CANADA

THE DETERMINATION OF LEAD BY A SOLVENT EXTRACTION-EDTA TITRATION PROCEDURE

A. HITCHEN

EXTRACTION METALLURGY DIVISION

DEPARTMENT OF MINES AND TECHNICAL SURVEYS, OTTAWA

MINES BRANCH

RESEARCH REPORT

R 128

Price 75 cents

MARCH 1965

Available by mail from the Queen's Printer, Ottawa,
and at the following Canadian Government bookshops:

OTTAWA
Daly Building, Corner Mackenzie and Rideau

TORONTO
Mackenzie Building, 36 Adelaide St. East

MONTREAL
Aeterna-Vie Building, 1182 St. Catherine St. West

or through your bookseller

A deposit copy of this publication is also available
for reference in public libraries across Canada

Price 75 cents Catalogue No. M38-1/128

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada
1965

Mines Branch Research Report R 128

THE DETERMINATION OF LEAD BY A SOLVENT EXTRACTION-EDTA TITRATION PROCEDURE

by

A. Hitchen*

ABSTRACT

A rapid, simple and precise method has been developed for the determination of 0.05 to 500 milligrams of lead, in mixtures of lead, titanium and zirconium precipitates used for the manufacture of ceramic transducers, and also in lead ores, concentrates and minerals. Lead is determined by titration with disodium ethylenediaminetetraacetate using Xylenol Orange as indicator, after separation from interfering elements by chloroform extraction of lead diethyldithiocarbamate. Complexation with cyanide and tartrate eliminates the interfering effect of most elements except bismuth, antimony, tin, manganese, and phosphate. The interference of all these except bismuth can be prevented by special procedures, which are described. In the case of bismuth, the method permits it to be determined along with the lead by a successive titration, and a procedure for accomplishing this is also given.

* Senior Scientific Officer, Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Direction des mines

Rapport de recherches R 128

LE DOSAGE DU PLOMB PAR LA MÉTHODE D'EXTRACTION PAR SOLVANT ET DE TITRAGE PAR ÉTHYLENE-DIAMINE-TÉTRAACÉTATE (EDTA)

par

A. Hitchen*

RÉSUMÉ

L'auteur a mis au point une méthode rapide, simple et précise pour déceler la présence de 0.05 à 500 mg de plomb dans les mélanges de précipités de plomb, titane et zirconium employés dans la fabrication des transducteurs en céramique, ainsi que pour doser le plomb dans ses minerais, concentrés et minéraux. Le titrage est réalisé à l'aide d'éthylène-diamine-tétraacétate disodique, le xylenol orange servant d'indicateur, après séparation du plomb et des éléments gênants par l'extraction au chloroforme du diéthyldithiocarbamate de plomb. La conversion en complexes de cyanure ou de tartrate élimine les effets gênants de la plupart des éléments, sauf le bismuth, l'antimoine, l'étain, le manganèse et les phosphates. La perturbation introduite par ces derniers, à l'exception du bismuth, peut être empêchée par l'utilisation de procédés spéciaux, que l'auteur décrit. Dans le cas du bismuth, la méthode permet son dosage en même temps que le plomb par des titrages successifs, procédé que l'auteur décrit également.

*Agent scientifique senior, Division de la métallurgie extractive, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

INTRODUCTION

Research work is being carried out in the Mines Branch laboratories on the development of a chemical process for the production of electronic ceramics of closely controlled composition and of greater purity and uniformity than those available commercially (1). Because one of the aims of this research program is to investigate the effect of small changes in stoichiometry on electrical and physical properties, the present investigation was undertaken to develop a simple, rapid, accurate and precise method for determining lead in mixtures of lead, titanium and zirconium precipitates used for the manufacture of ceramic transducers and in the solutions used in the production of mixed precipitates.

At the beginning of this project the lead determination was carried out by the usual gravimetric sulphate method (2). The results showed, however, that the precipitation was incomplete. It was possible to compensate for this loss, but the overall procedure could not be modified to provide the extremely high precision necessary to establish the exact stoichiometry of the sample materials submitted.

It is known that lead can be determined accurately and precisely by titration with ethylenediaminetetraacetic acid (EDTA) (3). Because EDTA forms complexes with titanium and zirconium, as well as with a large number of elements commonly occurring in minerals or metallurgical products, such as copper, zinc, calcium and magnesium, prior isolation of the lead is a necessity. If the lead is separated as lead sulphate prior to titration with EDTA, the result is subject to negative error because of solubility losses. On the other hand, elements that are co-precipitated and are also titrated by EDTA will lead to positive errors.

Diethyldithiocarbamate has been used for the extraction of many metals as the complex diethyldithiocarbamates, using ethyl acetate, chloroform, carbon tetrachloride, and other solvents (4). Kinnunen and Wennerstrand have utilized this behaviour for the determination of lead in materials such as brass, bronze, zinc ores and lead concentrates (5), extracting the lead with diethyldithiocarbamate from an ammoniacal-tartrate-cyanide solution and using Eriochrome Black T as the indicator for the EDTA titration. They reported no detailed study of interfering elements but mentioned that manganese and bismuth would interfere. They minimized this interference of manganese by addition of potassium cyanide prior to the titration of the lead with EDTA. To minimize interference from bismuth, they extracted the lead from a sodium hydroxide-tartrate-cyanide solution rather than from an ammoniacal solution.

It was considered that a similar approach could be adapted to the determination of lead in mixtures of lead, titanium and zirconium hydrous

oxide precipitates, and in solutions of these metals. Accordingly, experimental studies were undertaken to establish the effect on the method of titanium and zirconium and other elements that might be present as impurities in the raw materials used.

This report describes the successful application of a modification of Kinnunen and Wennerstrand's procedure to the determination of lead in mixtures and solutions of lead, titanium and zirconium precipitates used for the manufacture of ceramic transducers. The method was extended to include the analysis of complex copper-lead-zinc concentrates, galena, and sphalerite.

A procedure is also described for the successive determination of bismuth and lead after their extraction as the complex diethyldithiocarbamates. This procedure may find application in the analysis of lead-bismuth-titanium-zirconium ceramic materials and also of other bismuth-bearing materials.

APPARATUS AND REAGENTS

Apparatus

Separatory funnels, Squibb type, 125 or 250 ml, Teflon stopcock.
pH meter or narrow range pH papers.

Reagents

Ethylenediaminetetraacetic acid, disodium salt (EDTA). Prepare a 0.01M solution by dissolving 3.722 grams of the dihydrate salt in one litre of water. Standardize this solution against a pure lead solution prepared from 99.99 per cent pure lead metal.

Potassium cyanide, reagent grade -- 20 per cent aqueous solution.

Sodium acetate buffer solution, pH 6. Adjust a 0.2 M sodium acetate solution to pH 6 with 0.2 M acetic acid.

Sodium diethyldithiocarbamate. Prepare a 2 per cent aqueous solution fresh every two days and filter before use. Make the solution slightly alkaline with ammonium hydroxide to help stabilize it.

Sodium potassium tartrate (Rochelle salt), reagent grade--20 per cent aqueous solution. (NOTE: Sodium or ammonium tartrate or citrate may be used instead of Rochelle salt.)

Xylenol Orange--0.1 per cent aqueous solution.

EXPERIMENTAL PROCEDURE

The procedure finally adopted was as follows:

1. Lead-Titanium-Zirconium Compounds

A. Solid Samples

Transfer a weighed sample, containing 100 to 200 mg of lead (Note 1), to a beaker, and add about 5 ml of concentrated sulphuric acid. Digest at fuming temperature for 5 minutes to ensure the dissolution of titanium and zirconium oxides. Cool, dilute with about 20 ml of water, and add 4 to 5 grams of solid tartaric acid. Neutralize the solution by the addition of concentrated ammonium hydroxide until a flocculent precipitate of lead tartrate appears (Note 2). Then add 10 ml in excess, all at once, to dissolve the precipitate. If a slight residue remains, allow the solution to stand for about 1 hour, after which time the precipitate should have dissolved.

Transfer the solution quantitatively to a 125 or 250 ml separatory funnel (Note 3), and add sufficient 2 per cent diethyldithiocarbamate solution to precipitate all the lead (usually 20 ml is sufficient for 100 to 200 mg Pb). Extract the lead by shaking vigorously for 1/2 to 1 minute with 10 to 15 ml of chloroform. Allow the two phases to separate and carefully drain the chloroform phase into a clean 250 ml beaker. Add a few ml of diethyldithiocarbamate solution to the aqueous phase remaining in the separatory funnel, to make sure all the lead has been precipitated. If not, add more diethyldithiocarbamate as required. Extract the solution again with three 5 to 10 ml portions of chloroform to ensure the complete extraction of lead. Combine

---

Note 1. The requirements of high accuracy and precision make it desirable to take as large an amount of lead as is practical.

Note 2. This step is an important part of the procedure and should be done carefully. If the pH is allowed to exceed 4, a non-flocculent precipitate of lead tartrate forms which is very difficult to dissolve with the excess ammonium hydroxide that is added in the next step. In the event that a non-flocculent precipitate is produced, add dilute nitric acid until a flocculent precipitate appears and then add the excess ammonium hydroxide all at once. If the difficulty is not cleared up by the foregoing treatment it may be necessary to start with another sample or aliquot.

Note 3. If potentially interfering elements, such as copper, nickel, etc., are expected to be present, add 10 ml or more of 20 per cent potassium cyanide solution to the sample in the separatory funnel before adding the diethyldithiocarbamate solution.

the chloroform extracts. Add 5 to 10 ml of 8 M nitric acid to the chloroform extract, and remove the chloroform carefully by evaporation at low heat on a hot plate. Evaporate the solution to dryness to remove the nitric acid. Add a few drops of perchloric acid and nitric acid and fume to dryness.

Add 5 to 10 grams of solid ammonium chloride and 75 to 100 ml of water and heat to dissolve the lead residue. When the solution is clear, add 30 ml of sodium acetate buffer (pH 6) solution, cool to room temperature and then, using a pH meter, adjust the acidity to pH 5.8 to 6.0, if necessary, with either hydrochloric acid or ammonium hydroxide. Add several drops of Xylenol Orange indicator solution and titrate the solution with 0.01 M EDTA solution. Near the end-point check the pH, re-adjust it if necessary to the range 5.0 - 5.5, and complete the titration. Calculate the percentage of lead.

B. Solutions

Transfer an aliquot containing 100 to 200 mg of lead to a 125 or 250 ml separatory funnel, add 10 ml of 20 per cent sodium potassium tartrate solution, and add 10 ml of concentrated ammonium hydroxide in excess of that required to neutralize the solution. Follow the extraction procedure outlined in A, starting at the point where diethyldithiocarbamate is added.

2. Lead Ores, Concentrates and Minerals

Weigh a sample containing 5 to 200 mg of Pb and transfer it to a 250 ml beaker. Add 15 ml of concentrated hydrochloric acid, cover with a watch glass, and boil for a few minutes to dissolve any lead sulphide and expel hydrogen sulphide. Add 10 ml of concentrated nitric acid and continue to boil until the volume of the solution has been reduced to about 5 or 10 ml. Cool, add 20 ml of 9 M sulphuric acid, and evaporate to fumes of sulphur trioxide. If much silica is present, add 2 to 3 ml of concentrated hydrofluoric acid before evaporating to fumes of sulphur trioxide. If tin, arsenic, and antimony are present, they can be removed at this point by volatilization as bromides with hydrobromic and hydrochloric acids. Repeat this treatment, if necessary, to ensure complete removal of tin, etc., then cool, wash down the sides of the beaker with water, and evaporate to fumes of sulphur trioxide again. Continue the fuming for about 10 minutes. Cool, add 25 to 30 ml of water, and heat to dissolve the soluble salts. Add 10 to 30 ml of 20 per cent Rochelle salt solution, depending on the iron content of the sample; neutralize the solution with concentrated ammonium hydroxide, and then add 10 ml in excess. Transfer the solution to a 125 or 250 ml separatory funnel, add 10 to 30 ml of 20 per cent potassium cyanide solution, depending on the amount of copper, zinc, and similar interfering elements present, and allow to stand for 5 minutes or longer. Add 10 to 20 ml of 2 per cent diethyldithiocarbamate solution to precipitate the lead, and proceed with the extraction and determination of lead

as described previously for the lead-titanium-zirconium samples. With samples containing less than 10 mg of lead, greater accuracy is possible by titrating with 0.001 M EDTA solution. If large amounts of metals such as cadmium, copper, zinc, cobalt and nickel are present, better precision and accuracy will be obtained if the chloroform-diethyldithiocarbamate phase is backwashed with an ammoniacal-tartrate-cyanide solution similar in composition to that from which the lead was extracted initially.

PRELIMINARY INVESTIGATIONS

Determination of Lead in Synthetic Solutions Containing Titanium and Zirconium

Initial experiments on synthetic solutions containing titanium and zirconium were carried out, using the original Kinnunen and Wennerstrand procedure (3, 5). The results obtained are given in Table 1. The end-point of the titration was not sharp, and it is believed that this, rather than losses in extraction, is the greatest factor contributing to the erratic lead values obtained. The poor end-point observed is probably due to the presence of decomposition products of the diethyldithiocarbamate, which either mask the colour change or react with the indicator.

TABLE 1

Determination of Lead in Synthetic Solutions Containing Titanium and Zirconium, using the Kinnunen-Wennerstrand Procedure Employing Eriochrome Black T Indicator

Metals Taken			Lead Found
Lead (mg)	Titanium (mg)	Zirconium (mg)	(mg)
4.98	10	10	5.17, 5.12
9.97	10	10	8.50, 9.97
14.95	10	10	14.10,14.48

Because of this difficulty, the indicator-buffer system, Xylenol Orange-sodium acetate, suggested by Korbl and Pribil (6) was substituted for the Eriochrome Black T of the original procedure, and the following changes were made in the procedure:

1. The diethyldithiocarbamate associated with the lead in the extract was completely destroyed, using nitric and hydrochloric acids, to ensure that it would not interfere with the end-point.

2. Ammonium chloride was used to dissolve the lead residue remaining after the destruction of the diethyldithiocarbamate because amounts greater than 20 mg of lead could not be completely dissolved using the sodium acetate solution alone.

3. The amount of potassium cyanide used in the extraction step was reduced, since only negligible amounts of copper, zinc, etc., were expected to be present.

The results obtained in a series of tests using this modified procedure are given in Table 2, experiments 1 to 7. The end-point in these tests was much sharper and easier to detect than in the original procedure using Eriochrome Black T. The recoveries, however, were low, and this was attributed to the lack of sufficient tartrate to dissolve completely the lead, titanium, and zirconium. Accordingly, another series of tests, in which the amount of tartrate solution was increased from 5 ml of 20 per cent Rochelle salt solution to 10 ml or 20 ml, was carried out. The results of these tests (Table 2), experiments 9 to 17, show that the recovery of lead was quantitative, that the precision was excellent, and that addition of cyanide is unnecessary when only titanium and zirconium are present.

Attempts to determine lead using this modified procedure without completely destroying the diethyldithiocarbamate were unsuccessful. Neutralization of the excess nitric acid with ammonium hydroxide after removal of the chloroform did not eliminate the decomposition products that interfered with the detection of the end-point. On the other hand, complete destruction of the diethyldithiocarbamate by evaporation with nitric acid, followed by treatment of the residue with a few drops of perchloric acid, or by repeated evaporations with nitric or hydrochloric acids, resulted in an extremely sharp, precise colour change.

TABLE 2

Determination of Lead in Synthetic Solutions
Containing Titanium and Zirconium

No.	Metals Taken			Amount of KCN Solution Used, ml	Amount of Rochelle Salt Solution Used, ml	Extracted	Lead Found (mg)
	Lead (mg)	Titanium (mg)	Zirconium (mg)				
1.	19.93	10	10	10	5	Yes	19.91, 19.85
2.	29.90	10	10	10	5	"	29.71, 29.91
3.	9.97	20	20	10	5	"	8.91, 9.28
4.	19.93	20	20	10	5	"	19.80, 19.80, 19.60
5.	24.92	20	20	10	5	"	24.34, 24.55
6.	39.86	20	20	10	5	"	39.82, 38.16, 38.17
7.	49.83	20	20	10	5	"	49.31
8.	24.92	--	--	--	--	No	24.92
9.	24.92	--	--	10	10	Yes	24.92
10.	24.92	20	20	10	10	"	24.86, 24.96
11.	49.83	--	--	10	10	"	49.92
12.	49.83	20	20	10	10	"	49.92, 49.88
13.	24.92	20	20	--	10	"	24.88
14.	49.83	20	20	--	10	"	49.76
15.	124.6	60	60	--	10	"	124.7, 125.5
16.	503.8	100	125	10	20	"	503.5, 503.7
17.	503.8	200	250	10	20	"	503.9, 503.7

Effect of Ammonium Chloride, and of Variations in pH, in the Acetate Buffer Solution

Because it was found necessary to use ammonium chloride to dissolve the residue of lead remaining from the chloroform extract, it was decided to test the possibility that the ammonium chloride might itself be effective as a buffer without the necessity of adding sodium acetate. Experiments were therefore carried to determine the effect of ammonium chloride and of variations in pH in the acetate buffer solution on the determination of lead, particularly with reference to the ease of recognition and sharpness of the end-point. The results of these experiments are given in Table 3.

TABLE 3

Effect of Ammonium Chloride, and of Variations in pH, in Acetate Buffer Solution

(Lead taken, 50.32 mg; volume of solution titrated, 100 ml)

Test No.	Acetate Buffer (pH 6) (ml)	Ammonium Chloride (g)	Initial pH	Final pH	Volume EDTA (ml)	End-point Comments
1	30	Nil	4.00	3.75	24.0 - 24.2	Indistinct
2	"	"	4.50	4.32	24.18	Sharp
3	"	"	5.00	4.90	24.18	"
4	"	"	5 50	5.26	24.19	Very sharp
5	"	"	6.00	5.50	24.20	" "
6	"	"	ca 6	6.00*	24.18	Sharp
7	"	"	ca 6	6.60*	24.19	Not sharp
8	"	"	6.50**	5.62	24.16	Sharp
9	"	"	7.00**	5.72	24.12	"
10	"	"	7.50**	5.72	24.18	"
11	"	5	4.00	3.90	23 - 24	Indistinct
12	"	"	6.00	4.60*	24.18	Sharp
13	"	"	5.00	4.90	24.18	Very sharp
14	"	"	6.00	5.40	24.18	" "
15	"	"	ca 6	5.80*	24.18	Sharp
16	"	"	7.00**	6.10	24.1 - 24.2	Not sharp
17	Nil	"	6.5	5.30*	24.18	Very sharp
18	"	10	6.5	5.40*	24.18	" "
19	"	5	5.9	6.20*	-	Indistinct

* The final pH was adjusted to this value just prior to the end-point of the titration.

** A precipitate appears in the solution at this pH

Determination of Lead in Synthetic Solutions Containing No Other Metal Ions

Experiments were carried out with pure lead nitrate solutions to establish the range over which lead could be determined precisely and accurately. In these experiments, aliquots of a standard lead solution were taken, the lead was determined by direct titration with EDTA in acetate solution buffered to pH 5.0 - 5.5, and the results were compared with those that were obtained by taking identical aliquots of lead solution and extracting the lead with diethyldithiocarbamate by the proposed procedure. Cyanide was added to the solutions used in these extractions, since it would be present in a general procedure if metals such as copper, nickel, zinc, etc., were present. The results of these experiments are given in Table 4.

TABLE 4

Determination of Lead in Synthetic Solutions Containing No Other Metal Ions

Pb Taken (mg)	Pb Found (mg)	
	Not Extracted	Extracted
0.051	0.052*	0.052*
0.102	0.104*	0.114, 0.110*
0.204	0.204*	
0.511	0.512*	0.520, 0.512*
1.022	1.024*	1.024, 1.022*
10.22	10.22 **	10.24, 10.22 **
51.12	51.11 **	51.11, 51.09 **
102.23	102.22 **	102.22, 102.24**
204.46	204.44 **	204.34, 204.34**

* Titrated with 0.001 M EDTA.
** Titrated with 0.01 M EDTA.

Standard Deviation and Confidence Limits of the Method

Twenty-four identical aliquots, each containing approximately 100 mg of lead, taken from a solution of lead nitrate were analysed for lead. Twelve of these aliquots were extracted and the lead determined by the proposed procedure. In these extractions, potassium cyanide solution was added for reasons previously given. As a basis for comparison, the lead in the remaining twelve aliquots was titrated directed with EDTA without being extracted. The results of these experiments are given in Table 5.

TABLE 5

Precision of the Lead Determination

	mg Pb Found	Standard Deviation, mg Pb
Extracted	102.33, 102.18, 102.22, 102.22, 102.18, 102.22, 102.26, 102.22, 102.24, 102.22, 102.24, 102.22.	$s = \pm 0.0386$
Not Extracted	102.22, 102.22, 102.26, 102.22, 102.22, 102 24, 102.22, 102.26, 102.22, 102.22, 102.22, 102.22.	$s = \pm 0.0167$

Effect of Diverse Ions

Copper, nickel, zinc, cadmium, titanium, zirconium and iron are among the many elements that are also precipitated by diethyldithiocarbamate in either acid or basic solution. In addition, such elements as magnesium, aluminum, iron, titanium and zirconium will be precipitated together with the lead, by the addition of ammonium hydroxide to a solution containing these elements, unless a complexing reagent is present. Some degree of selectivity in the precipitation and extraction of lead may be attained by using either tartrate or citrate and/or cyanide as complexing reagents and by adjustments in the pH of the solution (4). Oxalate cannot be used as a complexing reagent because it would precipitate calcium, magnesium, lead and several other elements in a basic solution.

Tartrate or citrate can be added to prevent the precipitation of hydrous oxides of lead, iron, titanium, zirconium, aluminum, magnesium, strontium, calcium, bismuth, antimony, tin, chromium, thorium, uranium and cerium

in alkaline solution and, in addition, to prevent the formation of insoluble salts of lead with molybdate, tungstate, vanadate, arsenate, and chromate. The alkaline tartrate solution, however, does not prevent the precipitation of copper, nickel, cobalt, zinc and cadmium with diethyldithiocarbamate, and these elements would be extracted and interfere with the determination of lead. This can be prevented by the addition of cyanide to complex them

The solution can then be made strongly basic (pH 10-11) by the addition of an excess of ammonium or sodium hydroxide. Under these conditions lead is extractable and there are relatively few interferences.

Several series of tests were next undertaken to evaluate the effectiveness of the steps proposed above for the elimination of the interference of the various elements.

The first series of tests was carried out to determine the effect of several of the impurities that might be encountered in the materials used in the preparation of the lead-titanium-zirconium mixed precipitates. The amount of impurity added was about 100 times that which was likely to be present in the samples to be analysed, so that any significant interference would be immediately apparent. No cyanide was added except where noted. The results are given in Table 6.

In addition, the possible interference from varying amounts of other ions commonly present in lead ores, and in galena and sphalerite, was investigated separately on test solutions containing 5 or 50 mg of lead. In these tests cyanide was added to solutions containing elements, such as calcium, magnesium, aluminum and uranium, even though these elements do not form cyanide complexes, because cyanide would be included as part of a general procedure in the analysis of complex ores. Ascorbic acid was added to one of the manganese test solutions to see whether it might be effective in preventing the extraction of manganese. In the tests conducted at the 5 mg level of lead, no ammonium chloride was added to dissolve the lead residue remaining after destruction of the organic extract, because the amount of lead residue was relatively small and it dissolved readily in the acetate buffer solution. The results of these tests are given in Tables 7, 8 and 9. The criterion used to decide if an element interfered was whether or not recovery of the lead at the 50 mg level was within $\pm$ 0.1 mg of the amount taken.

In other attempts to prevent the extraction and interference of bismuth, antimony, tin, manganese, magnesium, and phosphate, a series of tests was carried out in which 3 g of EDTA (disodium salt) was added to the solution of the metals prior to the addition of the tartrate, ammonia and cyanide. Possible interference due to barium was also checked. The results of these tests are given in Table 10.

Kinnunen and Winnerstrand (5) state that the extraction of bismuth is negligible from a sodium hydroxide-tartrate-cyanide solution. Accordingly, a series of tests was carried out in this medium to determine whether the extraction of bismuth, tin, antimony, manganese, barium, and phosphate could be prevented. In these tests, 5 ml of 50 per cent sodium hydroxide solution was substituted for the 10 ml of concentrated ammonium hydroxide used in the regular extraction procedure. The results of these tests are given in Table 11.

TABLE 6

Determination of Lead in Synthetic Solutions Containing Foreign Elements

(Lead taken, 50.42 mg)

Foreign Metal Present (mg)	Amount of 20% KCN Solution Used (ml)	Lead Found (mg)
None	0	50.42, 50.42
10 Al^{+3}	0	50.46
4 Ca^{+2}	0	50.42
28 Ce^{+4}	0	50.44
4 Fe^{+3}	0	50.42
42 Fe^{+3}	10	50.42
6 Mg^{+2}	0	50.32
5 Cu^{+2}	0	Interference is stoichiometric
10 Cu^{+2}	10	50.42
5 Zn^{+2}	0	Interference is stoichiometric
10 Zn^{+2}	10	50.45
10 Bi^{+3}	10	Interferes, indistinct end-point
10 Sn^{+2}	10	Interferes, indistinct end-point

TABLE 7

Effect of Diverse Ions on the Determination of Lead by the Proposed Method

(Lead taken, 5.032 mg)

Taken (mg)	Amount of 20% KCN Solution Used (ml)	Lead Found* (mg)	
		Procedure A**	Procedure B***
125 Cu^{+2}	30	5.249	5.042
125 Ni^{+2}	30	5.042	5.040
125 Co^{+2}	30	5.228	5.032
125 Zn^{+2}	30	5.166	5.022
250 Fe^{+3}	30	5.166	5.034
56 Cd^{+2}	30	5.373	5.042

* Titrated with 0.001 M EDTA solution

** Procedure A: The lead was extracted without a backwashing step.

*** Procedure B: The lead was extracted and the chloroform phase was backwashed once with a mixture of 20 ml of 20 per cent Rochelle salt solution, 20 ml of 20 per cent potassium cyanide solution and 10 ml of concentrated ammonium hydroxide. The aqueous phase was then washed twice with 5-10 ml portions of chloroform. The chloroform extracts were combined.

TABLE 8

A. Extraction as Diethyldithiocarbamates from Ammonium Hydroxide-Tartrate-Cyanide Medium

(30 ml 20% KCN present)
(Titration with 0.01 M EDTA)

I. Non-Interfering Elements

	Elements that do not Interfere with the Determination of Lead (10-100 mg Element; 50 mg Lead)
Cations	Ag^{+}, Al^{+3}, As^{+3}, As^{+5}, Ba^{+2}, Ca^{+2}, Ce^{+4}, Co^{+2}, Cr^{+3}, Cr^{+6}, Cu^{+2}, Fe^{+3}, Hg^{+2}, Mo^{+6}, Ni^{+2}, Sr^{+2}, Th^{+4}, Ti^{+4}, V^{+5}, W^{+6}, Zn^{+2}, Zr^{+4}.
Anions	F^{-} Br^{-} (as HBr, up to 5 ml of concentrated acid)

TABLE 9

A. Extraction as Diethyldithiocarbamates from Ammonium Hydroxide-Tartrate-Cyanide Medium

(Titration with 0.01 M EDTA)

II. Interfering Elements

Taken (mg)	Amount of 20% KCN Solution Used (ml)	Lead Taken (mg)	Lead Found (mg)
11 Bi^{+3}	10	50.42	Interferes
22 Cd^{+2}	10	50.42	51.72
56 Cd^{+2}	30	50.42	50.59
56 Cd^{+2}	50	50.32	50.40
56 Cd^{+2}	50	50.32	50.36
56 Cd^{+2}	50	50.32	50.32*
12 Mg^{+2}	10	50.42	50.42
125 Mg^{+2}	30	50.42	50.21
125 Mg^{+2}	30	50.32	45.78
20 Mn^{+2}	10	50.42	50.28
125 Mn^{+2}	30	50.42	Interferes
100 Mn^{+2}	30	51.06	51.25**
10 PO_4^{-3}	10	51.06	51.01
100 PO_4^{-3}	30	50.32	Interferes
13 Sb^{+3}	10	50.42	50.45
30 Sb^{+3}	30	50.42	50.35
100 Sb^{+5}	30	50.32	Interferes
100 Sb^{+5}	30	50.32	50.22***
10 Sn^{+4}	10	50.42	Interferes
10 U^{+6}	10	50.42	50.24
50 U^{+6}	30	50.42	50.00

* Chloroform phase backwashed once with NH_4OH - Tartrate-Cyanide Solution.

** About 1 gram of ascorbic acid was added to the solution before adding the diethyldithiocarbamate.

*** Sb volatilized with HBr + HCl treatment after extraction of Sb and Pb.

TABLE 10

B. Extraction of Diethyldithiocarbamates from EDTA-Ammonium Hydroxide-Tartrate-Cyanide Medium

(Titration with 0.01 M EDTA)

Taken (mg)	Amount of 20% KCN Solution Used (ml)	Lead Taken (mg)	Lead Found (mg)
100 Ba^{+2}	30	50.32	18.73
100 Bi^{+3}	30	50.32	Interferes
125 Mg^{+2}	30	50.32	50.34
100 Mn^{+2}	30	51.06	29.30, 36.03
100 PO_4^{-3}	30	50.32	16.01, 23.31
100 Sb^{+5}	30	50.32	8.95
100 Sn^{+4}	30	50.32	Interferes

TABLE 11

C. Extraction of Diethyldithiocarbamates from Sodium Hydroxide-Tartrate-Cyanide Medium

(Titration with 0.01 M EDTA)

Taken (mg)	Amount of 20% KCN Solution Used (ml)	Lead Taken (mg)	Lead Found (mg)
50 Ba^{+2}	10	51.06	51.05
100 Bi^{+3}	30	50.32	Interferes
100 Mn^{+2}	30	51.06	51.12
100 Mn^{+2}	30	51.06	51.00*
10 PO_4^{-3}	10	51.06	51.17
100 PO_4^{-3}	10	51.06	51.01
100 Sb^{+5}	30	50.32	50.34
100 Sn^{+4}	30	50.32	50.38

* About 1 gram of ascorbic acid was added to the solution before adding the diethyldithiocarbamate.

The interference due to bismuth which was noted in this test was entirely unexpected, in view of the statement of Kinnunen and Wennerstrand that bismuth would not extract under these conditions. Because it is possible to titrate bismuth and lead successively in the same solution with EDTA by making suitable pH adjustments, the possibility of determining both these elements in a single aliquot of the sample suggested itself. Accordingly, tests were carried out to establish whether or not bismuth could be quantitatively extracted from a sodium hydroxide-tartrate-cyanide medium. The procedure used was identical with that used for the simultaneous determination of bismuth and lead (see below), except that 5 ml of 50 per cent sodium hydroxide was substituted for the ammonium hydroxide in the extraction step, and no ammonium chloride was used to dissolve the residue remaining after the destruction of the diethyldithiocarbamate, since lead was absent. The bismuth was titrated with standard EDTA solution at pH 2.0. The results of these tests are given in Table 12.

TABLE 12

Extraction and Recovery of Bismuth from Sodium Hydroxide-Tartrate-Cyanide Medium

Bi Taken, mg	Bi Found, mg
1.012	1.008
10.12	10.04
101.2	101.2

DETERMINATION OF BISMUTH AND LEAD

Since, as has just been shown, extraction of both lead and bismuth from alkaline tartrate-cyanide medium is quantitative, it was decided to establish whether the two elements could be determined in the same solution from the same extraction. The advantage to be gained thereby is that it would then be unnecessary to remove the bismuth by hydrolysis as bismuth oxychloride after it has been extracted, along with the lead, using diethyldithiocarbamate.

Korbl and Pribil (6) state that bismuth and lead may be titrated successively with EDTA and Xylenol Orange indicator in a single sample solution by appropriate pH adjustments. Thus, it should be possible to titrate bismuth at pH 1 to 3 and lead at pH 5 to 6. Experiments were therefore carried out to confirm that bismuth could be quantitatively extracted together with lead and that these elements could be titrated successively with EDTA.

The procedure finally adopted is as follows:

Extract the bismuth and lead from an ammoniacal-tartrate-cyanide solution as directed for the analysis of lead ores. To the residue remaining after the destruction of the diethyldithiocarbamate extract, add about 20 ml of water, 5 g of solid ammonium chloride and 10 ml of 20 per cent Rochelle salt solution, and warm to dissolve the residue completely. Cool the solution to room temperature, dilute to 100 to 125 ml, and adjust the pH to 2.0 ± 0.5 with dilute nitric acid or ammonium chloride. Add a few drops of Xylenol Orange indicator solution and titrate the bismuth with standard EDTA solution. Near the end-point, adjust the pH again to 2.0 and finish the bismuth titration. Now add 30 ml of acetate buffer solution, pH 6, adjust the pH to 5.8 to 6.0, and titrate the lead with the standard EDTA solution. Calculate the bismuth and lead contents from the respective volumes of EDTA solution used.

The results of these experiments are given in Table 13. The table also includes, for comparison, the results obtained on similar solutions, containing bismuth and lead, which were not subjected to the extraction procedure.

TABLE 13

Determination of Bismuth and Lead

Solution	Metal Taken (mg)	Metal Found (mg)	
		Not Extracted	Extracted
1	Bi 101.22	101.22	101.34
	Pb 102.23	102.30	102.01
2	Bi 5.06	5.04	5.04
	Pb 102.23	102.22	102.22
3	Bi 101.22	101.11	101.22
	5.11	5.16	5.12

ANALYSES OF SAMPLES

To determine the accuracy of the proposed extraction -EDTA method, it was applied to a number of solutions and solid samples of lead-titanium-zirconium compounds and the results obtained were compared with values determined gravimetrically using the conventional lead sulphate procedure (2). These results are given in Table 14.

The method was also employed for the determination of lead in galena, in sphalerite, in lead ores, and in lead-copper-zinc concentrates. These results are given in Table 15.

TABLE 14

Determination of Lead in Mill Products--Comparison of Gravimetric and Extraction-EDTA Results

Sample	Other Constituents Present			Lead Found		
				Gravimetric-Method*		Extraction EDTA Method
	Ti (g/l)	ZrO_2 (g/l)	NO_3 (g/l)	A	B	
Solutions				g/l	g/l	g/l
2120	Pure $Pb(NO_3)_2$ solution			276.9, 277.9 276.9, 276.6		283.4, 284.0, 283.4
2120						283.2**
1931	1.77	4.67	32.3	16.50, 16.52		16.50, 16.51
1932	2.00	5.07	44.3	17.64, 17.64, 17.72, 17.68		18.03, 18.02
1933	1.90	5.71	50.0	17.88, 18.03, 18.28, 17.94		17.80, --
1934	1.90	6.15	49.7	18.29, 18.29		18.56, 18.59
1935	1.48	5.42	33.3	15.53, 15.44		15.74, 15.72
1936	1.24	5.38	31.0	14.44, 14.56		14.59, 14.58
1937	0.90	5.67	30.3	13.97, 13.95		14.16, 14.20
1938	1.91	1.35	26.0	8.10, 8.21		8.24, 8.24
2453	1.58	5.06	--		15.46, 15.54, 15.50	15.42, 15.44
2454	1.36	5.24	--		14.71, 14.56	14.72, 14.73
2455	1.16	5.55	--		14.11, 14.08	14.16, 14.16
2456	0.95	5.47	--		13.05, 13.06	13.11, 13.08, 13.05
2703	0.93	2.56	36.0		8.34, 8.36	8.36, 8.37
Solid Samples				%		%
2121	6.14	17.0	0.53	58.54, 58.38		59.05, 58.91, 58.91
2667	6.21	15.9	0.03	53.46, 53.46		53.59, 53.65, 53.56

NOTE:

*Gravimetric Method A consisted simply of precipitating the lead and weighing it as lead sulphate. Gravimetric Method B consisted of precipitating the lead, weighing it as lead sulphate, and, in addition, recovering the minute amount of lead in the filtrate electrolytically as PbO_2.

**The lead was determined by direct titration without extraction.

TABLE 15

Determination of Lead in Mill Products:
Comparison of Extraction-EDTA Method with Other Methods

Sample	Volumetric * $PbSO_4$/ $K_2Cr_2O_7$ (% Pb)	Polarographic Method ** (% Pb)		Extraction-EDTA Method (%Pb)
		A	B	
Galena	80.85, 80.38, 80.62	-	-	80.97, 80.95
Sphalerite	19.76, 19.83	-	-	19.87, 19.72
Copper-Lead-Zinc Concentrate	3.32, 3.32, 3.28	-	-	3.41, 3.39
Lead Ore	2.63, 2.66	2.69, 2.68	2.63, 2.67	2.77, 2.74

* Lead was separated as lead sulphate and determined volumetrically by the chromate method (see reference 2).

** Polarographic method A: The lead was separated as lead sulphate and dissolved in an ammonium acetate electrolyte.

Polarographic method B: The lead was separated as lead sulphate and dissolved in a hydroxylamine hydrochloride-potassium chloride electrolyte.

DISCUSSION

Effect on the End-Point Due to Ammonium Chloride and pH Variations in Acetate Buffer Solutions

The comments on the nature of the end-point, given in Table 3 and amplified below, are, of course, inherently subjective in nature and merely reflect the opinion of the observer. This difficulty has been discussed by Flaschka and Barnard (7).

At pH values less than 4 and greater than 6, the end-point of the titration is indistinct. The colour change is most distinct in a final pH range of 5.0 to 5.5, but the end-point is easily detected over a range of pH from 4.6 to 5.8. In acetate medium a precipitate appears in the solution at a pH above 6.3, but if ammonium chloride is also present the precipitate does not appear until the pH is 6.8 or greater. This precipitate dissolves on the addition of EDTA, and the end-point is sharp if the pH at the end-point is less than 5.8 and greater than 4.6. In the presence of ammonium chloride, however, and at initial pH values above 7, the precipitate dissolves but slowly and the titration is prolonged. The precipitate dissolves readily enough on warming the solution, but because the final pH is greater than 6 the end-point is not sharp.

Hydrogen ions are liberated during the course of the titration, and the magnitude of the decrease in pH is dependent on the amount of lead titrated and the amount of buffer solution used. With large amounts of lead, i.e. 50 to 200 mg, a change in pH of 0.5 to 1 unit can occur under the conditions used in the procedure. In order to ensure that the end-point is observed in the pH range necessary for the sharpest colour change, it is recommended that for the titration of less than 50 mg of lead the initial pH of the solution should be adjusted to between 5.8 and 6.0. When amounts of lead in excess of 50 mg are titrated, it is necessary to readjust the pH of the solution to the proper range shortly before the end-point is reached.

The results also show that lead can be titrated precisely in a solution containing only ammonium chloride. The end-point of the titration in the pH range of 5.0 to 5.5 is very sharp. However, the buffering capacity of a solution having a concentration of 5 to 10 g of ammonium chloride per 100 ml is insufficient to cope with the hydrogen ions liberated during the titration. Frequent readjustment of the pH is necessary, particularly when approaching the end point. The addition of sodium acetate is therefore recommended, since it provides the necessary buffering capacity.

Determination of Lead in Synthetic Solutions Containing No Other Metal Ions

The results in Table 4 show that lead can be quantitatively extracted with diethyldithiocarbamate and determined precisely and accuractely by titration with EDTA over a range from 0.05 to 200 mg of lead, and the results of experiments 16 and 17, given in Table 2, show that the range may in fact be extended up to at least 500 mg of lead without loss of accuracy and precision. In the range of 1 to 200 mg of lead, the precision and accuracy is 1 part per thousand, which is the precision desired for the determination of lead in the lead-titanium-zirconium compounds. With amounts of lead less than 1 mg, the precision is not so great but it is still adequate for most purposes.

Standard Deviation and Confidence Limits of the Method

From the data given in Table 5, the standard deviation and confidence limits of the method may be calculated. The standard deviation has been calculated, using the equation

$$s = \sqrt{\frac{\Sigma d^2}{n-1}}$$

where d = the individual deviation of each value from the mean, and n = the number of values. The results given in Table 5 show that for the unextracted set of samples s = 0.0167, and for the extracted set of samples s=0.0386. The difference between these values reflects the error to be expected as a result of the extraction step in the procedure, while the second value is an indication of the overall error of the method.

The 99 per cent confidence limits for the mean value (8) of the 12 observations can be expressed as $\pm$ (0.936)(0.0386) = $\pm$ 0.036 mg of lead. A calculation of the combined uncertainty resulting from the errors in reading the burette during (a) the standardization of the titrant and (b) the titration of the sample, indicates that it is sufficient to account for almost all the error in the overall method.

The colour change of the Xylenol Orange from red to yellow is extremely sharp and it is this property that contributes greatly to the high precision with which lead can be determined.

Diverse Ions

Table 6 shows that magnesium, calcium, iron, aluminum and cerium have no significant effect on the extraction and determination of lead at the levels of interference investigated. Copper and zinc are extracted quantitatively and interfere seriously. The addition of cyanide before extraction, however, complexes these elements and prevents their extraction and subsequent titration with EDTA.

Bismuth and tin are extracted together with the lead, even in the presence of cyanide. These elements are partly removed by hydrolysis in the sodium acetate buffer solution but, nevertheless, they interfere, causing an indistinct end-point with slow attainment of equilibrium. Bismuth can be completely eliminated as the oxychloride in a hydrochloric acid medium, or determined successively with the lead by proper adjustment of the pH conditions (see page 26). Tin can be removed by volatilization of its bromide with hydrobromic and hydrochloric acids.

The results given in Table 7, Procedure B, show that small amounts of lead can be extracted from moderate amounts of interfering metals such as copper, zinc, and nickel, and determined precisely, if the organic phase is backwashed with an ammoniacal-tartrate-cyanide solution. No significant amount of lead is lost in this operation. Failure to backwash the organic phase results in lead recovery values that are substantially too high (Procedure A).

The results given in Table 8 show that many elements do not interfere and can be tolerated in large amounts relative to lead. Excellent recoveries of lead at the 50 mg level were obtained. In addition to the fluoride and bromide anions mentioned, large amounts of nitrate, chloride, sulphate and perchlorate can be tolerated. These ions will result if the corresponding acid is used to dissolve the sample. If perchlorate is present, potassium salts (e.g., Rochelle salt) should not be used, in order to avoid the precipitation of potassium perchlorate. In this circumstance sodium tartrate or citrate may be substituted for the Rochelle salt.

The results given in Table 9 show the interference encountered when an ammoniacal-tartrate-cyanide medium was used. No backwashing of the chloroform phase was attempted, except with the one sample of cadmium as noted. Undoubtedly the inclusion of a backwashing step in the procedure would further improve the accuracy and precision, but for most purposes this additional step would be unnecessary.

The results show that the degree of interference of an element depends to some extent not only on the particular element in question, but also on the amount that is present. Thus, in an ammoniacal-tartrate-cyanide medium, a small quantity of manganese can apparently be tolerated but large amounts interfere seriously. The addition of ascorbic acid, however, prevents the air-oxidation of manganese and hence its subsequent extraction and interference with lead. A small amount of magnesium can be tolerated but the presence of large amounts lead to low recoveries of lead. Small amounts of phosphate do not seriously interfere but large amounts form a precipitate with lead that cannot be completely redissolved in the ammoniacal-tartrate-cyanide solution, at least under the conditions and at the level of phosphate investigated. Slightly low results were obtained in the presence of uranium[+6]. If insufficient cyanide is used, cadmium is partially extracted and interferes.

Increasing the amount of cyanide is of some help in reducing the interference of cadmium, but if the organic phase is backwashed with a fresh ammoniacal-tartrate-cyanide solution the cadmium is eliminated entirely. Bismuth, tin and antimony interfere at all concentrations but can be eliminated as discussed previously. Included in the table is the result of a test in which antimony was extracted with the lead and then, after destruction of the organic material, the antimony was volatilized as its bromide from a mixture of hydrobromic and hydrochloric acids. The recovery of lead in this case was satisfactory.

The results given in Table 10 show that the addition of EDTA to the solution prior to extraction prevented the interference of magnesium but not that of bismuth, antimony, tin, barium, manganese, and phosphate. Bismuth and tin were extracted with the lead. Very low recoveries of lead were obtained when barium, antimony, manganese and phosphate were present.

The results given in Table 11 show that interference from antimony, tin and manganese is prevented if the lead is extracted from a sodium hydroxide-tartrate-cyanide solution. The addition of ascorbic acid is not necessary to prevent the extraction and interference of manganese from this medium, as is the case when an ammoniacal solution is used. The manganous ion is very easily oxidized by air in an alkaline solution, and in an ammoniacal solution it forms, with diethyldithiocarbamate, a highly coloured purple complex (presumably manganic) that is soluble to some extent in chloroform. In a sodium hydroxide solution, on the other hand, a dark brown complex is formed that is not soluble in chloroform. The exact nature of these complexes is unknown but apparently the ammonia present in an ammoniacal solution forms part of the complex that is extractable with chloroform. The complex formed in a sodium hydroxide solution is not extractable.

In addition to the elimination of the above-mentioned elements, barium is not extracted from a sodium hydroxide-tartrate-cyanide medium. Furthermore, phosphate does not prevent the extraction of lead and thus larger amounts of this ion can be tolerated than when an ammoniacal-tartrate-cyanide solution is used. It was noted that bismuth is extracted from this medium, contrary to Kinnunen and Wennerstrand's observation. In the next section, the application of this observation to the development of a procedure for the successive determination of bismuth and lead is discussed.

Extraction and Recovery of Bismuth from Sodium Hydroxide-Tartrate-Cyanide Medium

The results given in Table 12 show that bismuth, in the range from 1 to 100 mg, is quantitatively extracted and recovered from a solution containing sodium hydroxide, tartrate and cyanide using diethyldithiocarbamate and chloroform. Bismuth would thus constitute a serious interference in the

determination of lead since its extraction from either an ammoniacal or a sodium hydroxide-tartrate-cyanide medium cannot be prevented.

The interference of bismuth can be overcome, however, by the procedure that is described for the successive determination of bismuth and lead after these elements have been extracted by diethyldithiocarbamate.

The Determination of Bismuth and Lead in a Single Sample

The results given in Table 13 show that it is possible to extract and determine bismuth and lead precisely and accurately by the proposed method if these metals are present in a single sample in the range of 5 to 100 mg of each metal. Amounts of metal outside this range were not investigated, but the other data presented in this report would indicate that smaller or greater amounts would be quantitatively extracted.

Since the bismuth must be determined first, the feasibility of a successful determination of bismuth and lead when present together depends on the ratio of these two metals. Thus the determination of a very small amount of bismuth, e.g. 0.1 mg or less, in the presence of 200 mg of lead would have a better chance of success than the inverse determination, since the bismuth could be titrated with dilute, i.e. 0.001 M, EDTA solution and the lead with a more concentrated, i.e. 0.02-0.05 M, EDTA solution. A small error in overshooting the end-point in the titration of bismuth would have a negligible effect on the determination of lead. If, on the other hand, bismuth predominates in the mixture, it may prove to be impossible to detect small amounts of lead, because a slight excess of the 0.02 M EDTA solution used to titrate the bismuth would combine with the small amount of lead present.

It should be noted, of course, that in this procedure any error in the determination of bismuth would be reflected in the determination of lead. If the bismuth end-point is overshot, the value obtained for lead will be low; and, conversely, high values for lead will be obtained if the bismuth end-point is undershot.

Tin and antimony, which will also be extracted if present, can be removed, after extraction, by volatilization as their bromides as mentioned previously. Other elements, except possibly manganese and phosphate, will not interfere. Alternatively, a sodium hydroxide-tartrate-cyanide medium can be utilized to avoid the interference of the above-mentioned elements.

It was found necessary to add both ammonium chloride and tartrate solution to the residue remaining after destruction of the diethyldithiocarbamate. The ammonium chloride was required for the dissolution of the lead, and the tartrate was necessary to prevent the hydrolysis and precipitation of the bismuth in the presence of the chloride during the pH adjustment.

Analysis of Samples

Table 14 shows that the results obtained by the proposed extraction-EDTA method are in excellent agreement with those obtained by a modified gravimetric lead sulphate method (Gravimetric Method B), in which the small amount of lead sulphate remaining in the filtrate after the lead sulphate separation was determined by electrolytic deposition as lead oxide. The results obtained by the conventional lead sulphate procedure (Gravimetric Method A) indicate the magnitude of error inherent in this method. Negative errors are associated with the solubility of lead sulphate in aqueous media, while positive errors are attributed to co-precipitation or hydrolytic deposition of the titanium and zirconium with the lead sulphate.

Table 15 shows that the proposed method is applicable to the determination of large and small amounts of lead in lead-bearing ores, concentrates and minerals. The slightly higher results by the extraction-EDTA method are attributed to more complete recovery of the lead, inasmuch as both the volumetric and polarographic methods utilize a preliminary separation of the lead as lead sulphate. It was also found that the values that were obtained using a hydrogen sulphide precipitation to isolate the lead prior to the extraction-EDTA method agreed very closely with the results obtained by using the extraction-EDTA method directly.

Smaller amounts of lead (less than 1 per cent) can be determined by simply taking a larger sample or by using a more dilute solution of EDTA for the titration. It is recommended that in either procedure the chloroform phase be backwashed with an ammoniacal-tartrate-cyanide solution to eliminate any gross contaminants and to improve the accuracy and precision.

CONCLUSIONS

The procedure presented in this report is applicable to the determination of from 0.05 to 500 mg of lead. It is a rapid, simple and precise method and the results are highly reproducible under routine conditions. The method is substantially more precise than the gravimetric procedure and is useful over a much greater range of concentration of lead. Elements that interfere are very few, and procedures are given to eliminate them if they should be present. A procedure is also given by which bismuth and lead may be determined simultaneously. This latter procedure would be extremely useful for the analysis of lead-bismuth-titanium-zirconium ceramic transducer material. In addition, the procedure should find application for the determination of bismuth in bismuth-bearing materials, whether or not lead is required.

ACKNOWLEDGEMENTS

The author would like to express his thanks to D.J. Barkley, who determined the lead gravimetrically as lead sulphate in the lead-titanium-zirconium samples and who assisted in devising the technique of dissolving the solid samples of these compounds. Thanks are due also to W. Zbitnew, who determined the lead in the samples of sphalerite, galena, etc., by the other methods used for comparison with the extraction-EDTA method, and to Mrs. E.M. Donaldson for her critical reading and constructive comments on the manuscript.

REFERENCES

1. V.M. MacNamara and W.A. Gow, "A Chemical Precipitation Method for the Production of a Homogeneous, High Purity Powder Applicable to the Lead Zirconate Titanate Solid-Solution Series", Mines Branch Investigation Report IR 63-39, Department of Mines and Technical Surveys, Ottawa, Canada (1963).

2. W.F. Hillebrand et al., "Applied Inorganic Analysis", 2nd Ed., John Wiley and Sons, Inc., New York. (1953).

3. F.J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid", D. Van Nostrand Company, New York (1957).

4. G.H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley and Sons, Inc., New York (1957).

5. J. Kinnunen and B. Wennerstrand, "Chemist-Analyst", 43, 65-67 (1954).

6. J. Korbl and R. Pribil, "Chemist-Analyst", 45, 102 (1956).

7. H.A. Flaschka and A.J. Barnard, Jr., in "Comprehensive Analytical Chemistry", ed. by C.L. Wilson and D.W. Wilson, Vol. 1B, Chapter 9, pp.315-316, Elsevier Publishing Company, London (1960).

8. ASTM Manual on Quality Control of Materials, Special Technical Publication 15-C, Part 2, January 1951, p. 43; by American Society for Testing Material, 1916 Race Street, Philadelphia 3, Pa., U.S.A.