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A method is described for the colorimetric determination of concentrations greater than 0.1 p.p.m. of lead in telluric acid. Lead is concentrated into not more than 0.5 g of tellurium by reducing a solution of telluric acid at pH 1.6 to 2.3 with a suitable amount of hydrazine. The normal dithizone method for the isolation and colorimetric determination of traces of lead is not applicable in presence of sexavalent tellurium, but up to 0.5 g of the quadrivalent form can be tolerated.

LEAD is a common impurity in tellurium, and in work on the purification of this element it became necessary to determine traces of lead, particularly in telluric acid. The usual methods for separating lead from other materials depend on an extraction procedure involving the use of diethyldithiocarbamate or dithizone, and dithizone is also the most satisfactory reagent for the colorimetric determination of traces of lead.¹ Preliminary experiments indicated that diethyldithiocarbamate cannot be used, as it is extensively oxidised by telluric acid. The latter also suppresses the formation of lead dithizonate in strongly ammoniacal solution, so that, when the double-extraction procedure first described by Snyder² and later modified by Sandell¹ is used, recovery of lead is incomplete in presence of 0.5 g of telluric acid.

EXPERIMENTAL

EFFECT OF QUADRIVALENT TELLURIUM ON ISOLATION AND DETERMINATION OF LEAD WITH DITHIZONE-

Tellurium (obtained from J. Lowenstein Co. Ltd.) having a purity of 99.9999 per cent. was dissolved in diluted nitric acid (1 + 1) to give a solution of quadrivalent tellurium. An 8.3- μ g portion of lead, as nitrate, was added to each of different amounts of this solution, and the lead in the samples was isolated and determined as described by Sandell¹; the results were—

Tellurium present, g	••	0.0	0.002	0.012	0.06	0.23	0.57
Lead found, μg	••	$8 \cdot 2$	$8 \cdot 2$	8.1	8.3	$8 \cdot 2$	8.3

The presence of up to 0.5 g of quadrivalent tellurium, therefore, has no effect on the determination of traces of lead by this method. The citrate reagent used during the extraction with dithizone forms a complex with quadrivalent tellurium, which, under the alkaline conditions used, is precipitated if more than 0.5 g of tellurium is present. When this occurs the recovery of lead is low.

Quadrivalent tellurium appears to react with dithizone under the conditions of this extraction procedure. The final carbon tetrachloride solution in which the colour of the lead dithizonate is measured becomes increasingly yellow as the amount of tellurium present in the original solution increases. This colour cannot be produced by any oxidation products of dithizone formed during the preliminary extraction, as such products would hardly be extracted by dilute nitric acid (1 + 100) and should not therefore appear in the final determination. This yellow colour does not interfere with the determination of lead; at the wavelength used for measuring the dithizone colour (520 m μ) it has a low absorption, equivalent to less than 0.1 μ g of lead. Maximum absorption occurs at 425 to 430 m μ , and Mabuchi,³ who used widely different conditions, found that quadrivalent tellurium and dithizone formed a complex having a maximum at 430 m μ . When only sexavalent tellurium is present, no yellow colour is formed.

RECOVERY OF LEAD FROM SOLUTIONS OF TELLURIC ACID-

A few preliminary experiments were carried out without control of the pH. An excess of hydrazine hydrate solution was added to a solution of 0.5 g of telluric acid containing added lead, and all the tellurium was precipitated; analysis of the precipitate showed that it contained most of the added lead. However, it is usually necessary to take a weight of telluric acid considerably greater than 0.5 g in order to have present an amount of lead suitable for determination, and the lead must be concentrated into not more than 0.5 g of tellurium. This may be accomplished by using only enough hydrazine to precipitate a small proportion of the tellurium; all the lead is co-precipitated.

In a series of recovery experiments, $25 \cdot 0 - \mu g$ portions of lead were added to separate solutions containing 1.5 g of purified telluric acid, and tellurium was precipitated by 2 ml of a 10 per cent. solution of hydrazine hydrate (purified as described under "Reagents") from solutions at different pH values. The results were—

Original nH	-	1.10	1.20	1.30	1.44	1.60	1.75	1.90	2.05	2.20	2.30
ongmarphi	••	1 10	1 20	100		1 00	1 10	1 50	200	2 20	200
pH after precipitation	• •	1.42	1.61	1.68	1.82	2.04	2.16	2.25	$2 \cdot 34$	2.49	2.63
Lead found, $\mu g \dots \dots$	• •	19.2	$24 \cdot 9$	$25 \cdot 4$	$25 \cdot 1$	25.6	24.7	$25 \cdot 3$	24.7	24.0	$23 \cdot 9$

The change in pH caused by adding 2 ml of purified hydrazine hydrate solution (pH 9), subsequently precipitating and boiling is governed by the extent to which the solution is buffered. In the experiments mentioned above, the increase was 0.3 to 0.4 unit of pH, whereas when 15 g of telluric acid were present in the sample solution and 2 ml of hydrazine hydrate solution were used, the increase was only 0.05 unit of pH. For a solution containing 15 g of purified telluric acid at pH 1.20, the final pH was 1.25, and the recovery of 8.3 μ g of added lead was only 1.5 μ g. Since at this initial pH recovery of added lead was complete in presence of 1.5 g of telluric acid, the pH after precipitation is the controlling factor. The results above show that recovery of added lead is complete in the pH range 1.6 to 2.35; at lower pH values precipitation of lead is incomplete, and at higher pH values there is difficulty because the amount of tellurium precipitated increases to more than the tolerable limit (0.5 g).

Completeness of precipitation of lead with a small proportion of tellurium-

To check the completeness of precipitation of lead by the method described above, attempts were made to determine the amount of lead remaining in solution. Since most of the lead is precipitated, the bulk of any lead remaining in solution should be precipitated when a further small proportion of the tellurium present is reduced to the element. Lead was therefore determined in second precipitates. This was done in presence of up to 15 g of telluric acid, and up to 25 μ g of lead were added; the largest amount of lead found was 0.2 μ g, and the reagent blank value was 0.7 μ g of lead. Within these limits the recovery of lead in one precipitation was complete.

EFFECT OF CHLORIDE, SULPHATE AND CITRATE ON RECOVERY OF LEAD-

The presence in telluric acid of other cations as impurities would not be expected to interfere, as, if these ions were also precipitated when the telluric acid was reduced, they would be separated during the isolation of lead. However, the formation of lead - anion complexes might prevent co-precipitation of lead. Nitrate was without effect, as lead was added in nitric acid solution, but the effects of three other common anions, chloride, sulphate and citrate, were examined. Portions of lead ($25 \mu g$) were added to separate solutions each containing 1.5 g of purified telluric acid and one of these anions, and lead was recovered by the proposed procedure. The final pH of each solution was between 1.92 and 2.06; the results were—

Foreign anion		Chloride	Sulphate	Citrate
Concentration of anion, M		0.3	0.25	0.1
Lead found, μg	••	25.9	$25 \cdot 1$	0.0

These results show that, although chloride and sulphate ions are without effect, citrate ions, even in lower concentrations, prevent co-precipitation of lead with tellurium.

Method

Reagents-

The hydrochloric and nitric acids and ammonia solution used were obtained from the British Drug Houses Ltd. ("Lead-free for Foodstuffs Analysis").

Telluric acid—Remove lead from analytical-reagent grade telluric acid by passage through a column of Amberlite IR-120 in the hydrogen form at pH 4.

Hydrochloric acid, dilute (1 + 9).

Ammonia solution, diluted (1 + 1).

Nitric acid, concentrated and dilute (1 + 100).

Hydrazine hydrate solution—Adjust the pH of a 10 per cent. v/v aqueous solution of laboratory-reagent grade hydrazine hydrate to 9 with hydrochloric acid, and remove lead

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by shaking with successive portions of dithizone solution in carbon tetrachloride until there is no colour change. Remove excess of dithizone by shaking with successive portions of chloroform until colourless. (Hydrazine hydrate is more convenient to use than is the hydrochloride, as less adjustment of the pH is involved.)

Hydroxylamine hydrochloride solution—Prepare and purify as described by Sandell.¹ Potassium cyanide solution—Prepare and purify as described by Sandell.¹

Ammonia - cyanide - sulphite solution—Prepare and purify as described by Sandell.¹

Dithizone solution—Prepare and purify as described by Sandell.¹

Ammonium citrate solution—Adjust the pH of a solution containing 200 g of analytical-reagent grade citric acid in 250 ml of water to 9 by adding analytical-reagent grade ammonia solution, and cool the solution in ice as required. Dilute the final solution to 500 ml, and remove lead as described by Sandell.¹

Carbon tetrachloride-Analytical-reagent grade.

Standard lead solution—Dissolve 0.1667 g of dried analytical-reagent grade lead nitrate in 250 ml of dilute nitric acid (1 + 100), and dilute 5 ml of the solution to 500 ml with that acid. This gives a solution containing 4.17 μ g of lead per ml.

PREPARATION OF STANDARD GRAPH FOR LEAD-

Take 0, 0.5, 1.0, 1.5, 2.0 and 2.5-ml portions of standard lead solution, dilute each to 10.0 ml with dilute nitric acid (1 + 100), and carry out the extraction procedure described by Sandell¹ for isolating lead (see Note), with two exceptions. Instead of indicator solution, it is more convenient to use a pH meter; the capacity of 4-cm spectrophotometer cells necessitates an increase to 25 ml of the volume of organic phase in the subsequent determination, so an increase in the volume of the aqueous phase is desirable; this is done by increasing to 10 ml each of the portions of dilute nitric acid (1 + 100) used to secure reversion of lead to the aqueous phase.

To the combined nitric acid solutions add 20 ml of ammonia - cyanide - sulphite solution and 25 ml of dithizone solution. Shake for 1 minute, allow the layers to separate, filter the carbon tetrachloride layer through a plug of filter-paper, and measure its optical density in 4-cm cells at 520 m μ with a Unicam SP600 spectrophotometer. Use the solution containing no added lead as reference.

For 1-cm spectrophotometer cells, take 0, $1 \cdot 0$, $2 \cdot 0$, $4 \cdot 0$, $6 \cdot 0$ and $7 \cdot 0$ -ml portions of standard lead solution, and continue as described above; in this way the range 0 to 30 μ g of lead is covered. The maximum deviations of the graphs from linearity represented 0.2 and 0.9 μ g of lead for 4- and 1-cm cells, respectively.

Note—The procedure described by Sandell¹ differs considerably from that found in earlier editions of the book.

PROCEDURE-

Dissolve a suitable weight of telluric acid (up to 15 g) in 50 to 250 ml of water, and add hydrochloric acid to adjust the pH to a value between 1.6 for 1.5 g of sample and 2.0 for 15 g. Add 1.5 to 2.0 ml of hydrazine hydrate solution, heat just to boiling-point, and set aside for at least 3 hours. Measure the pH of the cold supernatant liquid, which should be in the range 1.6 to 2.1. Draw the supernatant liquid through a sintered immersion filter (porosity No. 2), wash the precipitate three times with water, and remove the washings. Dissolve the precipitate in 5 ml of concentrated nitric acid, boil to expel oxides of nitrogen, and isolate and determine lead as described for the standard graph. Use as reference a reagent blank solution prepared by treating 5 ml of concentrated nitric acid as described above.

RESULTS

The recovery of lead added to solutions of purified telluric acid is shown in Table I; it can be seen that recovery is complete over a wide range of conditions.

It is not possible to measure the complete reagent blank value, but only that portion of it subsequent to the precipitation. The reagent blank value as measured is in the range 0.7 to $1.2 \mu g$ of lead. The only reagents not covered by this value are a few drops of hydrochloric acid (containing not more than 0.005 p.p.m. of lead) and 2 ml of a 10 per cent. solution

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TABLE I

RECOVERY OF ADDED LEAD FROM SOLUTIONS OF PURIFIED TELLURIC ACID

Lead found in solution containing-				
	1.5 g of	15 g of		
Lead added,	telluric acid,	telluric acid,		
$\mu \mathrm{g}$	μg	$\mu \mathrm{g}$		
Optical density measu	ured in 1-cm cells—			
0.0	0.1	0.4		
4.2	4.1	5.3		
8.3	8.4	9.1		
16.7	16.6	16.8		
25.0	$25 \cdot 1$	$25 \cdot 2$		
$29 \cdot 2$	29.6	29.8		
Optical density measu	wed in 4-cm cells-			
1 0.0	0.1	0.3		
1.1	0.9	1.4		
$2 \cdot 1$	$2 \cdot 2$	$2 \cdot 4$		
4.2	4.3	$4 \cdot 2$		
6.3	6.2	6.4		
8.3	8.3			
10.5	<u> </u>	11.0		

of hydrazine hydrate, which has itself been purified. The total amount of lead in these reagents must be exceedingly small, so that the measured blank value may be considered to be the true value.

There appears to be no reason why weights of telluric acid greater than 15 g should not be used as sample. The lower limit for determining lead would then be below the 0.1 p.p.m. claimed for the proposed method.

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