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SEPARATION OF BISMUTH FROM LEAD WITH
(ETHYLENEDINITRIL) TETRAACETIC ACID
APPLICATION TO RADIOCHEMISTRY

SEPARAÇÃO DE BISMUTO E CHUMBO COM ÁCIDO ETILENODIANI-
NOTETRAACÉTICO (EDTA) — APLICAÇÃO À RADIOQUÍMICA

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Separation of Bismuth from Lead with (Ethylenedinitrilo)tetraacetic Acid

Application to Radiochemistry

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► Bismuth can be radiochemically separated from lead by using (ethylenedinitrilo)tetraacetic acid in a modification of the procedure proposed by Přibil and Čuta. The separation is successful when both elements are at tracer concentration or when one (or both) of them is at macro concentration. A single-step separation permits recovery greater than 90% of both elements with practically no contamination. The procedure involves simple and rapid manipulation and can be completed in less than 15 minutes, which is important when the half lives of the isotopes are short.

PŘIBIL and Čuta (7) described a separation of bismuth from lead when both cations are present in more than tracer concentration. This separation is accomplished by complexing the elements with (ethylenedinitrilo)tetraacetic acid (EDTA) and then adding calcium ion which replaces bismuth in the EDTA complex. If the solution is slightly ammoniacal, bismuth is precipitated as the hydroxide and can be filtered off. For gravimetric purposes, it is necessary to add equivalent amounts of calcium nitrate and EDTA to the lead-bismuth solutions; by using a large excess of the calcium salt, the precipitated bismuth hydroxide always contains some calcium, and it is necessary to dissolve and repurify it (7). The present authors have observed that the excess of calcium nitrate added to the lead-EDTA solution, in ammoniacal media, will slightly contaminate the bismuth hydroxide with lead and reprecipitation is necessary.

The separation of lead from bismuth is always an important radiochemical problem, as isotopes of both elements often occur together—for instance, in nuclear processes such as lead-204 (*d*, $2n$) bismuth-204 and lead-206 (*d*, $2n$) bismuth-206 (9, 10), and in natural radioactive lead-bismuth mixtures previously separated in the uranium, thorium, and actinium series.

To obtain radiochemically pure lead-212 and bismuth-212, Rudenko (8)

devised a method in which bismuth and lead are precipitated as bismuth gallate and lead sulfide, respectively. Titration of bismuth with EDTA in the presence of large amounts of lead has been described by Fritz (1). Traces of lead have been separated and determined in the presence of small amounts of bismuth by Moore (6), who precipitated bismuth sulfide with copper as a carrier in hydrochloric acid medium; lead remains in the filtrate.

The classical separation of lead from bismuth by precipitating bismuth hydroxide with sodium hydroxide and forming sodium plumbite, which is soluble, has the disadvantage that some lead is entrained with the bismuth precipitated. Also, bismuth is somewhat soluble in the excess sodium hydroxide required to form the lead plumbite and each fraction is contaminated by the other element.

Starting with the method suggested by Přibil and Čuta (7), a new method has been devised for the separation of lead from bismuth, whatever their relative concentrations, which avoids the use of calcium to dissociate the bismuth-EDTA complex; the method is especially useful in radiochemical problems when one or both elements are present at tracer level.

PRINCIPLES OF METHOD

Přibil and Čuta (7) have called attention to the different behavior of bivalent and trivalent metals with EDTA in connection with the possibility of precipitating the metals from EDTA solutions with ammonium hydroxide. The bivalent metals form very stable complexes with EDTA, which, with the exception of beryllium, cannot be precipitated out of solution by ammonium hydroxide. Some of the trivalent metal-EDTA complexes are also very stable even in relatively acid solutions and cannot be precipitated with ammonium hydroxide. However, sodium hydroxide will effect precipitation and will do so quantitatively, unless the amphoteric character of the metal

prevents this reaction, as is the case with aluminum (7).

The facts observed by the above authors suggested that the system of lead-bismuth EDTA complexes could be resolved and both cations separated by using only sodium hydroxide as precipitant, as it is not necessary to use calcium to replace the trivalent metal in the complex.

The complexing efficiency of EDTA with bismuth is greatly affected by the hydrolytic effect at high pH values. By adding sodium hydroxide to a mixture of the EDTA complexes of bismuth and lead, bismuth is precipitated as the hydroxide, and as no large excess of alkali is required to form the soluble sodium plumbite, the inconvenience of dissolution of some bismuth hydroxide is avoided. In the procedure described in the present paper, the amount of sodium hydroxide added to the mixture of EDTA complexes of lead and bismuth might be determined by the phenolphthalein end point. However, because a slight excess of EDTA prevents a quantitative precipitation of bismuth in solution made alkaline against phenolphthalein, an excess of sodium hydroxide was used over the end point of the indicator, the final sodium hydroxide concentration being about 0.1M. At this concentration the amount of sodium hydroxide present is not large enough to dissolve the bismuth hydroxide formed, but it is sufficient to precipitate the bismuth from the solution of EDTA.

APPARATUS AND REAGENTS

The activities of the radioisotopes were determined in a mica window Geiger counter with 1.2 mg. per sq. cm. of window thickness. A decimal scaling unit, Model 166 (Nuclear Chicago Corp.), was used as a register. For gamma scanning, a one-channel pulse analyzer (Instituto de Energia Atômica) was used; a linear amplifier (Technical Measurement Corp.), Model A1-4A, a decimal scaler, Model 181-A, and a sodium iodide-thallium well-activated scintillation crystal, Model XT-100 (both from Nuclear-Chicago Corp.) were also used. The gamma-

counting system was standardized by using lead-210 (0.047 m.e.v.), cadmium-109 (0.087 m.e.v.), tin-113 (0.393 m.e.v.), and cesium-137 (0.662 m.e.v.) sources.

Lead nitrate tagged with lead-210 was obtained from Canadian Radium and Uranium Corp., and was purified by pulp-paper chromatographic techniques using butyl alcohol in a 3*N* solution of hydrochloric acid (4, 5). Spectrographic analysis of the purified material is presented in Table I. Carrier-free lead-210 and bismuth-210 were obtained from old radium tubes used for radiotherapy. The tubes were smeared with a piece of cotton which was then treated with nitric acid, the solution was filtered and made 0.1*N* in nitric acid, and lead and bismuth were deposited by electrolysis on platinum electrodes which were boiled in nitric acid 1 to 1 to remove the radioisotopes.

The EDTA was of analytical grade and was purified further by dissolution in ammonium hydroxide and precipitation twice with hydrochloric acid. A standard solution was made by weighing the required amount of acid to make a 0.1*M* solution, dissolving it in ammonium hydroxide, ascertaining the pH to 8.0, and titrating with magnesium chloride using Eriochrome Black T as indicator. Solutions of other concentrations in EDTA were made by dilution.

PROCEDURE

The experiments were made in four groups depending on the relative amounts of bismuth and lead. In group A, macro amounts of lead and bismuth were present; in group B, lead was at macro amount and bismuth at tracer level; in group C, lead was at tracer level and bismuth in macro amount; and in group D, both elements were at tracer level.

The radioisotope solutions obtained from the nitric acid treatment of the platinum electrodes were boiled to eliminate excess of nitric acid and made to volume in 100-ml. volumetric flasks. Depending on the experimental group, carriers of bismuth and/or lead were added at this stage and the mixture was considered ready for separation.

The concentrations of the solutions in the various groups were 11.8 mg. per ml. of lead ion (groups A and B) and 13.4 mg. per ml. of bismuth ion (groups A and C). The amounts of radioactive isotopes of both elements in all four groups were from 0.006 to 0.2 μ c. per ml. of solution of lead-210 in secular equilibrium with bismuth-210. For the same set of experiments the concentration of the radioactive isotopes in the original solution was the same.

For the experiments, 1 ml. of solution was taken to a beaker and the volume of 0.01*M* EDTA solution required for complexation of the metals was added. For the experiments in group D, where

bismuth and lead were at tracer concentration, the volume of 0.01*M* EDTA was 1 ml. The solution was treated with 1*N* sodium hydroxide until the formation of a permanent pink color of phenolphthalein indicator, then an excess of alkali was added, and the volume was made to 20 ml.; the final concentration of sodium hydroxide was 0.1*M*. At this stage bismuth is precipitated as the hydroxide or there is the formation of a radiocolloid if it is present at trace concentration, the recovery of bismuth being over 98%. All steps were carried out on a hot plate.

Table I. Spectrographic Analysis of Lead Nitrate Tagged with Lead-210 After Chromatographic Purification

	Per Cent
Al	0.002
Si	0.0005
Ca	0.0001
Cu	0.0003
Fe	0.001
Mg	0.0001
Ag	0.0001

The precipitate or the radiocolloidal bismuth was filtered off, washed with a dilute solution of sodium hydroxide and water, and mounted for counting. Before filtering, the paper (Whatman No. 42) was treated with sodium hydroxide solution.

The purity of each fraction, the precipitate of bismuth hydroxide and the soluble lead, were determined next. Purity of the bismuth precipitated was checked by gamma spectrometry looking for the 0.047-m.e.v. photopeak for lead-210. Purity of the lead filtrate solution was verified by adding bismuth carrier to the filtrate (also, lead carrier when working with carrier-free lead, groups A and D) and precipitating both elements with bismuthiol I (2,5-dimercapto-1,3,4-thiadiazol), mounting the precipitates, and counting. The amount of bismuth present in the lead fraction was calculated by the method proposed by Lima (8).

Table II. Per Cent Bismuth Contamination of Original Amount of Lead Fractions (Columns *a*, cations previously complexed with EDTA; column *b*, no previous complexation)

A		B		C		D	
<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
0	8.0	1.7	37.0	3.8	34.0	0.1	27.0
0.8	5.8	0	35.0	4.1	10.5	2.1	21.5
0	4.8	1.0	9.5	4.0	11.0	7.6	15.0

To compare results, separations were also carried out by the classical precipitation of bismuth hydroxide (or radiocolloid formation if at tracer level) with sodium hydroxide and by forming the soluble sodium plumbite, without

having previously complexed the cations with EDTA.

To check the possibility of some contamination of the bismuth hydroxide precipitate with lead, when the bismuth-EDTA complex was broken by adding calcium ions, the precipitation of bismuth hydroxide was also carried out by this technique.

RESULTS AND DISCUSSION

Typical results for the percentage of contamination of the lead fraction with bismuth on the various groups of experiments are presented in Table II. Data are given for the cases where the precipitation was carried out by the method described in this paper and, for comparison, by using only sodium hydroxide without previous complexation of the cations. The percentage of contamination was calculated by using the formula given in (3)—i.e.,

$$a = 1 - (A' - A'')/A' \exp(-\lambda t') - A'' \exp(-\lambda t'')$$

where *a* is the fraction (contamination) of bismuth on the lead bismuthiol precipitate, *A'* and *A''* are the activities of the precipitate at times *t'* and *t''*, respectively, and λ is the disintegration constant for bismuth-210.

Table II shows that contamination of the lead fraction is practically absent for groups A and B, as compared to a large contamination when no previous complexation by EDTA is carried out. The largest percentage of contamination (7.6%) is observed in group D when both cations are at tracer level. Even in this group the results are much better than when the classical method of precipitating with sodium hydroxide alone is used, where extremely high values for contamination are found.

The contamination for the corresponding bismuth fractions of Table II was checked by γ -ray spectrometry of these fractions, as described. The results are present in Figure 1 for two typical

precipitates of each group. Curves *a* correspond to the bismuth fractions obtained when the two cations in the mixture were previously complexed with EDTA. Curves *b* are for the cases when bismuth hydroxide was

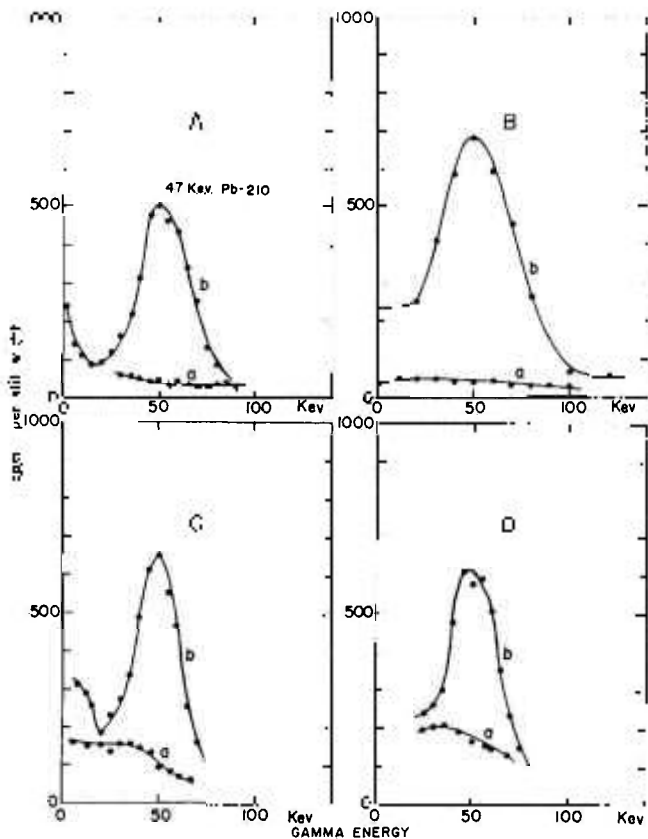


Figure 1. Gamma-ray scanning of the bismuth fractions

- a. Cations complexed with EDTA
- b. No previous complexation

Slit width, 20 k.e.v.; gain setting, 4

precipitated by sodium hydroxide with no previous complexation. In all four groups the results were reproducible and the 47-k.e.v. photoelectric peak of lead-210 could always be detected in the bismuth fraction that was precipitated without previous complexation with EDTA. By comparing the areas under the curves in Figure 1 with the areas obtained with the original lead-210 solutions, it is found that the contamination is about 8% for the case when the cations are not previously complexed with EDTA and sodium hydroxide is used as precipitant.

In groups C and D, where lead was present at tracer level, the bismuth hydroxide precipitate showed some contamination by lead when an excess of

calcium ion was used for disruption of the EDTA complexes. The small increase in concentration of lead ions, originating from an eventual exchange reaction between lead-EDTA complex and calcium ions, would favor an entrainment of lead by bismuth hydroxide; This entrainment would be in accordance with Fajans' rule (2), because lead ions, when present in macro amounts, will form the insoluble lead hydroxide; consequently, in accordance with Fajans' rule, lead ions, when at tracer concentration, would be coprecipitated with bismuth hydroxide. The entrainment of lead might also be due to an occlusion, in the bismuth hydroxide, of some lead-EDTA complex together with the calcium ion that is absorbed

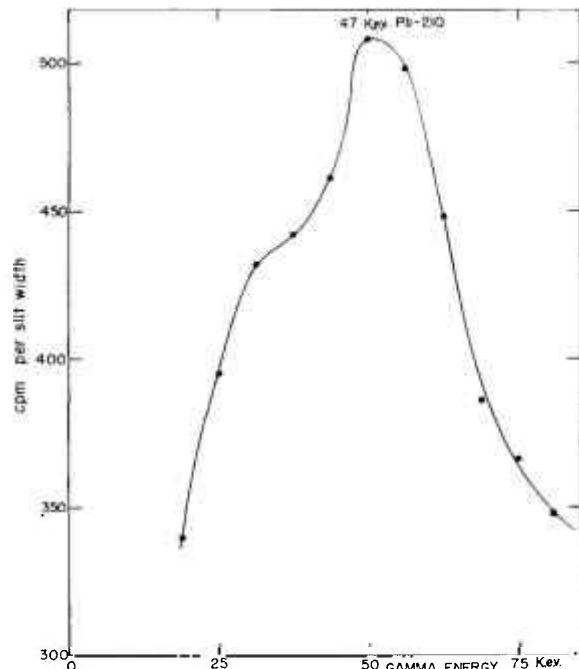


Figure 2. Gamma-ray scanning of bismuth fraction when calcium ion is used to break the bismuth-EDTA complex

Slit width, 20 k.e.v.; gain setting, 4

when this ion is used in excess. Figure 2 is a typical scanning of a bismuth hydroxide precipitate when calcium, in an excess of 10% over the equivalent amount of EDTA, was used to break the bismuth-EDTA complex.

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