min intervals). After the solution is diluted to 25 cm^3 with distilled water and deaerated with pure nitrogen for 5 min, the polarogram is recorded from −0.25 to −0.65 V. Lead is determined by the current peak height at −0.41 V.

Results and Discussion

Supporting Electrolyte. As a result of the investigation of various acids (such as hydrochloric, nitric, sulfuric, and perchloric acid), the most suitable supporting electrolyte was found to be hydrochloric acid in respect to the shape of the polarograms of lead and the ease of dissolution of hafnium hydroxide. So, hydrochloric acid was chosen as the supporting electrolyte for further studies. Then, the effect of the concentration of this acid on the current peak height was studied. As shown in Fig. 1, the current peak height was gradually decreased with increasing amounts of hydrochloric acid; however, a maximum and almost constant value was obtained over a concentration range from 0.5 to 2 mol dm^{-3} of hydrochloric acid. Accordingly, an acidity of 1 mol dm^{-3} was used in this experiment and obtained the highest current peak height.

In Table 1, the relation between the concentration of hydrochloric acid and the time required for the dissolution of hafnium hydroxide is also shown. From this, it can be seen that hafnium hydroxide is dissolved easily by the use of hydrochloric acid whose concentration is more than 3 mol dm^{-3}. In this Table, the results of experiments with zirconium hydroxide is also appended.

Effect of pH on Coprecipitation. The effect of the pH on the coprecipitation of lead with hafnium hydroxide was studied for a solution (100 cm^3) containing 20 μg of lead. The pH values were adjusted with 1:1 aqueous ammonia and 1 mol dm^{-3} hydrochloric acid. The results are shown in Fig. 2. The pH range in which about 100% recovery of lead was observed was found to be 7.0—11.5, which was wider by about 4 times than that of zirconium hydroxide.[7] In this experiment, a pH of about 10 was adopted for the coprecipitation with hafnium hydroxide.

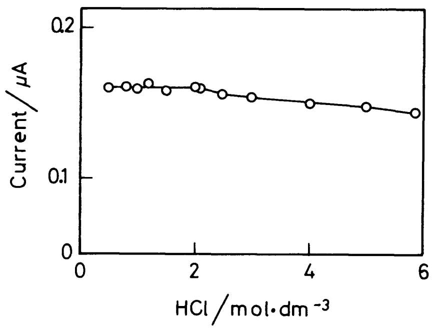

Fig. 1. Effect of the concentration of supporting electrolyte.
Pb: 20 μg/25 cm^3, Hf: 5 mg/25 cm^3, temperature: 25.0±0.1 °C.

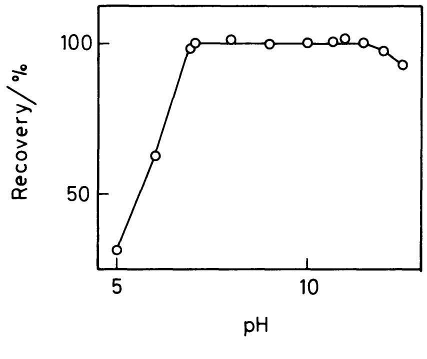

Fig. 2. Effect of pH on coprecipitation.
Pb: 20 μg/25 cm^3, Hf: 5 mg/25 cm^3, supporting electrolyte: 1 mol dm^{-3} HCl, temperature: 25.0±0.1 °C.

Effect of the Amount of the Coprecipitant. The effect of the hafnium concentration on the coprecipitation was studied with a solution (100 cm^3) containing 20 μg of lead and various amounts of hafnium. As the result, lead could be quantitatively collected by adding from 2 mg to at least 20 mg of hafnium.

Effect of Volume of Sample Solution. The relation between the recovery percentage of lead and the volume of the sample solution was studied by the recommended procedure, using various volumes (100—900 cm^3) of sample solutions which contain 20 μg of lead. The recovery percentage was approximately 100% when volumes from 100 to 500 cm^3 were used. However, in the case of using a volume of more than 500 cm^3, the percentage decreased considerably.

Effect of Aging of Precipitate on Lead Recovery. The relation between the recovery of lead and the aging time of the precipitate was investigated. The results indicated that the recovery of lead reached almost 100% at about 10 min after the precipitate was formed. After that, this percentage remained almost constant for at least 10 h. Then, the effect of the aging temperature of precipitate on the recovery of lead was also studied. It was found that almost a 100% recovery was always obtained within a temperature range from room temperature to 90 °C. In this experiment, therefore, the aging of the precipitate was carried out for more than 10 min at room temperature.

TABLE 1. RELATION BETWEEN CONCENTRATION OF HYDROCHLORIC ACID AND DISSOLUTION TIME OF PRECIPITATES

Concentration of HCl/mol dm^{-3}	$Hf(OH)_4$ min	$Zr(OH)_4$ min
1	*ca.* 2.5	*ca.* 50
2	*ca.* 1	*ca.* 12
3	*ca.* 10 s	*ca.* 3
6	*ca.* 5 s	*ca.* 1
9	(A)	*ca.* 1
12	(A)	*ca.* 0.5

10 mg of hafnium or zirconium was taken and 1 cm^3 of hydrochloric acid was used. (A): Precipitate dissolved instantaneously.

Filtration of Precipitate. In this experiment, we tried to filter the precipitate by means of suction using a glass filter and were able to considerably shorten the filtration time without any loss of precipitate. Also, the filtration and dissolution procedures of the precipitate were simplified. Whether the loss occurs or not by suction was examined by a comparison of the recovery of lead obtained by suction with that obtained by natural filtration (using Toyoroshi No. 5A filter paper). It was confirmed that almost the same recoveries were obtained for the both cases.

Calibration Curves. The calibration curves which were prepared by the recommended procedure were shown in Fig. 3. A linear relationship between the current peak height and the concentration was maintained over the range of 0.1—50 μg cm^{-3} for lead. In the absence of 5 mg of hafnium, the calibration curves were also prepared. It was recognized that the obtained curves were the same as the one which was prepared in the presence of hafnium. The reproducibility of the method, expressed by the relative standard deviation of the current peak heights which were obtained from ten repeated determinations, was 1.2% for 20 μg in 100 cm^3 sample solution. In order to investigate the temperature effect on the current peak height, a series of polarograms were also recorded at different temperatures. With a rise of temperature, the potential of the current peak shifted to more negative values and the current peak height increased. In this case, the temperature coefficient was calculated as 1.0%.

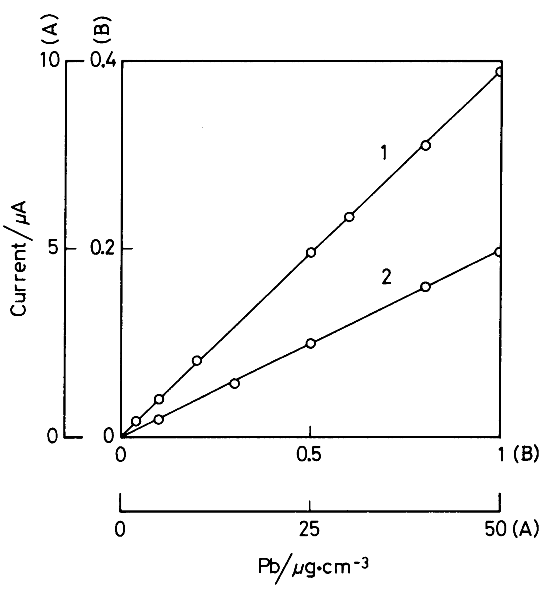

Fig. 3. Calibration curves.
Supporting electrolyte: 1 mol dm^{-3} HCl, Hf: 5 mg/25 cm^3, temperature: 25.0±0.1 °C, 1: utilize scale (A), 2: utilize scale (B).

Effect of Diverse Ions. The effect of twenty-three diverse ions on the determination of 20 μg of lead were examined by the application of the recommended procedure. The results are summarized in Table 2. Lead could be determined within a 5% error in the presence of 5 mg each of 8 cations, such as alkali metals, alkaline earth metals, aluminium, lanthanum, and molybdenum(VI), 0.5 mg each of 3 cations such as zinc, manganese(II), and nickel, and 0.1 mg each of 5 cations such as antimony(III), bismuth(III), cadmium, chromium(III), and cobalt. Tin(IV), copper, and iron(III), however, interfered with the determination even if they were present in a small amounts.

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Table 2. Effect of diverse ions

Ion	Amount added mg	Recovery %
Li^+	5.0	99.0
Be^{2+}	5.0	103.1
Mg^{2+}	5.0	104.0
Ca^{2+}	5.0	100.4
Ba^{2+}	5.0	100.1
Al^{3+}	5.0	98.0
Ga^{3+}	1.0	100.0
In^{3+}	0.05	97.0
Sn^{4+}	0.02	110.0
Sb^{3+}	0.1	99.2
Bi^{3+}	0.1	102.0
Cu^{2+}	0.02	94.8
Zn^{2+}	0.5	100.0
Cd^{2+}	0.1	98.0
La^{3+}	5.0	100.0
Zr^{4+}	1.0	100.0
Th^{4+}	1.0	100.0
Cr^{3+}	0.1	101.0
Mo(VI)	5.0	99.1
Mn^{2+}	0.5	98.0
Fe^{3+}	0.02	93.7
Co^{2+}	0.1	98.3
Ni^{2+}	0.5	101.0

20 μg of lead was taken.

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