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DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*DETERMINATION OF TIN IN ORES,
STEEL AND ALLOYS WITH GALLEIN AFTER
EXTRACTION AS THE IODIDE*

ELSIE M. DONALDSON

MINERAL SCIENCES DIVISION

JULY 1974

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Information Canada
Ottawa, 1974

Mines Branch Technical Bulletin TB 195

DETERMINATION OF TIN IN ORES, STEEL AND ALLOYS
WITH GALLEIN AFTER EXTRACTION AS THE IODIDE

by

Elsie M. Donaldson^{*}

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ABSTRACT

A method for determining up to about 3.5% of tin in ores and mill products is described. After sample decomposition, tin is separated from the matrix elements by toluene extraction of tin(IV) iodide from a 2 M sulphuric acid — 1.5 M potassium iodide-tartaric acid medium, then back-extracted into 2% sodium hydroxide solution. The red complex formed between tin(IV) and gallein is extracted into n-amyl alcohol from a mono-chloroacetic acid-ascorbic acid medium, and the absorbance of the extract is determined at 496 nm. Arsenic, antimony, germanium, and thallium are partly extracted as iodides under the proposed conditions, but large amounts of arsenic and moderate amounts of antimony, germanium, and thallium may be present in the sample solution without causing error in the results. The proposed method is also applicable to steel and copper-, aluminum-, zinc-, and zirconium-base alloys.

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Direction des mines
Bulletin technique TB 195

DOSAGE DE L'ÉTAIN DANS LES MINÉRAIS, LES ACIERS
ET LES ALLIAGES AVEC LA GALLÉINE APRÈS SON
EXTRACTION SOUS FORME D'IODURE

par

Elsie M. Donaldson*

RÉSUMÉ

On décrit une méthode afin de déterminer jusqu'à environ 3.5% d'étain dans les minerais et produits d'usine. Après la dissolution de l'échantillon, l'étain est séparé des éléments de la matrice par extraction au toluène de l'iodure d'étain (IV) à partir d'un milieu de 2M d'acide sulfurique -1.5M d'iodure de potassium et d'acide tartarique, puis extrait en retour par une solution à 2% de soude caustique. Le complexe rouge formé par l'étain (IV) et la galléine est extrait par l'alcool n-amylique en milieu acide monochloroacétique-acide ascorbique et l'absorbance de l'extrait est mesuré à 496 nm. Dans les conditions décrites, l'arsenic, l'antimoine, le germanium et le thallium sont partiellement extraits sous forme d'iodures, quoiqu'on puisse trouver d'importantes quantités d'arsenic et des quantités moindres d'antimoine, de germanium et de thallium dans la solution échantillon sans que les résultats en soient affectés. La méthode proposée peut également s'appliquer à l'acier et aux alliages à base de cuivre, d'aluminium, de zinc et de zirconium.

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INTRODUCTION

The preparation and characterization of ores for use as certified reference materials is a continuing project (Canadian Certified Reference Materials Project) sponsored by the Mines Branch. As part of this project, a zinc-tin-copper-lead ore, MP-1, and a zinc-lead-tin-silver ore, KC-1, have been issued with recommended values for tin (1,2). The accurate determination of tin in ores is generally troublesome (3-6), and this is evidenced by the wide range of values obtained in the inter-laboratory certification programs for the two certified ores (1,2,6). In such certification schemes, it is desirable to obtain results by as many diverse methods as possible, including spectrophotometric methods. Because of the paucity of suitable spectrophotometric methods for determining tin in ores, it was anticipated that none of the participating laboratories would use such methods. Consequently, the present investigation was undertaken either to develop such a method, or to modify and adapt an existing one, that would be applicable to the determination of both small and moderate amounts of tin in ores.

Many of the existing spectrophotometric methods for determining tin in ores involve phenylfluorone (7, 8), pyrocatechol violet (9, 10), or gallein (11-15) as the chromogenic reagent. Of these, gallein was chosen for use in the present work because it forms a stable tin complex that is readily extractable into certain organic solvents (13, 16-19). Gallein was first investigated by Wood (20,21) who applied it to the field determination of small amounts of tin in soils after separation of tin from the matrix elements by volatilization with ammonium iodide. A modification (22) of Wood's procedure has been used to determine tin in low-grade ores and tailing products (11, 12, 14, 15). However, none of these methods, which involve the volatilization of tin with ammonium iodide, were considered in the present work because it is known that tin bound in a silicate lattice or in cassiterite entrapped in silicates is not converted to tin(IV) iodide by this procedure (23). Moreover,

certain volatile, acid-soluble constituents could accompany the tin and subsequently interfere (24). A method involving the extraction of the tin-gallein complex, without prior separation of tin from the matrix elements (13), was also not considered because, due to the non-selectivity of gallein, it is subject to interference from other ions that are co-extracted with the tin.

Because precipitation techniques for separating tin from interfering elements and interfering elements from tin are prone to errors due to incomplete precipitation and co-precipitation effects, respectively (25), a solvent extraction technique was sought for the isolation of tin prior to its spectrophotometric determination. A procedure involving the extraction of tin (IV) iodide with benzene or toluene has been used by previous workers (26-28) and was selected for the present work because of its relative specificity.

This paper describes the successful application of a modification of an extraction method (16), involving the extraction of the tin-gallein complex into n-amyl alcohol, to the determination of tin in ores and mill products after the separation of tin from the matrix elements by toluene extraction as the iodide. The applicability of this method to the determination of small and moderate amounts of tin in various other materials is also established.

APPARATUS AND REAGENTS

Apparatus

Spectrophotometer: Unicam Model SP500.

pH meter: Sargent-Welch Model DR.

Centrifuge: Clinical type.

Reagents

Standard tin solution (1 ml = 1 mg of tin). Dissolve 0.2000 g of pure tin metal by heating in a 250-ml beaker with 50 ml of concentrated sulphuric acid. Cool, and dilute the solution to 200 ml with water. Dilute 20 ml of this stock solution to 100 ml with 25% sulphuric acid. Transfer 5 ml of the resulting solution to a 200-ml volumetric flask, add 20 ml of concentrated hydrochloric acid, and dilute to volume with water. Prepare fresh as required (1 ml = 5 µg of tin).

Gallein (4,5-dihydroxyfluorescein) solution, 0.06% w/v in ethyl alcohol. This solution is stable for at least one month.

Monochloroacetic acid solution, 40% w/v.

Ascorbic acid solution, 5% w/v. Prepare a fresh solution every five days.

Hydrochloric acid, 10% v/v.

Sulphuric acid, 2.8 M. Add 310 ml of concentrated sulphuric acid, slowly and while stirring, to approximately 1600 ml of water in a 2-litre beaker. Allow the solution to cool to room temperature, transfer it to a 2-litre volumetric flask, and dilute to volume with water.

Sulphuric acid, 50% v/v.

Tartaric acid solution, 25% w/v.

Potassium iodide solution, 5.3 M. Dissolve 220 g of the reagent in approximately 230 ml of water and dilute to 250 ml. Prepare fresh as required.

Potassium iodide - sulphuric acid wash solution, 1.5 and 2 M, respectively. Add 40 ml of 5.25 M potassium iodide solution to 100 ml of 2.8 M sulphuric acid. Prepare fresh just before use.

Sodium hydroxide solution, 2% w/v. Store in a polyethylene bottle.

N-amyl alcohol. Analytical reagent-grade.

Toluene. Analytical reagent-grade.

PROCEDURES

Preparation of Calibration Curve

To six 100-ml beakers, add, by burette, 1, 2, 3, 4, 5, and 6 ml, respectively, of standard 5 $\mu\text{g}/\text{ml}$ tin solution, and dilute each solution to exactly 20 ml with 10% hydrochloric acid. Add 20 ml of 10% hydrochloric acid to a seventh beaker; this constitutes the blank. Add 5 ml of 40% monochloroacetic acid solution, 2 ml of 5% ascorbic acid solution, and 2 ml of concentrated ammonium hydroxide to each beaker, in succession, mix thoroughly and cool the solutions to room temperature in a water-bath. Using a pH meter, adjust the pH of each solution to 2.25 ± 0.01 (Note 1) with concentrated ammonium hydroxide and/or 10% hydrochloric acid as required. Transfer the resulting solutions to 60-ml separatory funnels, marked at approximately 50 ml, and dilute to the mark with water (Note 2). Add exactly 1 ml of 0.06% gallein solution, stopper, shake, and allow the solutions to stand for 15 minutes to complete the complex formation. By pipette, add 10 ml of n-amyl alcohol to each funnel, stopper, and shake for 2 minutes. Allow several minutes for the layers to separate, then drain off and discard the lower aqueous layer. Drain the n-amyl alcohol

extracts into dry 15-ml centrifuge tubes, and centrifuge for 1 minute. Determine the absorbance of each tin-gallein extract, at 496 nm, against the blank as the reference solution, using 1-cm cells. Plot μg of tin vs. absorbance.

General Procedures

In the following procedures a reagent blank is carried along with the samples.

Ores and mill products

Depending on the expected tin content, transfer 0.25 - 0.5 g of powdered sample to a 30-ml zirconium crucible, add 1.5 g each of sodium carbonate and sodium peroxide and mix thoroughly. Cautiously fuse the mixture (to avoid spattering) over an open flame, and maintain it in the molten state for approximately 30 seconds to ensure complete sample decomposition. Allow the melt to cool, then transfer the crucible to a covered 600-ml beaker containing 80 ml of water and 65 ml of 50% sulphuric acid. When the dissolution of the melt is complete, remove the crucible after washing it thoroughly with water, cover the solution (Note 3) and evaporate it to approximately 125 ml. Remove the cover and evaporate the solution to fumes of sulphur trioxide to dehydrate silica and to remove hydrogen peroxide. Cool, wash down the sides of the beaker with a small amount of water, and evaporate the solution to fumes again to ensure the complete removal of hydrogen peroxide. Cool, add approximately 20 ml of water and 10 ml of 25% tartaric acid solution, and dilute the solution to approximately 150 ml with water. Filter the resulting solution (Whatman No. 541 paper) into a 250-ml volumetric flask, wash the beaker twice with 25-ml portions of hot 2.8 M sulphuric acid, then wash the beaker, paper, and residue thoroughly with hot water. Discard the paper and residue. Cool the filtrate to room temperature, dilute to volume with water, and mix (Notes 4 and 5).

Transfer a 20 - 50-ml aliquot, containing up to approximately 1 mg of tin, to a 125-ml separatory funnel, marked at approximately 50 ml and, if necessary, dilute to the mark with 2.8 M sulphuric acid. Add 20 ml of 5.3 M potassium iodide solution and 15 ml of toluene, stopper, and shake for 2 minutes. Allow several minutes for the layers to separate, then drain the lower aqueous layer into a second 125-ml separatory funnel. Wash the stem of the first funnel twice with 2.8 M sulphuric acid, contained in a plastic wash bottle, and collect the washings in the second funnel. Add 10 ml of toluene to the second funnel, and re-extract the sample solution once more by shaking for 2 minutes. Drain off and discard the aqueous phase. Add the second extract to the first one. Wash the stem of the second funnel twice with toluene, contained in a plastic wash bottle, and collect the washings in the first funnel. Wash the second funnel, including the stopper, twice with approximately 5-ml portions of toluene, and add the washings to the first funnel. Wash the stem of the funnel with toluene after each washing stage and add the washings to the first funnel. Drain off and discard the residual aqueous phase remaining in the first funnel. Wash the first funnel, including the stopper, with 10 ml of freshly prepared 1.5 M potassium iodide - 2 M sulphuric acid wash solution, then stopper the funnel and wash the toluene phase by gently inverting the funnel 6-8 times. Drain off and discard the aqueous layer. Repeat the washing step, drain off the aqueous layer, and wash the stem of the funnel with water to remove excess acid.

Add 10 ml of 2% sodium hydroxide solution to the combined extracts, stopper, and shake for 1 minute. Allow the layers to separate, then drain the lower aqueous layer into a 250-ml Teflon beaker. Wash the stem of the funnel thoroughly with water, and collect the washings in the beaker containing the aqueous layer. Strip the combined extracts two more times, by shaking for 30 seconds each time, with 5-ml portions of 2% sodium hydroxide solution, and combine the aqueous layers with the first layer (Note 6). Evaporate the resulting solution to approximately 20 ml and cool to room temperature. Transfer the solution to a volumetric flask of appropriate size (50 - 500-ml) and dilute to volume with water.

Transfer a 10 - 20-ml aliquot of both the sample and blank solutions to 100-ml beakers and, if necessary, dilute to exactly 20 ml with water. Add 2 ml of concentrated hydrochloric acid, 5 ml of 40% monochloroacetic acid solution, and 2 ml of 5% ascorbic acid solution, in succession. Mix thoroughly, then add 2 ml of concentrated ammonium hydroxide, cool the solutions to room temperature in a water-bath, and proceed with the pH adjustment, complex formation, and extraction of the tin-gallein complex as described above. Measure the absorbance of the sample extract against the reagent blank extract and determine the tin content of the aliquot by reference to the calibration curve.

Steel

Transfer 0.25 - 0.5 g of sample to a 400-ml beaker, add approximately 25 ml of water and 10 ml of concentrated nitric acid, cover the beaker, and heat until the decomposition of acid-soluble material is complete. Add 65 ml of 50% sulphuric acid, remove the cover, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with a small amount of water and evaporate the solution to fumes again to ensure the complete removal of nitric acid. Cool, dilute to approximately 150 ml with water, filter the solution (Whatman No. 541 paper) into a 600-ml beaker, and wash the beaker, paper, and residue thoroughly with hot water.

Transfer the paper and contents to a 30-ml zirconium crucible, burn off the paper at a low temperature, and ignite at approximately 600°C. Fuse the residue with 1.5 g of sodium peroxide, cool, and transfer the crucible to the beaker (covered) containing the initial filtrate. When the dissolution of the melt is complete, remove the crucible after washing it thoroughly with water. Cover the resulting solution (Note 3), evaporate it to approximately 125 ml, then proceed with the dehydration of silica and/or removal of hydrogen peroxide, the addition of tartaric acid solution, the filtration of the solution (Note 5), if necessary (Note 7), the extraction of tin iodide, and the subsequent determination of tin as described above.

Copper-, aluminum-, and zinc-base alloys. Decompose 0.25 - 0.5 g of sample as described above for steel samples. After the removal of nitric acid by evaporation of the solution to fumes of sulphur trioxide, add approximately 20 ml of water and 10 ml of 25% tartaric acid solution, dilute to approximately 150 ml with water, then proceed with the filtration of the solution (Whatman No. 40 paper) (Notes 4 and 5), if necessary (Notes 7 and 8), the extraction of tin iodide, and the subsequent determination of tin as described for ores and mill products.

Zirconium-base alloys. Transfer 0.25 - 0.5 g of sample to a 400-ml beaker, add 80 ml of 50% sulphuric acid and 5 - 10 drops of concentrated hydrofluoric acid, cover the beaker, and heat until the decomposition of the sample is complete. Remove the cover and evaporate the solution to fumes of sulphur trioxide twice to ensure the complete removal of hydrofluoric acid. Cool the solution, add approximately 20 ml of water and 10 ml of 25% tartaric acid solution, and dilute to about 150 ml with water. Transfer the resulting solution to a 250-ml volumetric flask, dilute to approximately 225 ml with water, cool to room temperature, dilute to volume with water, and proceed with the extraction and determination of tin as described for ores and mill products.

Notes

1. The pH meter employed should be capable of measuring pH accurately to within ± 0.01 divisions. Because of the high absorbance exhibited by gallein (approximately 0.24 in a 1-cm cell under the conditions of the present work) in the range of pH required for formation of the tin complex, erratic results will be obtained for tin if the addition of gallein solution is not rigidly controlled and if the pH of the tin solutions deviates by more than approximately ± 0.01 units from that of the reagent blank solution.

2. The volume of the aqueous phase before extraction should be kept relatively constant to eliminate volume changes in the extract resulting

from the partial solubility of n-amyl alcohol in water (i. e. , 2.19% by weight at 25°C).

3. To avoid loss by spattering, the solution should be kept almost completely covered during evaporation until almost all of the hydrogen peroxide has been removed.

4. If the sample contains lead, lead sulphate will precipitate after filtration and dilution of the sample solution. The solution can be allowed to either stand until the precipitate has settled or a suitable portion can be filtered through a dry (Whatman No. 42) filter paper.

5. If the sample contains tungsten, any insoluble tungsten compounds that precipitate after filtration and dilution of the solution to volume can be removed, prior to the extraction of tin iodide, by filtering a suitable portion of the solution through a dry (Whatman No. 42) filter paper.

6. The toluene can be used for subsequent extractions if the toluene phases are combined in a large separatory funnel and washed once by shaking with 20% sulphuric acid, and then three times by shaking with distilled water.

7. If filtration is not necessary, add 50 ml of 2.8 M sulphuric acid, transfer the solution to a 250-ml volumetric flask, dilute to volume with water, and proceed with the extraction of tin iodide as described.

8. If elemental silicon is present (e.g., in aluminum alloys) and the solution is not completely clear after dilution to volume, filter a suitable portion of the solution through dry (Whatman No. 42) filter paper prior to the extraction of tin iodide.

EXPERIMENTAL

Spectral Characteristics of the Tin-Gallein Complex

In most previous applications, the absorbance of the tin-gallein complex has been measured in aqueous media containing gelatin to prevent precipitation of the complex (22,24), or in the absence of gelatin (12,20, 21,29). The reported wavelength of maximum absorption of the complex under these conditions is approximately 520 - 525 nm. However, the results obtained by investigators (13, 16, 19) who extracted the complex into various alcohols and ketones show that the wavelength of maximum absorption of the extracted complex (495 - 500 nm) is appreciably lower than that of the complex formed in an aqueous medium. This was confirmed in the present work by measuring the absorbance of the complex in aqueous media containing gelatin, and after extraction of the complex (in the absence of gelatin which causes emulsification) into n-amyl alcohol. The results showed that extraction of the complex results in a decrease in the wavelength of maximum absorption from 510 to 496 nm. These tests also showed that extraction results in a corresponding increase in molar absorptivity from 25.8×10^3 to 41.1×10^3 l. mole⁻¹. cm⁻¹. The latter value is greater than that reported for cyclohexanone extracts of the tin complex (34.5×10^3 l. mole⁻¹. cm⁻¹) (13).

These findings together with the absorption spectra of the complex before and after extraction (Figure 1) show that the complex extracted into n-amyl alcohol is not identical to that formed in an aqueous medium. A mole-ratio study carried out in an aqueous medium [Figure 2 (a)] gave definite evidence for the 1:2 complex previously reported by Wood (20). A similar study involving the extracted complex yielded inconclusive results because of the insolubility of the complex or complexes formed in the absence of a sufficient excess of gallein (Figure 2 (b), broken line). This insolubility also prevented further attempts to determine the nature of the extracted complex by the continuous variations method. However, the results shown

in Figure 2 (b) suggest that the extracted complex is probably a 1:3 complex, and this is supported by the ratio of the molar absorptivities of the two complexes (2:3.2) (30). According to Wood (20), the 1:2 complex formed in aqueous media does not contain coordinated halogens. Consequently, the complex extracted into n-amyl alcohol probably results from dehydration or removal of water molecules associated with the tin and subsequent replacement of these coordinated water molecules by an additional molecule of gallein. Because of the sensitivity and stability of the complex obtained after extraction into n-amyl alcohol, this extraction technique was employed in the present work.

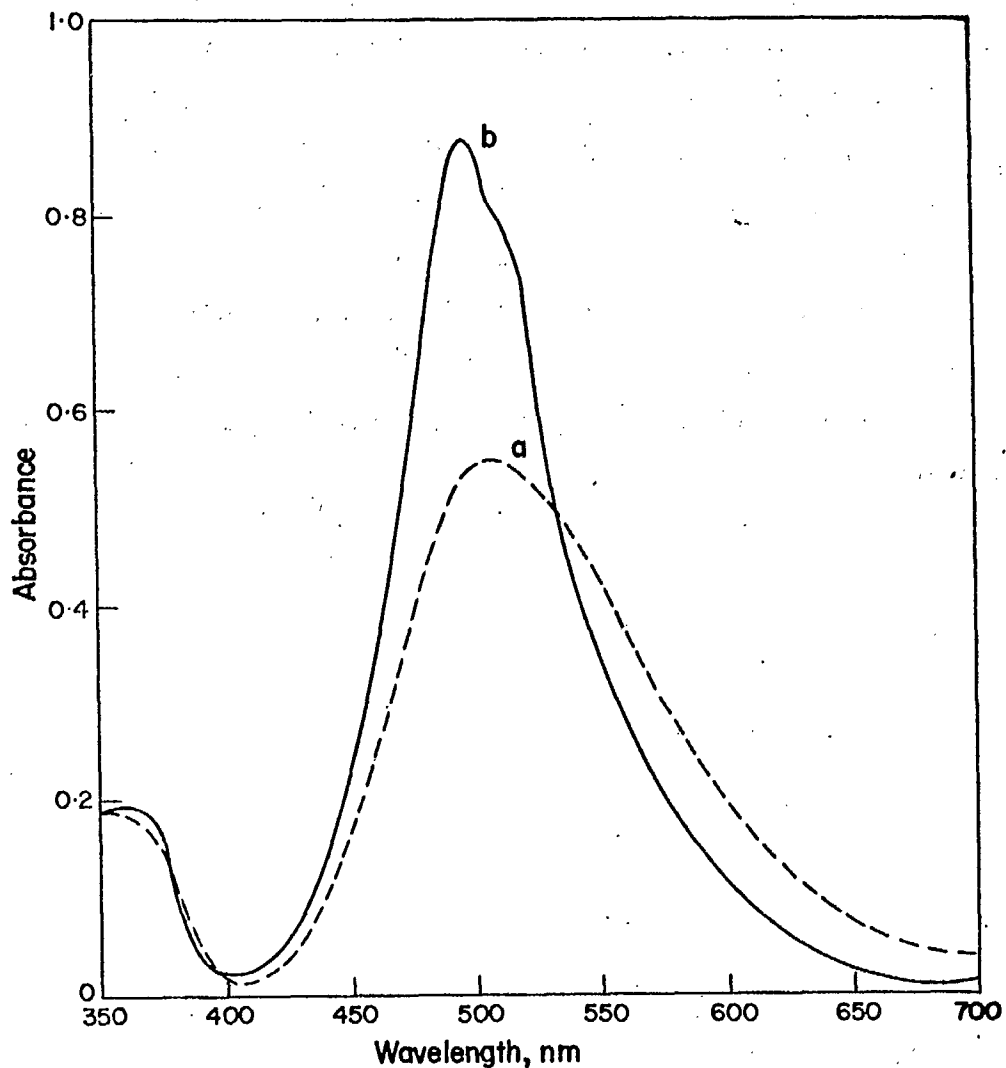


Figure 1. Absorption spectra of tin(IV) - gallein complexes

(a) Tin(IV) ($25\mu\text{g}$) - complex formed at pH 2.25 in presence of 5 ml 40% monochloroacetic acid solution, 1 ml 10% ascorbic acid solution, 1 ml 1% gelatin solution, 4 ml ethyl alcohol, and 1 ml 0.06% gallein solution - total volume 50 ml. Spectrum measured, after 45 minutes, against a reagent blank in a 5-cm cell.

(b) Tin(IV) ($25\mu\text{g}$) - complex formed as above in absence of gelatin and ethyl alcohol - extracted into 10 ml n-amyl alcohol. Spectrum measured against a reagent blank in a 1-cm cell.

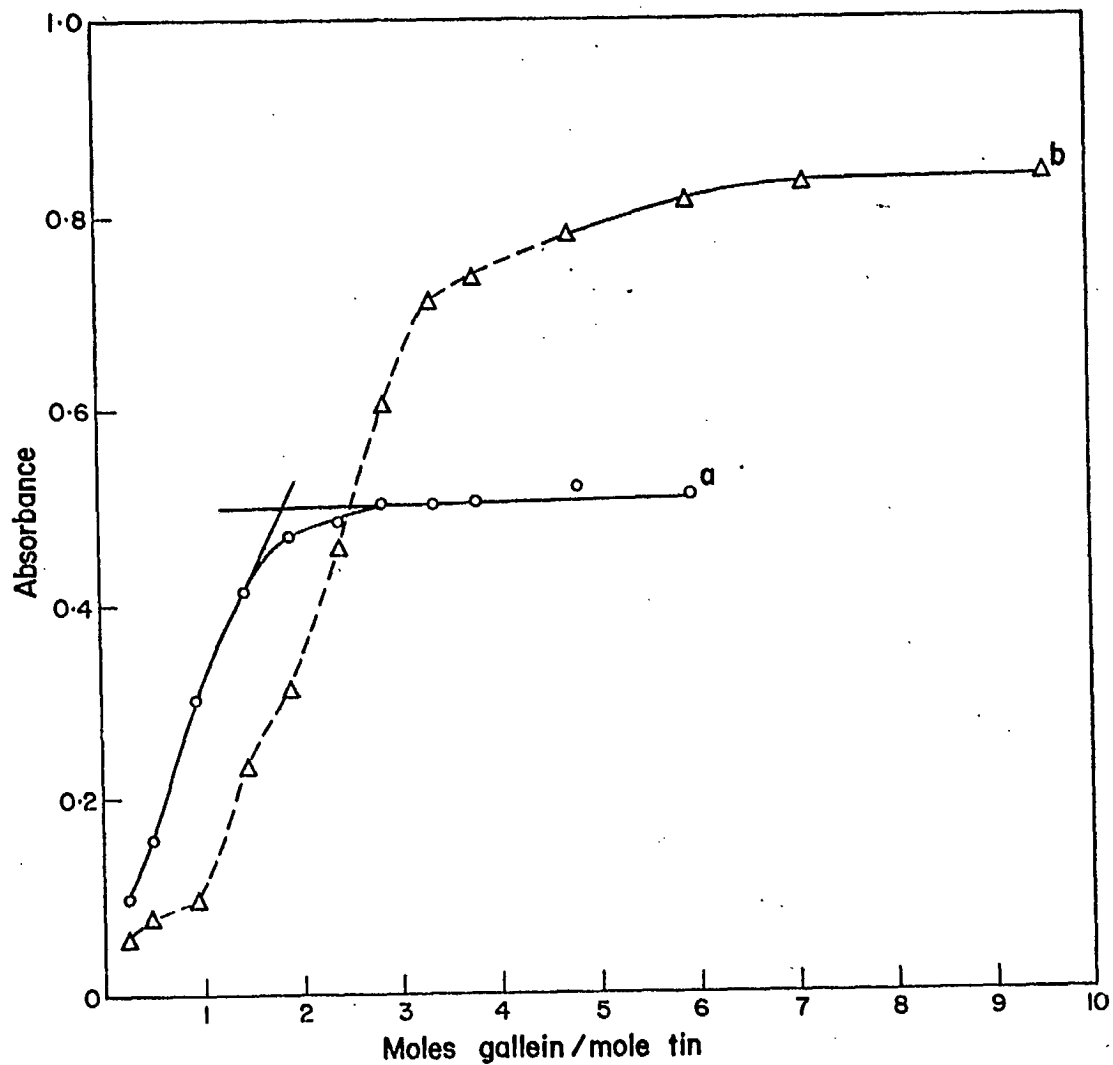


Figure 2. Mole-ratio plots for the tin(IV) - gallein complexes

(a) Tin(IV) (0.2μ moles) - complex formed and measured (at 510 nm) as described for Figure 1(a).

(b) Tin(IV) (0.2μ moles) - complex formed and measured (at 496 nm) as described for Figure 1(b).

Factors Influencing Formation and Subsequent Extraction of the Tin-Gallein Complex

Effect of pH

Although Wood (20, 21) found that the optimum range of pH required for formation of the 1:2 complex is approximately 2-3, most later investigators (14-16, 24) have found that the optimum range is approximately 2.0 - 2.5. Experiments to verify the effect of pH on the formation and subsequent extraction of the tin complex showed that the pH of the aqueous phase increases approximately 0.35 to 0.40 pH units during extraction because of the co-extraction of the monochloroacetic acid that is employed to prevent hydrolysis of tin (20, 21). Tests showed that sodium acetate behaved similarly. N-amyl alcohol, pre-equilibrated with a concentrated monochloroacetic acid solution of specified pH, could not be employed because some of the extracts were hazy and monochloroacetic acid separated from the pre-equilibrated solvent on standing. Furthermore, the volume of the pre-equilibrated n-amyl alcohol decreased during extraction from 10 ml to approximately 8 ml because monochloroacetic acid was transferred back to the aqueous phase. Tests performed with non-equilibrated n-amyl alcohol showed that the tin-gallein complex is formed completely, and extracted, in a single stage, with 10 ml of n-amyl alcohol when the initial pH of the aqueous phase is in the range 1.6 to approximately 2.4; the corresponding pH range after extraction is approximately 2 - 2.8.

Because of the high absorbance exhibited by gallein at low pH values, an initial pH of 2.25 was chosen for the present work.

Effect of gallein concentration

According to McDonald and Stanton (16), 400 μ g of gallein are sufficient for the complexation and subsequent extraction of up to 20 μ g of tin, and Beer's law is obeyed for up to 2.0 μ g of tin per ml of n-amyl alcohol. Although tests carried out in this laboratory confirmed the above statement, greater sensitivity is obtained if a larger amount of gallein is used. The

results of these tests showed that approximately 1 ml of 0.06% gallein solution is required for the complexation of up to approximately 30 μ g of tin under the conditions of the present investigation, and that Beer's law is obeyed for up to 3.0 μ g of tin per ml of n-amyl alcohol. The absorbance of the extract remains constant for at least 3 hours. In the absence of a sufficient excess of gallein, an insoluble purple complex, which remains at the bottom of the n-amyl alcohol layer, is obtained.

Effect of time

Previous investigators (12, 13, 16, 17, 19, 21, 22, 24, 29) have reported considerably different reaction times (2 - 60 minutes) for the complete formation of the tin-gallein complex. However, it has been reported that the formation of the complex is retarded by alcohol (22). Under the conditions of the present investigation (2% by volume of ethyl alcohol), approximately 15 minutes are required.

Separation of Tin by Extraction of Tin(IV) Iodide

Although many solvent extraction methods have been employed to separate small amounts of tin from various matrix elements, prior to its spectrophotometric determination, published data (26-28, 31) on the extraction of tin(IV) iodide indicated the simplicity and relatively high specificity of this separation method. Recently, Byrne and Gorenc (31) carried out a comprehensive investigation of the effect of sulphuric acid and potassium iodide concentrations on the extraction of tin, antimony, arsenic, germanium, mercury, and various other elements. Their extraction curves (acid concentration vs. % extraction; based on data obtained by performing a single-stage extraction with toluene) show that the extraction of antimony is minimal at high iodide concentrations (1.5 M); that the extraction of mercury is minimal at iodide concentrations greater than 0.05 M; and that the extraction of arsenic, tin, and particularly germanium increases with an increase in acid or iodide concentration. From their data, it was considered that a double-stage extraction of tin iodide from a 2 M sulphuric acid - 1.5 M potassium iodide

medium should provide an effective means of separating trace and moderate amounts of tin from most matrix elements, and might minimize the co-extraction of antimony and germanium, both of which interfere in the determination of tin with gallein (13,21,24). Although arsenic would be co-extracted under these conditions, neither trivalent nor pentavalent arsenic form complexes with gallein (21).

Preliminary experiments to assess the feasibility of extraction from 2 M sulphuric acid - 1.5 M potassium iodide media were carried out with pure tin solutions and with solutions containing 50 μ g of tin and 10 mg each of germanium and antimony. In these tests, tartaric acid was added to prevent hydrolysis of antimony. Tin was back-extracted into dilute sodium hydroxide solution and the co-extracted iodine was reduced with ascorbic acid (27) prior to the determination of tin by the described procedure. The results of these tests showed that up to at least 2 mg of tin can be quantitatively extracted in two stages with 15 and 10 ml of toluene, and that sufficient germanium (milligram-quantities) and antimony (approximately 70 μ g) are co-extracted, at the 10-mg level, to interfere with the determination of small amounts of tin. However, subsequent work showed that moderate amounts of antimony and germanium (up to at least 3 mg and 2 mg, respectively) can be present in the solution or aliquot taken for extraction without producing significant error in the tin result.

Effect of Diverse Ions

Because the potassium iodide and sulphuric acid concentrations employed in the present work are greater and less, respectively, than those used by previous investigators (26-28), and because the results obtained by Byrne and Gorenc (31) are based on tests performed with microgram-quantities of various elements, an investigation was made of the effects of milligram-quantities of common ions, and certain ions that are known to form extractable iodide complexes (32), on the extraction and subsequent determination of small amounts (50 μ g) of tin. The results of these tests showed that up to at least 50 mg each of iron(III), aluminum(III), copper(II), zinc(II), and zirconium(IV), and up to at least 10 mg each of cobalt(II), nickel(II), cadmium(II), manganese(II),

chromium(VI), titanium(IV), vanadium(V), molybdenum(VI), mercury(II), gallium(III), indium(III), bismuth(III), arsenic(III), and tellurium(IV) do not interfere in the determination of tin by the proposed method. Thallium(I) interferes in the extraction of tin iodide because it forms an insoluble yellow iodide precipitate that remains, to a large extent, in the toluene phase. However, up to approximately 1 mg can be present in the solution or aliquot taken for extraction without causing error in the tin result. Lead precipitates as the sulphate, and tungsten forms insoluble hydrolysis compounds in the sulphuric acid medium employed for extraction of tin, but moderate amounts of these elements do not interfere if the precipitates are removed by filtration prior to the extraction of tin iodide.

Applications

The proposed method was applied to the analysis of the zinc-tin-copper-lead ore, MP-1 (1), and to the zinc-lead-tin-silver ore, KC-1 (2). For each of these ores, tin was determined, according to the directives of the Mines Branch's Canadian Certified Reference Materials Project, by using five subsamples from each of two bottles. It was also applied to single samples of standard reference steel and non-ferrous alloys. The results of these analyses are given in Tables 1 and 2.

TABLE 1

Determination of Tin in Standard Reference Ores

Sample	Nominal composition, %	Certified value, % Sn	Sn found, %	Standard deviation, %	Average Sn found, %
MP-1 Zinc-tin-copper- lead ore	19.4 Si, 3.6 Al, 5.7 Fe, 3.4 Ca, 0.1 Ti, 11.8 S, 4.0 F, 16.3 Zn, 2.2 Cu, 1.9 Pb, 0.8 As, 0.1 Cd, 0.1 In, 0.1 K	2.50	Bottle 1 - 2.45, 2.50, 2.48, 2.49, 2.52 Bottle 2 - 2.48, 2.49, 2.49, 2.51, 2.51	0.02	2.49
KC-1 Zinc-lead-tin- silver ore	11.1 Si, 0.8 Al, 16.1 Fe, 0.3 Ca, 0.1 Cd, 28.1 S, 0.2 C, 20.4 Zn, 7.0 Pb, 0.1 Cu, 0.2 Na, 0.1 K, 0.1 Ag	0.68	Bottle 1 - 0.683, 0.685, 0.680, 0.706, 0.700 Bottle 2 - 0.697, 0.690, 0.692, 0.695, 0.709	0.01	0.694

TABLE 2

Determination of Tin in N. B. S. and B. C. S. Steel and Non-Ferrous Alloys

Sample	Nominal composition, %	Certified value and range, % Sn	Sn found, %
NBS-19 g Acid open-hearth steel	0.6 Mn, 0.05 P, 0.2 Si, 0.1 Cu, 0.4 Cr, 0.03 Ti, 0.03 Nb	0.008	0.0095
NBS-32 e Nickel-chromium steel	0.8 Mn, 0.3 Si, 0.1 Cu, 1.2 Ni, 0.7 Cr	0.011 [†]	0.013
NBS-36 A Chromium-molybdenum steel	0.4 Mn, 0.4 Si, 0.1 Cu, 0.2 Ni, 2.4 Cr, 0.9 Mo	0.011 (0.010-0.012)	0.012
NBS-50 c Chromium-tungsten-vanadium steel	0.3 Mn, 0.02 P, 0.3 Si, 0.1 Cu, 4.1 Cr, 1.2 V, 0.1 Mo, 18.4 W	0.018	0.018
NBS-125 High-silicon steel	0.1 Mn, 5.0 Si, 0.3 Al	0.007 (0.005-0.008)	0.0092
BCS-218/2 Carbon steel	0.6 Mn, 0.03 P, 0.2 Si, 0.2 Cu, 0.1 Cr, 0.2 Ni, 0.04 As	0.035 (0.032-0.037)	0.034
BCS-273 Mild steel	0.2 Cu, 0.3 Ni, 0.1 Cr	0.06 ₅ (0.060-0.068)	0.065
NBS-37 E Sheet brass	69.6 Cu, 27.9 Zn, 1.0 Pb, 0.5 Ni	1.00 (0.98-1.02)	1.01 ₅
NBS-62 D Manganese bronze	59.1 Cu, 37.1 Zn, 1.2 Al, 0.9 Fe, 0.7 Mn, 0.3 Ni, 0.2 Pb, 0.1 Si	0.38 (0.37-0.40)	0.403
NBS-157 A Copper-nickel-zinc alloy	58.6 Cu, 29.1 Zn, 11.8 Ni, 0.2 Mn, 0.2 Fe	0.021 (0.016-0.026)	0.024
NBS-158 Silicon bronze	90.9 Cu, 2.7 Si, 2.1 Zn, 1.5 Fe, 1.3 Mn, 0.5 Al	0.97 (0.96-0.99)	0.985
NBS-164 Manganese-aluminum bronze	63.8 Cu, 21.9 Zn, 6.2 Al, 4.7 Mn, 2.5 Fe, 0.2 Pb	0.63 (0.60-0.64)	0.673, 0.655
NBS-1101 Cartridge brass (wrought)	69.6 Cu, 30.3 Zn	0.016	0.017
NBS-1102 Cartridge brass (wrought)	72.9 Cu, 27.1 Zn	0.006	0.0058
NBS-1116 Composite commercial bronze	90.4 Cu, 9.4 Zn	0.044	0.043
BCS-Manganese brass "B"	58.8 Cu, 33.9 Zn, 1.0 Mn, 0.9 Fe, 1.6 Al, 0.8 Pb, 1.0 Ni, 0.05 Sb	1.75 (1.64-1.88)	1.74 ₃
NBS-94 B Zinc-base alloy	4.1 Al, 1.0 Cu	0.006 (0.005-0.006)	0.0056
NBS-87 Silicon-aluminum alloy	6.2 Si, 0.6 Ni, 0.5 Fe, 0.4 Mg, 0.3 Cu, 0.3 Mn, 0.2 Cr, 0.2 Ti	0.063 (0.05-0.077)	0.063
BCS-268 Silicon-aluminum alloy	1.3 Cu, 0.6 Mg, 4.9 Si, 0.4 Fe, 0.2 Mn, 0.1 Ni	0.03 ⁻	0.029
NBS-360 Zircaloy-2	0.2 Fe, 0.1 Cr	1.43 [†]	1.43 ₇

[†] NBS provisional result

DISCUSSION

Tables 1 and 2 show that the results obtained for the reference ores and for the National Bureau of Standards and British Chemical Standards samples of steel, brass, bronze, and copper-, aluminum-, zinc-, and zirconium-base alloys are in good agreement with the certified values. The precision of the results for the ores MP-1 and KC-1 is superior to that for many sets of volumetric and instrumental results used in the certification of MP-1 (1) and KC-1 (2).

The proposed method is suitable for samples containing up to approximately 3.5% of tin. A disadvantage of the method is the high absorbance of the reagent blank and the subsequent necessity for rigid pH control. However, the method is extremely sensitive, the technique required is simple, and accurate and precise results can be obtained with careful control of the pH and the volume of gallein added prior to the extraction of the tin-gallein complex.

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