# **Polarographic Determination of Tin in Ores**

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This work was undertaken as a part of a research program on the flotation concentration of tin ores. Existing methods of tin determination proved to be timeconsuming, inaccurate, or insensitive for this purpose. The present method has been applied to many different types of tin ores, and is believed applicable to all ores, alloys, compounds, or mixtures containing tin if no better than the usual polarographic precision is to be expected at any given concentration. The procedure involves fusing with sodium peroxide, filtering off the cations insoluble in sodium hydroxide, and making the filtrate approximately 6N hydrochloric acid. The tin is then determined polarographically from a known volume of this solution. Few ions produce waves that interfere with the tin wave, and those that do interfere are easily removed. The time necessary to complete one analysis is less than 2 hours, but on a routine basis averages under half an hour.

ANALYTICAL methods for the determination of tin are usually specific, and depend to a great extent not only on the amount of tin in the ore, but also on the number and kind of possible interfering ions. An investigation has been undertaken to develop a polarographic procedure for the rapid determination of small amounts of tin in any ore. A great deal is known about the polarography of tin (3), and successful attempts have been made to determine tin in alloys (2) and in ores (1). However, these procedures are either too long, or not of general enough applicability.

Both stannous and stannic tin can be reduced at the dropping mercury electrode. The reduction of stannous tin to the metal produces waves suitable for analytical purposes in supporting electrolytes of 1N hydrochloric acid, 1N nitric acid, 1N sulfuric acid. 1N sodium hydroxide, tartrate, and alkaline citrate. The reduction of stannic tin produces waves suitable for analytical purposes only in hydrochloric acid solutions where the concentration of chloride ion is greater than about 4N. Higher order tin-chloro complexes are formed with increasing chloride concentrations until the chlorostannate complex predominates (5). This highest order chloro complex produces two waves upon reduction, both of which are diffusion controlled. The first wave occurring at a half-wave potential of -0.25 volt vs. S.C.E. results from the reduction of the chlorostannate ion to the chlorostannite ion, and the second wave at a half-wave potential of -0.52volt vs. S.C.E. results in complete reduction to the metal. The second wave is best for analytical purposes.

#### APPARATUS AND REAGENTS

Polarographic data were obtained from a Leeds & Northrup Electro-Chemograph Type E, and an H-type polarographic cell with a saturated calomel electrode. The cell was kept at a temperature of  $25.0^{\circ} \pm 0.1^{\circ}$  C. in a constant temperature water bath. Dissolved oxygen was removed satisfactorily by bubbling nitrogen through the solution for 10 minutes before each polarographic determination. Oxygen was removed from the nitrogen stream by bubbling the stream through a vanadous sulfate solution (6). Characteristic polarographic properties of the capillary used were: drop time, 4.50 seconds per drop; *m* for the capillary, 1.59 mg. per second; and 1.75 mg.<sup>2/3</sup> sec.<sup>-1/2</sup> for  $m^{2/3}t^{1/6}$  at h = 65.8cm. Approximately 6N hydrochloric acid was the supporting electrolyte employed in all cases. CONSTANT BOILING HYDROCHLORIC ACID. Add 1000 ml of

CONSTANT BOILING HYDROCHLORIC ACID. Add 1000 ml. of concentrated hydrochloric acid (specific gravity, 1.19) to 850 ml. of distilled water and boil for one half hour. GELATIN SOLUTION, 2.0%. Dissolve 2.0 grams of gelatin in about 90 ml. of hot water. Cool and dilute to 100 ml. The standard tin samples used were Mallinckrodt's granulated

The standard tin samples used were Mallinckrodt's granulated 20-mesh tin metal, Baker's Analyzed stannous chloride, National Bureau of Standards cast-bronze standard sample No. 52c containing 7.85% tin, 89.25% copper, and 0.76% nickel; and a cassiterite sample containing 77.9% tin.

#### PROCEDURE

Thoroughly mix 1 gram of -100-mesh tin ore or other tin sample with 8 grams of sodium peroxide in an iron crucible. If the tin is in solution, evaporate to dryness first, or if much organic matter is present, roast the ore at about 725° C. Fuse the contents as quickly as possible over a Tirrell burner, allowing it to be at a bright red heat for 1 minute. During this 1-minute period the crucible should be swirled with the aid of a pair of tongs to ensure complete mixing of the sample with the molten sodium peroxide. Cool the crucible and its contents and place them in a 250-ml. beaker containing 150 ml. of distilled water. Heat the solution to its boiling point to dissolve the melt out of the crucible, and then remove the iron crucible from the solution with a pair of platinum-tipped tongs using about 25 ml. of distilled water from a wash bottle to wash the small amount of adhering solution from the crucible to the rest of the solution. Cool to room temperature and transfer the contents of the beaker to a 200-ml. volumetric flask. Use about 25 ml. of distilled water to rinse the remaining contents of the beaker into the volumetric flask and make up to the mark.

Filter about 50 ml. of this solution through a dry filter paper into a small dry beaker. Pipet 25 ml. of the filtrate into a 50-ml. volumetric flask and make up to the mark with concentrated hydrochloric acid. If the sample contains more than 2% tin, add 0.1 ml. of the prepared 2% gelatin solution before making up to the mark. Make a polarogram of the solution over the range of -0.4 to -0.8 volt vs. S.C.E. Convert the wave height to microamperes and find the per cent tin from the following equation:

% Sn = 1.075  $I_d$  (µa.)/sample weight (grams)

#### **RESULTS AND DISCUSSION**

The value of  $I_d/C$  for different tin samples shows excellent reproducibility considering the wide variety of samples used. For 14 determinations of the value of  $I_d/C$  on four different samples the range was 4.34 to 4.46, the average 4.40, and the coefficient of variation  $\pm 0.93\%$ . It makes little difference in what form the tin occurs, because it is all oxidized to the plus four oxidation state by the procedure employed and determined polarographically as the complex chlorostannate ion.

Table I.	Relationship	of Diffusio	n Current to	o Concen-
tration of	Various Stan	dard Tin Sa	amples in Hy	drochloric
	Acid and 0.0	004% Gelat	in at 25° C.	

Sample	Tin Conen., <i>C</i> , Millimoles/Liter	Diffusion Current $I_d$ , $\mu a$ .	$K = I_d/C$ , Dif- fusion Current, $\mu a./Millimole/$ Liter
Tin metal (100% Sn)	$\begin{array}{c} 0.0256 \\ 0.234 \\ 1.162 \\ 5.60 \end{array}$	$\begin{array}{c} 0.114 \\ 1.020 \\ 5.16 \\ 24.3 \end{array}$	$     \begin{array}{r}       4.46 \\       4.36 \\       4.44 \\       4.34 \\     \end{array} $
Cassiterite (77.9% Sn)	$\begin{array}{c} 0.104 \\ 0.852 \\ 5.64 \end{array}$	$0.457 \\ 3.74 \\ 24.9$	4,39 4,39 4,42
Stannous chloride assayed 99.2% SnCl <sub>2</sub> .2H <sub>2</sub> O (52.4% Sn)	$\begin{array}{c} 0.122 \\ 0.585 \\ 2.51 \end{array}$	$0.535 \\ 2.57 \\ 10.9$	$\begin{array}{c} 4.38 \\ 4.40 \\ 4.35 \end{array}$
National Bureau of Standards cast- bronze standard sample No. 52c (7.85% Sn)	$\begin{array}{c} 0.0147 \\ 0.174 \\ 0.832 \\ 2.31 \end{array}$	$\begin{array}{c} 0.0653 \\ 0.777 \\ 3.63 \\ 10.2 \end{array}$	$\begin{array}{c} 4.44 \\ 4.46 \\ 4.36 \\ 4.43 \end{array}$

The concentration range of the tin for which this procedure may be employed is given in Table I. As the values of concentration fall on a good straight line when plotted against the diffussion current, it is felt that higher and lower percentages of tin can be determined by extrapolation of this straight line. The concentration range can also be easily varied by the size of the aliquot taken after the filtration of the sodium hydroxide-insoluble cations.

The tin is not adsorbed or coprecipitated with the sodium hydroxide-insoluble cations. These precipitates consisting almost completely of the ferric hydroxide from the iron crucible are approximately of the same quantity for each determination. Since there is no trend in the constant of the ratio of the diffusion current to the concentration of the tin, no tin is lost in this step of the procedure.

If a supporting electrolyte containing approximately 6N hydrochloric acid is used, few ions interfere with the tin wave. Over 30 of the more common cations were tested for possible interfering effects by adding small amounts of the material to 100 ml. of 6Nhydrochloric acid and observing whether a polarographic wave was obtained in the region of the tin wave. It was known that nickel, tungsten, vanadium, and lead would produce possible interfering waves.

Nickel is quantitatively separated from tin by precipitation as the hydroxide upon addition of water to the sodium peroxide melt. One tenth of a gram of nickel chloride was added to 0.0551 gram of granulated tin metal. A polarogram made according to the above procedure gave a diffusion current for tin of 5.20  $\mu$ a. and a value of  $I_d/C$  equal to 4.47. The half-wave potential for nickel in this supporting electrolyte is -0.59 volt vs. S.C.E. The half-wave potential for tin under the same conditions is -0.54volt vs. S.C.E.

Tungsten is not eliminated. It produces a wave that interferes with the tin wave. The tungsten may be removed easily, however, by filtering the tungstic acid in the presence of cinchinone from the sodium peroxide solution, which has been made slightly acid by the addition of a small amount of hydrochloric acid. The tungsten may then be dissolved in constant boiling hydrochloric acid and determined polarographically. Filter paper should not be used in this separation because the decomposition products formed by its reaction with acids produce a wave that interferes with the tungsten wave. One tenth of a gram of sodium tungstate was added to 0.0547 gram of granulated tin metal. A diffusion current of 5.12  $\mu$ a. was obtained for the tin wave upon removal of tungsten, giving a value of  $I_d/C$  equal to 4.44. The half-wave potential for tungsten in this supporting electrolyte is -0.60 volt vs. S.C.E.

Vanadium can easily be separated from the tin, if present. A good indication of its presence is shown by the characteristic vanadium color of the solution produced upon the addition of water to the sodium peroxide melt, or from noticing that the tin and vanadium wave starts at a much more positive value and is much more drawn out than the wave produced by the tin alone. Starting the polarogram at -0.40 volt vs. S.C.E. a straight line is obtained always to the beginning of the reduction of the tin. With even small amounts of vanadium present this portion of the wave will be curved. As there is a large amount of ferric hydroxide produced from the decomposition of the iron crucibles, the vanadium may be precipitated quantitatively upon the addition of ammonium hydroxide to the sodium peroxide melt and water solution. Ammonium hydroxide alone does not precipitate vanadium; the ferric hydroxide must be present. One tenth of a gram of ammonium vanadate was added to 0.0550 gram of granulated tin metal. A diffusion current for the tin of 5.08  $\mu$ a. was obtained giving a value of  $I_d/C$  equal to 4.38. The halfwave potential for vanadium in this supporting electrolyte is -0.46 volt vs. S.C.E.

Lead gives a half-wave potential of -0.55 volt vs. S.C.E. in the supporting electrolyte used here. Advantage is taken of the property of ferric hydroxide to occlude small amounts of lead so that it does not interfere with the tin wave. Wilkie (7) found that five parts of ferric hydroxide removed one part of lead from solution. One tenth of a gram of lead nitrate was added to 0.0548 gram of granulated tin metal. A diffusion current of 5.13  $\mu$ a. was obtained for the tin wave giving a value of  $I_d/C$  equal to 4.44. Since large amounts of ferric hydroxide are formed from the fusion in the iron crucible, large amounts of lead can be tolerated. However, if very large amounts of lead are present, the lead wave may be subtracted from the tin wave by a method proposed by Lingane for the determination of tin in copper-base alloys (4).

It was believed that in addition to nickel, tungsten, vanadium, and lead, copper, arsenic, and molybdenum also interfere with the tin wave obtained. One tenth of a gram of each of these metals was added to a tin sample, and the tin determined. No change in the value of  $I_d/C$  for the tin wave was found for any of these additional metals. The National Bureau of Standards cast-bronze standard sample No. 52c contained 89.25% copper, and was used satisfactorily as a standard. Arsenic(V) is not reduced at the dropping mercury electrode. Molybdenum(VI) produces a wave far removed from the tin wave in this supporting electrolyte.

Aluminum, silver, gold, boron, barium, bismuth, calcium, cadmium, cobalt, chromium, iron, mercury, magnesium, manganese, phosphorus, platinum, rhodium, antimony, strontium, titanium, uranium, zinc, and zirconium were not expected to interfere in this tin analysis. However, a mixture of these elements in their various oxidation states was prepared and added to a tin sample. No effect on the shape of the tin wave or  $I_d/C$  was observed. A polarogram made with these possible interfering elements present gave a diffusion current of 5.23  $\mu$ a. for 0.0553 gram of granulated tin metal and a value of  $I_d/C$  equal to 4.48.

If it is necessary to determine iron or some other element in the ore that may be precipitated from an alkaline solution, the following type of separation may be employed:

Fuse the sample in the usual manner in a nickel crucible. After the melt is dissolved in water, the iron and other substances insoluble in sodium hydroxide are filtered off and determined by any appropriate procedure. The tin in the filtrate may be determined by boiling down the filtrate to a volume less than 50 ml., during which time concentrated hydrochloric acid is added so that the final solution is constant boiling hydrochloric acid. This solution is placed in a 50-ml. volumetric flask, and made up to the mark with constant boiling hydrochloric acid.

Lingane (5) suggested the use of a supporting electrolyte of 4Nammonium chloride and 1N hydrochloric acid to provide a high chloride concentration and a low hydrogen ion concentration. This results not only in the formation of the highest order chloro complex, but also the creation of a small enough hydrogen ion concentration to allow the formation of a well-defined diffusion current plateau for the tin wave before the start of the hydrogen wave. In this procedure the concentration of chloride ion is high, about 6N from the hydrochloric acid added (only 2.5 ml. of concentrated hydrochloric acid is used for neutralization of the sodium hydroxide). Lingane's supporting electrolyte is not used. because the final solution is almost saturated with sodium chloride, which produces the same effect on the tin wave as the ammonium chloride. For samples containing more than 0.01% tin, the hydrogen wave is far removed from the tin wave. However, at very small tin concentrations the tin and hydrogen waves approach each other, because the potential of the hydrogen wave varies with the magnitude of the current. This difficulty may be overcome by increasing the weight of the sample, increasing the chloride ion concentration with ammonium chloride, and decreasing the normality of the hydrochloric acid, or increasing the size of the aliquot of alkaline solution containing the melt.

The half-wave potential of the tin in the supporting electrolyte

used is -0.54 volt vs S.C.E. This value does not vary with the tin concentration over the range of concentrations listed in Table I. In all cases the half-wave potentials are well within the range of -0.53 to -0.55 volt vs. S.C.E. The half-wave potential increases to more negative potentials as the hydrogen ion concentration decreases.

Although this procedure has been developed for the analysis of tin ores, there is no reason to suppose that it could not be applied to tin alloys and other tin-containing materials; especially when the tin concentration is small and there are a large number of interfering ions. Over 200 various tin ores containing 0.01 to 10% tin have been analyzed with a standard deviation always less than 2%. An average time for one analysis is less than half an hour on a routine basis and under 2 hours for one complete analysis.

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## **Polarography in Molten Ammonium Formate**

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A wide variety of inorganic compounds has been investigated polarographically in molten ammonium formate at 125° C. Among the compounds studied were uranium, thorium, and plutonium, as well as typical fission products such as zirconium and the rare earths. Possible applications to qualitative and quantitative analyses of both water-soluble and water-insoluble inorganic compounds are suggested by the polarographic results obtained. Results indicate the relative ease of reduction of the various ionic species in the molten ammonium formate system under the conditions prevailing in this investigation.

**I** ONAQUEOUS polarography can be applied to advantage in the analysis of many organic substances that are insoluble in water. Polarography in nonaqueous solvents performed at room temperature often results in decreased sensitivity due to the lower diffusion coefficients of the reducible species as well as greater difficulty in removing interfering dissolved oxygen. Both of these disadvantages can be minimized if the boiling point of the nonaqueous solvent permits the polarographic determination to be made at higher than room temperature.

Nachtrieb and Steinberg (9, 10) report the use of ternary salt mixtures acting as both solvent and supporting electrolyte in qualitative and quantitative analysis of inorganic compounds by application of dropping mercury polarography in the temperature range  $125^{\circ}$  to  $150^{\circ}$  C. Lyalikov and Karmazin (7) report the use of solid microelectrodes in molten salt polarography at still higher temperatures. Apparently even under the latter conditions, concentration-dependent current-voltage curves are obtainable in certain cases. The present status of polarography in fused salt media has been reviewed by Lingane (6).

The main disadvantage of fused salt polarography is the tendency for reaction between the constituents of the system at high temperatures. In many cases the choice of salt and electrode system will help eliminate or control these side reactions, so that reproducible polarographic results can be obtained. Under these conditions, advantage can be taken of the excellent inorganicsolubility properties afforded by the use of molten salt media—for example, ordinarily insoluble oxides and carbonates are readily dissolved in many fused salt media.

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In the present investigation, molten ammonium formate was chosen as the solvent-supporting electrolyte system, as it afforded the advantage of an operating temperature of  $125^{\circ}$  C., which permitted use of a dropping mercury electrode without employing a ternary eutectic salt mixture. The heat stability and versatile solubility properties permitted a broad coverage of compounds investigated. In addition to demonstrating the possible application of fused salt polarography to the analysis of a variety of inorganic compounds, the results obtained indicate the relative ease of reduction under these conditions of the various component metal ions studied.

#### EXPERIMENTAL

**Polarography.** Polarographic measurements were made at  $125^{\circ} \pm 1^{\circ}$  C. with a Leeds & Northrup Electro-Chemograph, Type E. Temperature control was maintained using Arochlor (Monsanto Chemical Co.) fluid in a large stainless steel constant temperature bath (Precision Scientific Co., Catalog No. 10192). The solutions were deoxygenated by passing dry nitrogen gas through the molten ammonium formate for 10 minutes. A simple dropping mercury electrode assembly employing a mercury-pool anode-type cell (see Figure 1) with ground-glass connections was used. A capillary (E. H. Sargent Co., S-29351) was sealed into the end of the electrode assembly with Sauereisen No. 1 paste, (Sauereisen Cements Co., Pittsburgh, Pa.), followed by a coating of Fisher High-Pyseal (Eimer and Amend Co.) to seal the pore space within the rigid Sauereisen union. Capillary characteristics and polarographic properties employed at  $125^{\circ} \pm 1^{\circ}$  C. were: m = 3.04 mg, per second, drop time = 2.7 seconds at h = 37.5 cm., and  $m^{2/3}t^{1/6} = 2.10$  mg.<sup>2/3</sup> sec.<sup>-1/2</sup>

Under the conditions employed, the molten ammonium formate yielded a useful reduction voltage range of +0.1 to -0.9 vs. a mercury pool. A similar voltage span of -0.1 to -1.1 vs. an external anode containing mercury, the ternary salt mixture, and potassium chloride was observed by Nachtrieb and Steinberg (10).

Freshly opened sample bottles of c.P. anhydrous ammonium formate (Baker & Adamson) were used in each polarographic run. Check polarograms were made from time to time on the ammonium formate alone to ensure its continued purity. Passing nitrogen gas through the solutions at the elevated temperature removed traces of water.

To ensure anhydrous conditions during sample preparation, the ammonium formate and the easily hydrolyzed materials such as uranium(III) chloride, uranium(IV) chloride, zirconium chloride, thorium chloride, aluminum chloride, and the anhydrous rare earth salts were all weighed out and melted within a dry box. Polarography on the plutonium compounds was performed inside an alpha-box.