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AN EVALUATION OF THE TITRIMETRIC AND ATOMIC ABSORPTION DETERMINATION OF TIN IN THE CERTIFIED REFERENCE MATERIALS, MP-1 AND KC-1

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ATOMIC ABSORPTION DETERMINATION OF TIN IN THE CERTIFIED

REFERENCE MATERIALS, MP-1 AND KC-1

by

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ABSTRACT

An investigation has been undertaken into the determination of tin in the certified reference materials, MP-1 and KC-1, by the titrimetric and atomic absorption methods. The effect of the nature of the metal used to reduce Sn(IV) to Sn(II) in the titrimetric method has been evaluated.

It has been shown that there is no significant difference between the results obtained by the titrimetric method when properly applied and those obtained by the atomic absorption method using the standard additions technique. The mean value for tin in MP-1 and KC-1 by both methods are 2.43% and 0.683% respectively. The value for MP-1 is lower than the recommended value.

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Direction des Mines

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UNE EVALUATION DU DOSAGE DE L'ETAIN PAR METHODE TITRIMETRIQUE ET

D'ABSORPTION ATOMIQUE DANS LES MATERIAUX TYPES DE REFERENCE, MP-1 ET KC-1

par

H.F. Steger*

RESUME

L'auteur a entrepris des recherches sur le dosage de l'étain utilisant les méthodes titrimétrique et d'absorption atomique, dans les matériaux de référence MP-1 et KC-1. Il a évalué, par la méthode titrimétrique, l'action du caractère du métal, utilisé pour la réduction de Sn(IV) à Sn(II).

Il a été démontré qu'aucune différence significative n'existe entre les résultats obtenus par la méthode titrimétrique, lorsqu'elle est appliquée correctement, et ceux obtenus par la méthode d'absorption atomique utilisant l'étalonnage par ajouts dosés. La valeur moyenne de l'étain, donnée par les deux méthodes dans MP-1 et KC-1, est de 2.43% et de 0.683% respectivement. La valeur de MP-1 est plus basse que la valeur recommandée.

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INTRODUCTION

As part of the Canadian Certified Reference Materials Project sponsored by the Mines Branch, 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 difficulty that is generally experienced in the accurate determination of tin in ores [3-5] is illustrated by the wide range of values obtained in the inter-laboratory certification programs for these ores [1,2,6]. In particular, an assessment of the results for MP-1 indicated that certain modifications of the titrimetric (i.e., volumetric) method gave lower results than did the methods involving an instrumental finish. The same trend, but to a lesser magnitude, was also observed in the results for KC-1[2]. Consequently, this present investigation was undertaken to define the causes for the variation in the tin content of MP-1 and KC-1 with the type of method used.

Table I illustrates the correlation of tin results for MP-1 with the analytical methods used[6].

TABLE I

Correlation of Tin Results for MP-1 with Analytical Methods

Analytical Method	No. of Labs.	No. of Results	Mean % tin
Titrimetric			
Fe reduction	4	55[a]	2.48
Ni reduction	1	10	2.40
Al reduction	1	10	2.23
Pb reduction	4	40	2.22
Other	1	4	2.28
Total	11	119	2.36
Instrumental			
Polarographic	3	30	2.40
Atomic absorption	6	63[a]	2.58
X-ray fluorescence	2	20	2.39(2.27)[b]
Spectrophotometric	1	10[a]	2.49
Total	12	123	2.49

[a]Table I contains results that were obtained subsequent to the certification program[1]; ten by the Fe-reduction method, nineteen by atomic absorption spectroscopy and ten by spectrophotometry[7].

[b]One laboratory has re-submitted results that are appreciably lower than the original, thereby yielding a lower mean %Sn.

The results in Table I suggest that the effectiveness of the titrimetric method depends on the nature of the metal used to reduce Sn(IV) to Sn(II). This present investigation, therefore, included the determination of the tin content of MP-1 by the titrimetric method using iron, aluminum, nickel and lead as the reducing agent in an attempt to define the causes of any significant variation in the tin value of MP-1 with the nature of the reducing metal.

The tin value obtained by the instrumental methods is higher than that by the titrimetric method. A close assessment of the results by the individual instrumental methods, however, shows that the higher total value is, in fact, due to the larger number of atomic absorption results compared to those by the other methods*.

It was imperative, therefore, that an investigation of the effectiveness of the atomic absorption method to determine tin in MP-1 and KC-1 be undertaken.

PROCEDURES

Fusion decomposition of MP-1 and KC-1

Four grams each of sodium carbonate and sodium peroxide and 0.55 g or 2.00 g of MP-1 or KC-1 respectively were thoroughly mixed in a zirconium

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*The mean %Sn by spectrophotometry is also higher than that obtained by all titrimetric methods. However, because this method gave eleven results higher than, six in agreement with, and three lower than, the certified values for twenty-one other reference materials, there is a good probability that the value of 2.49% tin in MP-1 is also high.

crucible, fused over a blast burner and kept molten at red heat for one minute. When the melt had cooled, the crucible was transferred to a 600-ml (covered) beaker containing 200 ml of water. After being washed with concentrated hydrochloric acid and water, the crucible was removed and concentrated hydrochloric acid was added to the beaker until a pale yellow solution was obtained. This solution was diluted to approximately 400 ml with water, boiled to expel carbon dioxide and decompose residual peroxide and then rendered slightly ammoniacal by the dropwise addition of concentrated ammonium hydroxide. After the further addition of 5 ml ammonium hydroxide, the precipitate of hydrous oxides was allowed to stand for ten minutes, then filtered through a Whatman No. 541 paper and washed with hot water. The bulk of the precipitate was transferred to the original beaker with a jet of hot water and the small amount remaining on the paper was dissolved by repeated washing with hot 50% hydrochloric-2% hydrofluoric acid solution and water.

The walls of the beaker were washed down with 80 ml of concentrated hydrochloric acid and sufficient concentrated hydrofluoric acid was added to dissolve the gelatinous zirconium hydrous oxide. For the titrimetric determinations of tin, the resulting solution was transferred to a 500-ml Erlenmeyer flask and diluted to approximately 200 ml with water. For the determination of tin by atomic absorption spectroscopy, the resulting solution was cooled, transferred to a 250-ml volumetric flask and diluted to volume with water.

Titrimetric method

Apparatus:

500-ml Erlenmeyer flasks capped with a rubber stopper equipped with an L-shaped glass siphon tube.

Reagents

Standard tin solution: 3.000 g of high purity tin were dissolved in 100 ml of concentrated hydrochloric acid and 5 ml of 30% hydrogen peroxide with heating. The solution was cooled, an additional 100 ml acid was added and the solution was diluted to 1ℓ.

Potassium iodate titrant: Approximately 3.6 g potassium iodate, 10 g potassium iodide and 2 g sodium hydroxide were dissolved in water and diluted to 2ℓ.

Indicator solution: Five grams each of Thyodene and potassium iodide were dissolved in water and diluted to 100 ml.

Antimony trichloride solution: 1% w/v in concentrated hydrochloric acid.

Iron granules: British Chemical Standards No. 149/2 (tin content 0.002%).

Nickel powder:)
Aluminum foil:) Tin content less
)   than 0.01%.
Test lead shot:)

Procedure for the determination of tin in ores

Iron- and nickel-metal reduction

Five grams of iron granules or nickel powder and 8 drops of 1% antimony trichloride solution were added to the contents (prepared as above) of the 500-ml Erlenmeyer flask which were then boiled until most of the metal had dissolved. The flask was capped with the rubber stopper such that the outlet of the L-shaped tube was immersed in a saturated sodium bicarbonate solution and the boiling was continued for several minutes after the complete dissolution of the metal. The flask was then cooled to room temperature and finally in an ice bath. After removal of the rubber stopper, two sodium bicarbonate tablets and 10 ml of indicator solution were added to the flask and potassium iodate titrant was added to the blue starch-iodine end point.

Aluminum-metal reduction

Three grams of aluminum foil, rolled into a tight ball, and 5 drops of 1% antimony trichloride were added to the 500-ml Erlenmeyer flask which was then swirled continuously until the vigorous reaction had subsided. The flask was capped immediately and the contents boiled for ten minutes. Thereafter, tin was determined as in the iron-metal reduction.

Lead-metal reduction

Three grams of test lead shot and five drops of 1% antimony trichloride were added to the Erlenmeyer flask and the contents were boiled for 20 minutes.

Thereafter, tin was determined as in the iron-metal reduction.

Standardization of potassium iodate titrant

The potassium iodate titrant was standardized for each metal by the procedures described above. Herein, however, the 500-ml Erlenmeyer flask contained a suitable aliquot of standard tin solution, 80 ml of concentrated hydrochloric acid and sufficient water to give a volume of approximately 200 ml. The titer obtained was corrected by subtracting that obtained for a blank which was simultaneously carried through each reduction procedure.

Atomic absorption method

Apparatus:

Varian-Techtron AA5 atomic absorption spectrophotometer.

Reagents

Standard tin solution (STS): Same as for the titrimetric method. Other standard tin solutions, ST(n),n = 1,3, of lower tin concentration were prepared by diluting 3,5 and 10 ml of STS + 40 ml concentrated hydrochloric acid to 500 ml with water.

Determination of tin in ores

The widely accepted method of standard additions[8] was used in this study. Four 10-ml aliquots of the solution from the fusion of a single sample of the ore were mixed with a 10-ml aliquot of either 8% hydrochloric acid or the standard tin solutions ST(n), n = 1,3. The absorbance readings of the solution were plotted against the added concentration of tin, $[Sn]_{ADD}$ (Fig. 1). The graph obtained is the solid line. The "true" calibration curve would be parallel to it, but passing through the origin. The value of [Sn] in the sample may thus be read at C_{Sn}[8].

The absorbance of the diluted (but otherwise unmodified) aliquot is due to the tin present plus background absorbance. The spurious enhancement of the absorbance of the sample due to background absorbance can be determined by measuring the absorbance at the Sn resonance line of a tin-free synthetic solution of overall composition as close as possible to that of the sample solution. These synthetic
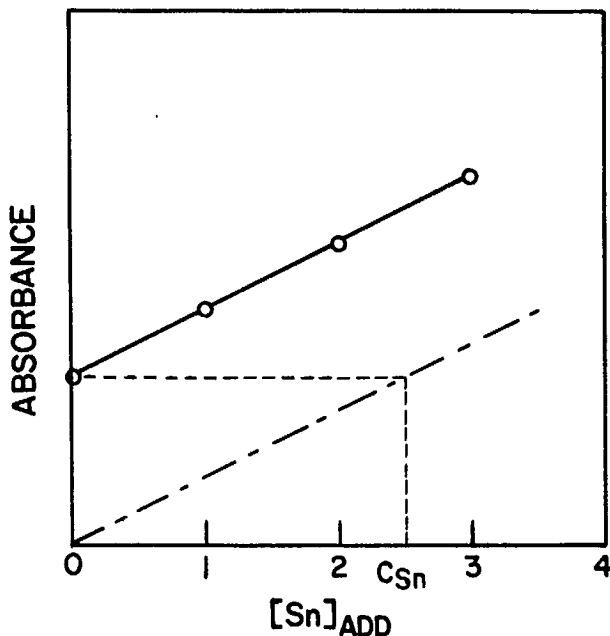

Fig. 1. — Method of Standard Additions

blank solutions were prepared from the oxides or anionic salts of the eight and five most abundant elements in MP-1 and KC-1 respectively. The appropriate mixtures were fused with sodium carbonate and sodium peroxide and thereafter treated in the same manner as samples of MP-1 and KC-1.

The tin content of MP-1 and KC-1 was determined in the following manner. A minimum of four samples of MP-1 were run at any one time. One "true" calibration curve for these samples was calculated by linear regression to give:

$$A_{Sn} - A = m[Sn]_{ADD} + b$$

where A and A_{Sn} represent the absorbance of the diluted but otherwise unmodified sample and tin-added sample respectively. The concentration of tin in the unmodified sample, C_{Sn}, is given by

$$C_{Sn} = \frac{(A - A_{bs}) - b}{m}$$

where A_{bs} represents the enhancement due to background absorbance and

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scatter. The %Sn in the ore is given by

$$\frac{\frac{1}{2} c_{Sn} \times 100}{wt \ ore} .$$

It should be noted that this formula is applicable only for the experimental condition of this present work.

All measurements were performed with an acetylene/nitrous oxide flame. Instrumental parameters such as lamp alignment, burner height, wavelength setting and acetylene/nitrous oxide fuel ratio were adjusted to optimize the sensitivity for tin.

RESULTS AND DISCUSSION

Because the variation in the tin content with the analytical method was appreciably greater for MP-1 than for KC-1, the investigation into the titrimetric method was concerned mainly with MP-1. It was assumed that the conclusions reached for MP-1 would apply also to KC-1. The titrimetric determination of tin in KC-1 was, therefore, restricted to the iron reduction technique. Both ores, however, were studied by atomic absorption spectrometry.

In order to avoid any possible bottle-to-bottle inhomogeneity, all titrimetric analyses of MP-1 were performed on subsamples taken from the same bottle. Because of complete consumption thereof, it was necessary to perform the atomic absorption determination of tin on a second bottle, the contents of which were also analyzed for tin by the Fe-reduction titrimetric method and found to agree with the first bottle. For KC-1, however, the contents of two bottles were analyzed.

Titrimetric method

Behaviour of reducing agents

The reduction of Sn(IV) to Sn(II) by both iron granules or nickel powder proceeds smoothly with continuous non-violent evolution of hydrogen gas. Approximately 25 minutes are required for complete dissolution of the metal. The nickel reduction is less satisfactory because of the dark green colour (due to Ni^{2+}) of the resulting solution which renders the blue iodine-starch end-point less well defined than for iron reduction.

The dissolution of aluminum, on the other hand, occurs in less than 5 minutes and because of the vigorous reaction, the flask must be shaken continuously to control the frothing due to the evolution of hydrogen gas. Indeed, if the aluminum foil is not pressed into a tight ball, the reaction becomes uncontrollable. Just subsequent to the dissolution of the aluminum, a fine black precipitate may be observed; specimens of this have been isolated and found, by X-ray diffraction, to be β-tin. Great care must be taken to ensure that the subsequent period of heating is long enough to dissolve this tin completely or the results obtained will be low. Undissolved tin metal will, of course, not be titrated with the iodate solution.

The reduction of Sn(IV) by test lead shot proceeds with slow evolution of hydrogen gas, but no visible dissolution of the lead. The solutions reduced by lead were found to be extremely sensitive to air-oxidation and extra care was taken to ensure that the flasks were tightly capped. Indeed, on the basis of the experience described above, the author recommends that iron metal be used as the reductant in the titrimetric determination of tin.

Statistical treatment of results

The results of the titrimetric determination of tin in MP-1 are summarized in Table II. There does appear to be some variation in the tin values of MP-1 with the nature of the metal-reducing agent. The magnitude of this variation, 0.05% Sn, is appreciably less than that, 0.26% Sn, observed in the inter-laboratory certification program[6]. It should be pointed out that, with the exception of aluminum, the trend in the value of %Sn with a change in the metal-reducing agent is the same in the present investigation and in the certification program.

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TABLE II

Results of Titrimetric Analysis of MP-1 (Bottle #1)

| Sample | % Sn Reducing Agent | | | |
	Fe	Al	Ni	Pb
1	2.44	2.44	2.40	2.39
2	2.39	2.43	2.41	2.40
3	2.40	2.44	2.39	2.38
4	2.36	2.43	2.40	2.39
5	2.40	2.46	2.38	2.37
6	2.44	2.43	2.41	2.40
7	2.48	2.43	2.40	2.39
8	2.43	2.44	2.39	2.40
9	2.43	2.45	2.40	2.38
10	2.45	2.44	2.41	2.39
11	2.43			
12	2.44			
13	2.42			
14	2.41			
15	2.41			
16	2.42			
17	2.42			
18	2.42			
19	2.42			
Average	2.422	2.439	2.399	2.389
95% confidence limits	2.41-2.43	2.43-2.45	2.39-2.41	2.37-2.40
Overall average	2.41 (2.37-2.45)			

A one-way analysis of variance of the 49 results for tin in Table II showed that there is a significant chemical difference with respect to the nature of the metal-reducing agent. Herein, the results were treated as though they satisfy the model[9].

$$x_{ij} = \mu + y_i + e_{ij}$$

where

x_{ij} = the jth result reported for metal i;

μ = the true value that is estimated by the overall mean $\overline{x}$;

y_i = the discrepancy between the mean of the values using metal i and μ; and

e_{ij} = the discrepancy of x_{ij} from the mean of the values using i.

It is assumed in this analysis that both y_i and e_{ij} are normally distributed, with the means of zero and variances of ω^2 and σ^2, respectively. The existence of ω^2 can be detected by comparing the ratio of "between-metal" mean squares to "within-metal" mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

The true value, μ, can be estimated by the overall mean $\overline{x}_{..}$, thus

$$\overline{x}_{..} = \sum_{i=1}^{k} \sum_{j=1}^{n_i} x_{ij}$$

with the variance of this overall mean being given by:

$$V[x_{..}] = \frac{\sum_{i=1}^{k} n_i}{\left(\sum_{i=1}^{k} n_i\right)^2} \omega^2 + \frac{1}{\sum_{i=1}^{k} n_i} \sigma^2$$

where

n_i = the number of results reported for metal i; and

k = the number of metal-reducing agents.

The 95% confidence intervals were then calculated according to the number of metal-reducing agents. The overall mean and corresponding 95% confidence limits are shown in Table II.

Tin-equivalent of iodate titrant

One of the more important factors in the titrimetric determination of tin is the standardization of the potassium iodate titrant. Theoretically, the tin equivalent value of the iodate (mg/ml), TE_{Sn}, should be constant for all metal-reducing agents. That this is not so is illustrated in Table III.

TABLE III

Tin-Equivalent of Iodate

Metal-Reducing Agent	TE_{Sn} (mg/ml)
Al	3.020
Fe	2.976
Ni	2.985
Pb	3.030

The variation in TE_{Sn} with the nature of the metal-reducing agent would be of no consequence provided that it also pertains to solutions derived from MP-1 and KC-1. However, as Table IV shows, this is not the case. TE_{MP}, the tin-equivalent of the iodate for solutions derived from MP-1, is given by $W\mu/V$ where W is the mean of the weights of samples of MP-1, V is the mean of the corresponding volumes of iodate for ten samples using aluminum, nickel and lead, twelve samples for iron, and μ is the true (unknown) tin content of MP-1. If the tin-equivalent of the iodate exhibited the same variation for both the standardization solutions and those derived from MP-1, TE_{MP}/TE_{Sn} would be essentially constant.

TABLE IV

Tin-Equivalent of Iodate Based on MP-1

Metal	Mean wt of MP-1, W(mg)	Mean vol Titrant, V(ml)	TE_{MP} ($\overline{mg/ml}$)	$\dfrac{TE_{MP}}{TE_{Sn}}$
Al	552.47	4.460	123.87μ	41.02μ
Fe	554.71	4.533	122.35μ	41.12μ
Ni	552.77	4.460	123.94μ	41.53μ
Pb	557.56	4.402	126.66μ	41.80μ

Tin-equivalent of iodate for MP-1 solutions

To further investigate the effect of the metal-reducing agent on the variation of the tin-equivalent of the iodate, 23 mg of cassiterite ore concentrate (NBS 137, 56.64% Sn) were added as an internal standard to one of a pair of samples of MP-1, each $\sim$0.55 g with a weight difference of less than 0.2 mg, and both samples were fused and treated as described previously. The tin-equivalent of the iodate for solutions derived from MP-1 and cassiterite, TE_{CASS}, is readily calculated from the difference between the volume of iodate and was found to be 3.26* ± 0.01 (6 determinations) for iron reduction, 3.45 ± 0.04 (4 determinations) for nickel reduction and 3.51 ± 0.05 (4 determinations) for lead reduction. If it is assumed, as seems reasonable, that the addition of the cassiterite to MP-1 does not significantly alter the behaviour of the metal-reducing agent, TE_{CASS} and TE_{MP} should be equal. The value of TE_{MP}/TE_{CASS} can, therefore, be used as a basis for estimating the "goodness" of the corresponding value of TE_{MP}/TE_{Sn}. TE_{MP} was calculated to be 133.71μ, 141.83μ and 144.20μ mg/ml for iron, nickel and lead respectively. TE_{MP}/TE_{CASS}, therefore, is 41.02μ, 41.11μ and 41.08μ respectively. It is evident that the procedure of standardization of the iodate against solutions of tin alone is satisfactory for aluminum and iron, but is not so for nickel and lead. The results of eight determinations of tin in MP-1 by each of iron, nickel and lead reduction (and using appropriate value of TE_{CASS}) are shown in Table V. The results by iron reduction pertain to MP-1 in Bottle #1, whereas by nickel and lead reduction pertain to MP-1 in Bottle #2.

TABLE V

Results of Titrimetric Analysis for Tin in MP-1

Sample	% Sn		
	Fe	Ni	Pb
1	2.43	2.44	2.42
2	2.44	2.43	2.43
3	2.45	2.44	2.44
4	2.44	2.42	2.43
5	2.43	2.43	2.41
6	2.43	2.43	2.43
7	2.44	2.44	2.41
8	2.45	2.43	2.43
Mean	2.438	2.433	2.425

*These values refer to an iodate titrant different from that for which data are given in Tables III and IV.

The cause of the differences in the effectiveness of the metal-reducing agents in giving satisfactory results in the titrimetric analysis for tin is not clearly understood at this time. There appears to be a relationship between this effectiveness and the reduction potential of iron, nickel and lead[10] (Fig. 2). The plot in Fig. 2 suggests that a reduction potential of approximately -0.45 volts is sufficient to give satisfactory results. Aluminum cannot, of course, give better than satisfactory results even though it has a much more negative reduction potential -1.76 volts; the anomalous position of aluminum in Fig. 2 is due to this insensitivity towards its reduction potential.

In solutions containing tin alone, tin exists as monomeric chloride complexes and is the only reducible species present. In solutions derived from MP-1, however, other elements such as Fe(III), Pb(II), Zn(II), Cu(II), Zr(IV), Ti(IV), Si(IV) and As(V) are present. It is possible that complex species composed of tin and other element(s) are present and that the tin in these species is reduced with greater difficulty than in monomeric chloride complexes. Therefore, the more powerful the metal is as a reducing agent, the more effective is its use.

Interference in the titrimetric method

The variation in the effectiveness of the metal-reducing agent in yielding satisfactory results is, of course, a result of interference in the titrimetric determination of tin in MP-1. Because this interference is inherent in MP-1, it must also occur in samples containing MP-1 + added cassiterite. The interference should, therefore, be reflected in the tin-equivalent value of the iodate and "accurate" tin values for MP-1 should be obtained. Nevertheless, these values remain appreciably lower than the mean value found by the instrumental methods in the inter-laboratory program[1]. This observation explains why low results were reported by many analysts who used the titrimetric method but were unaware of the variation of the tin-equivalent values of the iodate for the different metal-reducing agents. It remains a fact that certain laboratories did report low results explainable partly by the above reasoning.
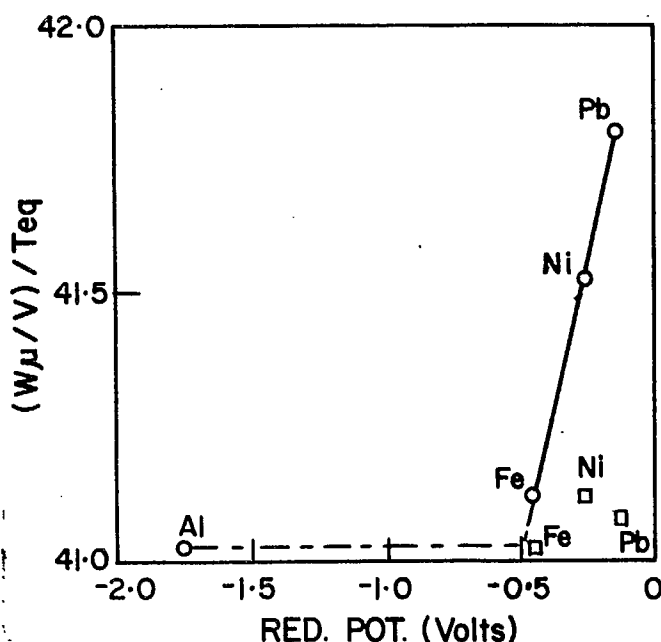

Fig. 2. The Relationship Between the the Reduction Potential of the Metal and the Value of the Ratio of the Tin-Equivalent of Iodate Solution for Solutions Derived from MP-1 to that for Solutions Containing Tin Alone (o) or that for Solutions Derived from MP-1 + added cassiterite (□).

Comments on titrimetric analysis of MP-1

This investigation indicates that the use of aluminum or iron as the reducing agents permits the accurate determination of tin in MP-1 by the titrimetric method when the iodate is standardized against solutions of tin alone. (Better results for iron are obtained when the iodate is standardized against samples of MP-1 + cassiterite.) If either nickel or lead is the reducing agent, the iodate must be standardized against samples of MP-1 and cassiterite for satisfactory results to be obtained. It is considered, therefore, that the computation of the mean tin values in MP-1 should be restricted to those values obtained under optimum experimental conditions. Therefore, it is

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TABLE VI

Results of Titrimetric Determination of Tin in MP-1

Bottle	No. of Determs.	Mean % Sn	95% Confid. Limits
1	18	2.439	2.434 - 2.444
2	30	2.432	2.429 - 2.435
Total	48	2.433	2.430 - 2.436

TABLE VII

Titrimetric Results of %Sn in KC-1 by Iron Reduction

Bottle	%Sn	
	Bottle #1	Bottle #2
1	0.681	0.680
2	0.679	0.684
3	0.681	0.684
4	0.682	0.682
5	0.680	0.682
Mean	0.681	0.682
Overall mean	0.682	
95% confidence limits	0.672 - 0.692	

recommended that the mean tin value in MP-1 for Bottle #1 should be computed using the values obtained by aluminum reduction (Table III) as well as those by iron reduction (Table V).

The titrimetric determination of tin in MP-1 with iron reduction was performed for Bottle #2 on the same samples used in the atomic absorption determination of tin in MP-1 (see Table VIII). Herein, a 200-ml aliquot was taken from the 250-ml volumetric flask. The tin-equivalent of the iodate was 3.264. The individual titrimetric results are given in Table VIII. The titrimetric results for Bottle #2 using nickel or lead reduction are shown in Table V.

The mean tin values and corresponding 95% confidence limits for each bottle and the overall total are shown in Table VI. A one-way analysis of variance of the results in Table VI indicated no significant difference between the two bottles and this is in accord with the findings of the inter-laboratory program to certify MP-1[1].

Analysis of reference ore KC-1

The results of the titrimetric determination of tin in reference ore KC-1 using iron as the metal-reducing agent are shown in Table VII. Herein, the tin equivalent of the iodate was determined using solutions containing tin alone.

Atomic absorption method

The accurate determination of Sn is difficult by atomic absorption, A.A. In addition to tin having poor sensitivity relative to other commonly determined elements, the maximum sensitivity for tin is strongly dependent on instrumental parameters such as nebulization rate, fuel ratio, etc. Furthermore, the sensitivity of AA to tin is also dependent on the nature of the matrix. Specifically, it was found that the sensitivity for tin in the matrix derived from MP-1 and KC-1 was less than that for solutions containing tin alone.

An attempt to establish the accuracy of the standard additions method in the AA determination of tin was made. Herein, four samples of approximately 24 mg cassiterite ore concentrate (NBS 137, 56.69 %Sn) and 44.7 mg Fe_2O_3 were fused with sodium carbonate and sodium peroxide and thereafter treated in the same manner as samples of MP-1 and KC-1. One other sample consisting of 44.7 mg Fe_2O_3 alone was prepared similarly. With the subtraction of the absorbance of the iron-only sample from that of each of the four samples containing cassiterite, a mean value of 56.8 ± 0.2% for NBS 137 was obtained. The AA method evidently yields satisfactory results.

The results of the AA determination of tin in MP-1 and KC-1 are shown in Tables VIII and IX respectively. Also shown in Table VIII are the titrimetric results for the same samples of MP-1 which were obtained in the manner described previously.

Background absorbance

It should be noted that subsequent to the AA determination of tin in MP-1 and KC-1, an attempt was made to measure, by use of the hydrogen continuum lamp[11], the background absorbance and scatter in solutions derived from these ores. Three samples of MP-1 (samples 12-14 in Table VIII) were investigated and it was found that the non-atomic absorbance as measured by the hydrogen continuum lamp was essentially the same as the absorbance of the synthetic MP-1 solution as measured with the tin hollow cathode lamp.

Two different Techtron AA-5 spectrophotometers were used in this study. At no time was a steady absorbance reading attained on either instrument. The reading accepted was, in fact, an estimate of the mid-point of slight oscillation of the needle. Unfortunately, because of the low sensitivity for tin, the use of the scale expansion mode was imperative which, in turn, increased the magnitude of this oscillation. At the setting of instrumental parameters and sample weights used in this investigation, it has been estimated, therefore, that the AA results for tin in MP-1 and KC-1 have a precision of ± 0.06 and ± 0.003% respectively.

The results of the AA determination of tin in MP-1 and KC-1 are in excellent agreement with those by the titrimetric method, but are appreciably lower than the AA results reported in the inter-laboratory certification program[1,2]. The cause of this discrepancy is not understood, particularly for those results which were also obtained by the standard additions method. Results obtained by the interpolation method may be subject to error. In this approach, the absorbance of the sample is compared with that of two synthetic standards having a higher and lower tin concentration and the tin concentration of the sample is either read off graphically or determined mathematically. The tin

TABLE VIII

Results of AA Analysis of MP-1
(Bottle #2)

Sample	% Sn AA	% Sn Titrimetric	Sample	% Sn AA	% Sn Titrimetric
1	2.38	2.44	8	2.46	2.44
2	2.45	2.43	9	2.45	2.43
3	2.39	2.44	10	2.44	2.43
4	2.46	2.44	11	2.41	2.44
5	2.40	2.45	12	2.44	2.44
6	2.41	2.42	13	2.45	2.43
7	2.45	2.44	14	2.45	2.44

Mean value for AA 2.431
95% confidence limits
limits 2.415 - 2.447

Mean value for titrimetric results 2.436
95% confidence limits 2.431 - 2.440

TABLE IX

Results of AA Analysis of KC-1

Sample	% Sn Bottle #1	% Sn Bottle #2
1	0.677	0.690
2	0.694	0.691
3	0.694	0.670
4	0.683	0.678
5	0.677	0.686
Mean	0.685	0.684

Overall mean 0.685
95% confidence
limits 0.680 - 0.690

concentration so determined must be somewhat in error if the sensitivity towards tin is different for the sample than for the synthetic standards. It is important, therefore, to establish that there is no significant difference in sensitivity. This is most easily accomplished by a comparison of the change in absorbance per given change in added tin concentration for the sample with that of the synthetic standards. In effect, however, this procedure requires that the standard additions method be applied to both the sample and to the synthetic standards.

CONCLUSIONS

The present investigation has indicated that there can be a significant difference between results by the titrimetric method with the nature of the metal-reducing agent if the iodate is standardized against solutions of tin alone. Although the use of nickel and lead leads to low values of tin in MP-1, these metals, nevertheless yield more satisfactory results than was suggested by the inter-laboratory program. It has been shown that when the iodate is standardized by the standard additions method (i.e., with cassiterite) nickel and lead also give excellent results.

It has also been shown that there is no significant difference between the tin values for MP-1 and KC-1 by the titrimetric method or by the atomic absorption method. It is the author's opinion that the atomic absorption method is somewhat less satisfactory because of the poor sensitivity for tin compared to other commonly determined elements.

REFERENCES

1. G.H. Faye, "Zinc-Tin-Copper-Lead Ore, MP-1: Its Characterization and Preparation for Use as a Standard Reference Material". Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Technical Bulletin TB 155, September (1972).

2. G.H. Faye, W.S. Bowman and R. Sutarno, "Zinc-Lead-Tin-Silver Ore, KC-1: Its Characterization and Preparation for Use as a Standard Reference Material". Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Technical Bulletin TB 193, July (1974).

3. T.R. Sweatman, Y.C. Wong and K.S. Toong, Trans. Inst. Min. Met., 76B, 149 (1967).

4. B.J. Hefferman, R.O. Archbold and T.J. Vickers, Aust. Inst. Min. Met. Proc., 223, 65 (1967).

5. B. Lister and M.J. Gallagher, Trans. (Section B) Inst. Min. Met., 79, B213 (1970).

6. G.H. Faye, W.S. Bowman and R. Sutarno, Anal. Chim. Acta., 67, 202 (1973).

7. E.M. Donaldson, "Determination of Tin in Ores, Steels and Alloys with Gallein after Extraction as the Iodide". Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Technical Bulletin TB 195 (1974).

8. W.J. Price, "Analytical Atomic Absorption Spectrometry". Heydon and Son, Ltd., New York, pp 80-1, (1972).

9. K.A. Brownlee, "Statistical Theory and Methodology in Sciences". John Wiley and Son, Inc., New York (1961).

10. R.C. Weast, ed., "Handbook of Chemistry and Physics", 48th edition, The Chemical Rubber Co., Cleveland, Ohio, p. D86 (1967).

11. Reference 8, p. 92.