BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 734—737 (1971)

The Determination of Tin in Tin Metal and in Zircaloy by Precise Coulometric Titration

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(Received October 12, 1970)

The purities of tin metals are determined directly by precise coulometric titration. The sample is dissolved with hydrochloric acid in a nitrogen atmosphere. The solution is then introduced into a hot antimony column. The reduced tin(II) ions are titrated with electrolytically-generated iodine. The titration is accomplished in a special cell by the use of which any disturbance of atmospheric oxygen is avoided. The titration efficiency under these acidic media was decreased when the current density was increased more than several mA/cm^2. The results obtained by two different analysts for the sample of the pure tin metal (5-nine) were 99.996 and 99.991%. The standard deviations of the results were 0.025 and 0.016% respectively. The tin in the other tin metals and in Zircaloy samples was determined satisfactorily without the use of any experimental factor.

The purity of a metal has generally been estimated by analyses of the impurities in the sample and then by the substraction of the sum of their contents from 100%.

In order to distinguish a sample of 99.9% purity from that 99.8% pure by the direct analysis of the bulk constituent, the relative error of the determination must be less than 0.05%. This is, however, less than the maximum accuracy of ordinary analytical methods.

The maximum accuracy of a precise coulometric titration is 0.003% as a standard deviation, while the value of 0.007% is obtained in ordinary laboratories.[1] This method has been used to estimate the purities of several primary standard substances for a volumetric method directly. The accuracy of this method, however, has not been yet used to estimate other metallic

1) T. Yoshimori and I. Matsubara, This Bulletin, **43**, 2800 (1970).

samples, *etc.*

Only one relevant report could be found in the literature; in it the purity of a tin metal was determined directly by the following volumetric method:[2] tetravalent tin was reduced to the divalent state with metallic nickel under a carbon dioxide atmosphere. Most of the tin(II) ions were then oxidized with an accurately-weighed amount of pure potassium iodate, while the remainder were titrated with a standard solution of potassium iodate. Because of the sensitiveness of tin(II) ions to the oxygen in air, this method sometimes gives lower results. A small amount of air on the surfaces of the potassium iodate crystals, and also the oxygen dissolved in the standard solution, may be introduced into the sample solution; they serve to oxidize the tin(II) ions.[3]

Caton and Freund[4] determined the content of tin in Zircaloy by coulometric titration. They used a hot antimony column for the reduction of tetravalent tin to the divalent state, and then titrated the tin(II) ions with electrolytically-generated iodine. Increasing the accuracy for the measurements of the electricity, the present authors determined the purities of several tin metals directly by precise coulometric titration using a biamperometric end-point location. Several improvements of the ordinary analytical treatments were necessary to obtain more accurate results.

Experimental

Apparatus. A sample tin metal was dissolved with hydrochloric acid under an atmosphere of nitrogen. The apparatus is shown in Fig. 1. Figure 2 shows in detail the antimony column used to reduce tin(IV) ions. The column was heated electrically with a flexible heater, while its temperature was controlled by the adjustment of the voltage applied to the heater.

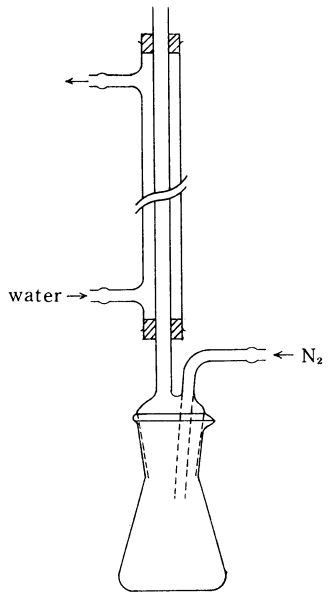

Fig. 1. Decomposition apparatus.

Figure 3 shows the coulometric titration cell. All the steps in the preparation of the electrolyte in the cell and in the washing of the cell could be performed without any disturbance of the atmospheric oxygen.

The chromium(II) chloride solutions were useful for removing traces of the oxygen in nitrogen (Fig. 4). The solutions and the liquid zinc amalgams were stirred continuously

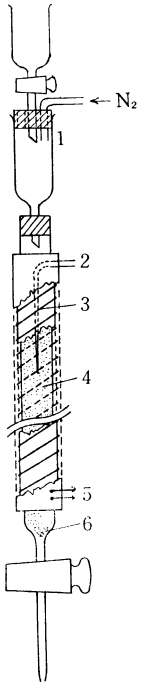

Fig. 2. Reduction column.

1. Funnel 2. Thermocouple 3. Heater
4. Antimony (20—30 Mesh) 5. To variable voltage supply 6. Glass wool

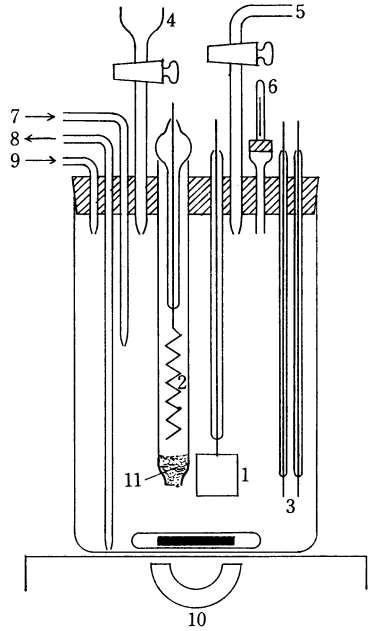

Fig. 3. Titration cell.

1. Generator electrode 2. Auxiliary electrode
3. Indicator electrodes 4. Reductor column
5. 1M KI solution inlet 6. Bunsen valve 7. N_2
8. To aspirator 9. Washing water
10. Magnetic stirrer 11. Silica gel membrane

2) S. Kalimann, *Anal. Chem.*, **22**, 729 (1950).
3) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley, New York (1929), p. 239.
4) R. D. Caton and H. Freund, ASTM Special Technical Publication. No. 272, 207 (1959).

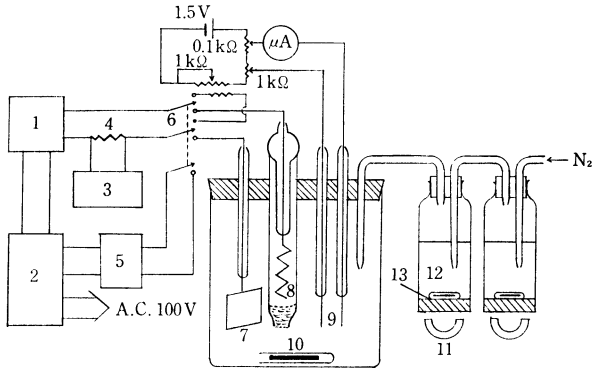

Fig. 4. Whole assembly.
1. Constant current source 2. Constant voltage source 3. Potentiometer 4. Standard resistor 5. Electronic stop watch 6. Switch 7. Generator electrode 8. Auxiliary electrode 9. Indicator electrodes 10. Titration cell 11. Magnetic stirrer 12. $CrCl_2$ solution 13. Liquid Zn amalgam

with magnetic stirrers. This stirring was advisable to keep the chromium ions under the divalent state.

A precise potentiometer and a standard resistor of 1 ohm were used to measure the electrolytic current. Their accuracies had been certified within 0.05% and 0.01% respectively. The constant-current source used here was the same instrument as that shown previously.[1,5] If we consider the errors of the above measuring devices as 3σ, a relative standard deviation of 0.02% may be expected for the measurement of the current, including the reliability of the standard cell used.

An electronic stop watch based on the frequency of a quartz crystal (Nippon Electric Co., Type 102) was used to measure the time of the electrolysis. The relative error, based on the time measurement, did not exceed 0.01%.

The "dead-stop" method using a microammeter (fullscale 10 μA) was used to locate the end-point of the titration. The whole assembly of the apparatus is illustrated in Fig. 4.

The indicator electrodes were frequently washed by dipping them into concentrated nitric acid for 20 minutes. Platinum foil (about 114 cm^2) was used as the generating electrode.

A silica-gel diaphragm[6] was advisable for the present purposes. It was prepared by the following procedure: glass wool was packed tightly at the bottom of the cathode compartment and then soaked in a sodium silicate solution (50%). Hydrochloric acid (3N) was then repeatedly introduced into the compartment until the acid did not leak through the diaphragm. The diaphragm was stored in hydrochloric acid (3N) and could be used several times.

The other precautions in measuring the electricity and the weighing of the sample were the same as those reported previously.[1]

Reagents. All the reagents were of an analytical grade, and all were used without further purification. The antimony metal (20—30 mesh) was washed with boiling 3N hydrochloric acid and then packed in a glass tube (Fig. 2). The purity of the metal was higher than 99.9%.

Procedure. *Dissolution of the Sample*: A sample tin metal was weighed into the decomposition flask (Fig. 1). Nitrogen was allowed to flow through the flask to remove the atmospheric oxygen. Then 20 m*l* of concentrated hydrochloric acid was added; a reflux condenser was necessary to prevent any loss of tin tetrachloride.

The addition of a small piece of an antimony metal to the flask was advisable in order to dissolve the pure samples more quickly. If necessary, the flask was warmed gently. When any black residue was found in the flask, a drop of a hydrogen peroxide solution (30%) was added to the flask and the solution was heated more gently. In this case, the introduction of the nitrogen was unnecessary. Zircaloy samples were placed in a Kjeldahl flask and then dissolved with hot hydrochloric acid and with the drop-by-drop addition of hydrofluoric acid.

After the dissolution of the sample was complete, the solution was cooled to room temperature under an atmosphere of nitrogen.

Preparations of Column and Cell: The solution in the column was boiled for 20 min. Oxygen-free nitrogen was then allowed to flow through the cell. After the temperature of the column had been adjusted to about 100°C, the column was washed with about 50 m*l* of 3N hydrochloric acid. Then the washings in the cell was removed carefully with an aspirator, avoiding any introduction of atmosperic oxygen into the cell. From this period to the end of the titration, the purified nitrogen should be allowed to flow through the cell continuously at a rate of about 150 m*l* per min.

Twenty milliliters of concentrated hydrochloric acid and 50 m*l* of a 1M potassium iodide solution freed from atmospheric oxygen were added to the cell from their reservoirs. Pure nitrogen was introduced into the solution for more than 30 min, and then the gas was allowed to flow over the solution to prevent any spattering of the solution in the cell. If the hydrochloric acid or the potassium iodide solution contained any oxidizing materials (for example, dissolved oxygen or chlorine), some iodine was produced in the mixture. The error based on this iodine could be corrected by reading the indicator current during this period and by continuing the coulometric titration to the point which the indicator current after the end-point was again raised to the same value as in the previous measurement.

Reduction of the Tin(IV) Ion and Coulometric Titration: A sample solution prepared as above was poured into the funnel on the column and then allowed to flow through the column at a rate of 1 ml/min. The flask and the column were washed thoroughly with 150 m*l* of 3N oxygen-free hydrochloric acid.[7] This was done by the introduction of the nitrogen over the solution on the top of the column.[8] From the last period of the washing, the tin(II) ions could be titrated with the coulometrically-generated iodine. During the titration, the generator current was kept constant. This method has already been described elsewhere.[1]

After the end-point, the indicator current began to rise. At this moment, the generator current was stopped; then both the indicator current and the time of the electrolysis were recorded. Again the solution was titrated for a short period, after which both the indicator current and the time were recorded. This short-period titration was repeated several times in order to obtain the titration curve clearly.

Results and Discussion

Dissolution of the Sample. The sample was dissolved in various kinds of glassware. A fairly large loss of tin ions by the spattering or by the vaporization of tin(IV) chloride was found even by the use of a

5) T. Yoshimori, Y. Hino, and T. Takeuchi, *Bunseki Kagaku*, **15**, 1234 (1966).
6) G. Marinenko and J. K. Taylor, *J. Research Natl. Bur. Standards*, **67A**, 453 (1963).
7) M. A. Salam Khan and W. I. Stephen, *Anal. Chim. Acta*, **41**, 43 (1968).
8) C. Yoshimura, *Nippon Kagaku Zasshi*, **74**, 818 (1953).

tall-form beaker or an Erlenmeyer flask. These losses of tin were overcome by the introduction of nitrogen into the flask to prevent the oxidation of the tin(II) ions. The dissolution time for the sample of high purity was shortened considerably by the addition of a piece of an antimony metal to the flask.

Column and Its Use. Instead of the antimony column, several other metals have been used for the reduction of tetravalent tin. Aluminum, iron, and nickel, however, all have relatively low hydrogen overvoltages and produce much hydrogen during the reduction process. Therefore, none of them can be used as the constituent of the column. Lead is sometimes used as the reducing material for the tin(IV) ion. This metal, however, was not adopted for the present purpose because lead ions dissolved in the solution produce lead chloride as a precipitate.[4]

Antimony was thus chosen as the constituent of the column. The flow rate of the sample solution was adjusted between 0.5 ml/min and 1 ml/min so as to accomplish the complete reduction of the tin(IV) ions.

The ordinary reduction procedure by boiling with metals was not successful because the introduction of air into the tin(II) solution was unavoidable during the process of separating the residual metals from the solution, and also while setting up the cell for the coulometric titration. The residual metals in the solution reduced the excess iodine generated after the endpoint and disturbed the location of the point.

Analysis of Pure Tin Metal (five-nine). A commercially-obtainable tin metal (so-called five-nine) was analyzed by the proposed method. The results of the analysis of the impurities obtained by the authors and by the producer are shown in Table 1. The purities obtained by this method are tabulated in Table 2. The relative standard deviation, as calculated from these results, was less than 0.02%.

Current Efficiency: First, the current density for the generation of the titrant was 13.3 or 8.8 mA/cm^2. In this case, the results obtained were rather high. This indicates that the titration efficiency of tin(II) ions with the electrolytically-generated iodine is less than 100% in this electrolyte.

Marinenko and Taylor[10] measured the current efficiencies for the generation of iodine in various solutions and showed that the efficiencies were somewhat decreased in acidic solutions. Recently Iritani *et al.*, in potentiometrically titrating mixtures of iodide ions and iodine with a potassium iodate standard solution in acidic media, they found that iodine monochloride was formed in the media with more than 3N hydrochloric acid.[11] With the current densities of *ca.* 10 mA/cm^2, some iodine monochloride may perhaps be formed; its current efficiency is unknown.

With reference to the results shown in Table 2, the authors considered that the titration efficiency of tin(II) ions with the electrolytically-generated iodine was 100% when the current density was kept below 1 mA/cm^2.

Oxygen in the Washing Solution: The oxygen in the washings produces hydrogen peroxide by reacting with the antimony in the column[7] and oxidizes the tin(II) ions. This disturbance can be avoided by the introduction of pure nitrogen into the solution on the top of the column.

Coulometric Titration of Several Tin Metals. The purities of the tin metals of various grades were analyzed by the proposed method. The results obtained are shown in Table 3. It can be concluded from these results that the proposed method is satisfactory for estimating the purities of various tin metals directly.

Table 1. Some analytical results of pure tin metals (5-nine) (ppm)

Pb[a]	Cu[a]	O[b]	H[c]	Total sum
1	<1	8	1.1	11

a) Obtained from the producer (spectroscopic method).
b) Obtained in the authors' laboratory by a carrier gas method.
c) The same as b, *cf.* Ref. 9.

Table 2. Direct determination of purity of the pure tin metal (5-nine) (Diaphragm: Silica gel)

Current density (mA/cm^2)	No. of exp.	Purity (%)	σ(%)
1	18	99.945[a]	0.028[b]
13	2	100.055	0.070
9	6	100.028	0.051
0.9	9	99.996[c]	0.025[b]
0.9	6	99.991[c]	0.016

a) Diaphragm was tissur membrane.
b) $\sqrt{V}$ value.
c) Obtained by the different analyst.

Table 3. Analytical results of tin metals and zircaloy samples

Sample	No.of Exp.	Sn Content (%)	σ(%)
Sn (99.7%)[a]	4	99.670	0.034
Sn (99.9%)[a]	3	99.907	0.024
Zircaloy 1	3	1.491	0.004
Zircaloy 2	3	2.148	0.003
Zircaloy 3	3	1.540	0.005
Zircaloy 4	4	0.875	0.005

a) Shown by the producer.

Determination of Tin in Zircaloy. The tin contents in Zircaloy samples were also determined by means of the authors' apparatus. The samples were dissolved in a Kjeldahl flask with hydrochloric and hydrofluoric acids. The results are shown in Table 3. The errors of the results are diminished considerably compared with the case of the value obtained previously.[4]

When the results were compared with those obtained in other laboratories, these values were found to be the highest. The authors believe that the difference shows the effect of the atmospheric oxygen on the tin(II) ions in the other volumetric procedure.[3]

The authors express their sincere thanks to Professor S. Hirano (Toyo University) and Professor T. Takeuchi (Nagoya University) for their valuable suggestion.

9) T. Yoshimori and S. Ishiwari, *Talanta*, **17**, 349 (1970).

10) G. Marinenko and J. K. Taylor, *Anal. Chem.*, **39**, 1568 (1967).

11) N. Iritani, Y. Takino, and N. Kuroda, *Bunseki Kagaku*, **18**, 583 (1969).