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The Polarographic Determination of Trace Elements In High Purity Zinc and Zinc Die-Casting Alloys.

A thesis presented by

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THE POLAROGRAPHIC DETERMINATION OF COPPER, LEAD AND CADMIUM IN HIGH PURITY ZINC ALLOYS*

INTRODUCTION

Metallurgists have found in recent years that traces of lead, cadmium and tin in zinc-base die-casting alloys tend to cause intergranular corrosion, which results in a serious weakening of the alloy. For this reason specifications for the manufacture of these alloys are very rigid, often requiring that lead shall not exceed 0.003 per cent, cadmium 0.003 per cent, and tin 0.001 per cent. The purpose of this investigation was to develop a system of analysis for zinc die-casting alloys of the "Mazak" type in which the polarograph could be used with advantage to determine trace amounts to 10^{-4} per cent with high precision and accuracy.

The determination of trace quantities by wet methods of analysis is exceedingly difficult. It is usually necessary to use large samples (100 gm. or more), and to make repeated time-consuming separations. The polarographic method, on the other hand, is essentially a micro-method, the very nature of which greatly reduces the necessity for making separations, and is a procedure which compared very favourably with the spectrochemical method with respect to the limits of determination possible. In addition, a polarographic determination, where applicable, is considerably cheaper than a spectrochemical determination, and can often be carried out more rapidly.

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Heyrovsky[6] in a review of the applications of polarography noted that it is possible to determine lead and cadmium in zinc. Curves are given for a 0.5 gm. sample in 5 ml. of HCl in which the concentration of Pb is 0.0050 % and Cd is 0.0037 %. Terui[12] determined lead and cadmium to the nearest 1 x 10^{-3} % by dissolving 8 gm. of zinc in 70 ml. of 5N HCl with a few drops of HNO_3 and evaporating to 50 ml. Enslin[5] reported a method for lead and cadmium in pure zinc using the polarograph in which the zinc was dissolved in nitric acid, and the resulting solution combined with different base solutions. The lead and cadmium were determined separately; the lead with an accuracy of 20 % of the total amount present from 3 x 10^{-3} % to 5 x 10^{-4} % on what would correspond to a 100 gm. sample in one litre of solution. Krossin[9] applied the polarograph to the analysis of coppe and aluminum-bearing zinc alloys for lead and bismuth by means of a precipitation with sodium sulphide. Seith and Esche[10] determined lead, cadmium, bismuth, thallium and tin in zinc by the polarographic method. The lead, cadmium and bismuth were determined simultaneously by treating a 5 gm. sample with HCl and diluting to 25 ml. before electrolysis at 28 °C. The thallium and tin were determined by difference from the sum of cadmium and thallium, and lead and tin respectively. Results are reported to the nearest 1 x 10^{-3} % except for tin which is limited to 1.5 x 10^{-3} %. Hohn[7] in a review of polarographic methods of analysis outlined a method for copper, lead and cadmium in zinc, but made no mention of the accuracy or precision of the method.

In the work reviewed above, only one paper deals with the determination of impurities in zinc alloys, and this involves an objectionable sulphide separation with its attendant errors. The present investigation was undertaken in an effort to develop a method for the direct determination of copper, lead and cadmium in high purity zinc-base die-casting alloys of the "Mazak" type with special emphasis on the accuracy and precision in the region of 10^{-4} %.

As an indication of the types of impurities in zinc and zinc die-casting alloys, as well as the concentrations employed, the following tables are included.

Table I

Composition of Zinc Die-Casting Alloys [1*]

	S. A. E. No. 903 A. S. T. M. No. XXIII	S. A. E. No. 921 A. S. T. M. No. XXI	S. A. E. No. 925 A. S. T. M. No. XXV
Copper	0.10 Max.	2.5-2.5	0.75-1.25
Aluminum	3.5-4.3	3.5-4.5	3.5-4.3
Magnesium	0.03-0.08	0.02-0.10	0.02-0.08
Iron-Max.	0.100	0.100	0.100
Lead-Max.	0.007	0.007	0.007
Cadmium-Max.	0.005	0.005	0.005
Tin-Max.	0.005	0.005	0.002
Zinc	Remainder	Remainder	Remainder

Table II

Wrought Zinc and Zinc Alloys [1*]

Composition per cent.

Grades	Pb	Fe Max	Cd	Cu	Mg	Zn
A	0.05 max.	0.010	0.005 max.	0.001 max.		remainder
B	0.05-0.12	0.012	0.005 max.	0.001 max.		remainder
C	0.30	0.020	0.20-0.35	0.005 max.		remainder
D	0.05-0.12	0.012	0.005 max.	0.65-1.25		remainder
E	0.05-0.12	0.015	0.005 max.	0.75-1.25	0.007-0.02	remainder

[*] The maximum limit of impurities has been materially reduced in recent years, and so the above tables are merely an indicator of the trend.

Table III

A. S. T. M. recognized commercial zincs [1*]

	Lead	Iron	Cadmium	Aluminum	Sum of Pb, Fe, Cd
(1a) Special High grade, Max., per cent	0.007	0.005	0.005	None	0.010
(1) High grade, max., per cent	0.07	0.02	0.07	None	0.10
(2) Intermediate, max., per cent	0.20	0.03	0.50	None	0.50
(3) Brass Special, max., per cent	0.60	0.03	0.50	None	1.0
(4) Selected, max., per cent	0.80	0.04	0.75	None	1.25
(5) Prime Western, max., per cent	1.60	0.08	----	----	----

Table IV

Percentage-Concentration

(Basis-8 gm. in 50 ml.)

Element	Composition (per cent)	Concentration (molar)
Copper	0.01	2.5×10^{-4}
Aluminum	1.0	6.02×10^{-2}
Magnesium	0.01	6.56×10^{-4}
Iron	0.01	2.86×10^{-4}
Lead	0.001	7.72×10^{-6}
Cadmium	0.0001	1.42×10^{-6}
Tin	0.0001	1.35×10^{-6}
Zinc	10.0	2.43×10^{-1}

It is not uncommon for zinc to contain the following elements,[2] Tin, antimony, arsenic, lead, bismuth, cadmium, copper, iron, nickel, cobalt, manganase aluminum, thallium, indium, silver, mercury, as trace elements. Magnesium and aluminum are used as alloying elements in Zamak type die-casting alloys. Traces of germanium and gallium are also to be found, (cf. Bur. Stds. Zinc Spelters Nos. 108 and 110).

Apparatus and Reagents

The preliminary studies were made with a Leeds and Northrup "Electro-chemograph*, and the work was concluded with an Heyrovsky Polarograph Model XI (E. H. Sargent and Co.). The galvanometer sensitivity on the Sargent instrument was 0.0027 uA/mm. at 1 metre. The same capillary was used throughout the investigation. The capillary constant in 4.8 M $ZnCl_2$ was found to be 1.37 mg.$^{2/3}$ sec.$^{-\frac{1}{2}}$ when h = 36.5 cms., t = 3.3 secs., and temp. = 25±0.5 °C.

When the curves showed irregularities traceable to fluctuations in the drop-time the capillary was cleaned[†] with conc. HNO_3 as directed by Kolthoff and Lingane[8]. The pressure on the dropping electrode was maintained by using the Leeds and Northrup electrode assembly in conjunction with a large flask to serve a a pressure regulator. This kept the pressure constant to within ±0.5 mm.

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*The L and N "Electro-chemograph" was kindly loaned to us by the University of Toronto.

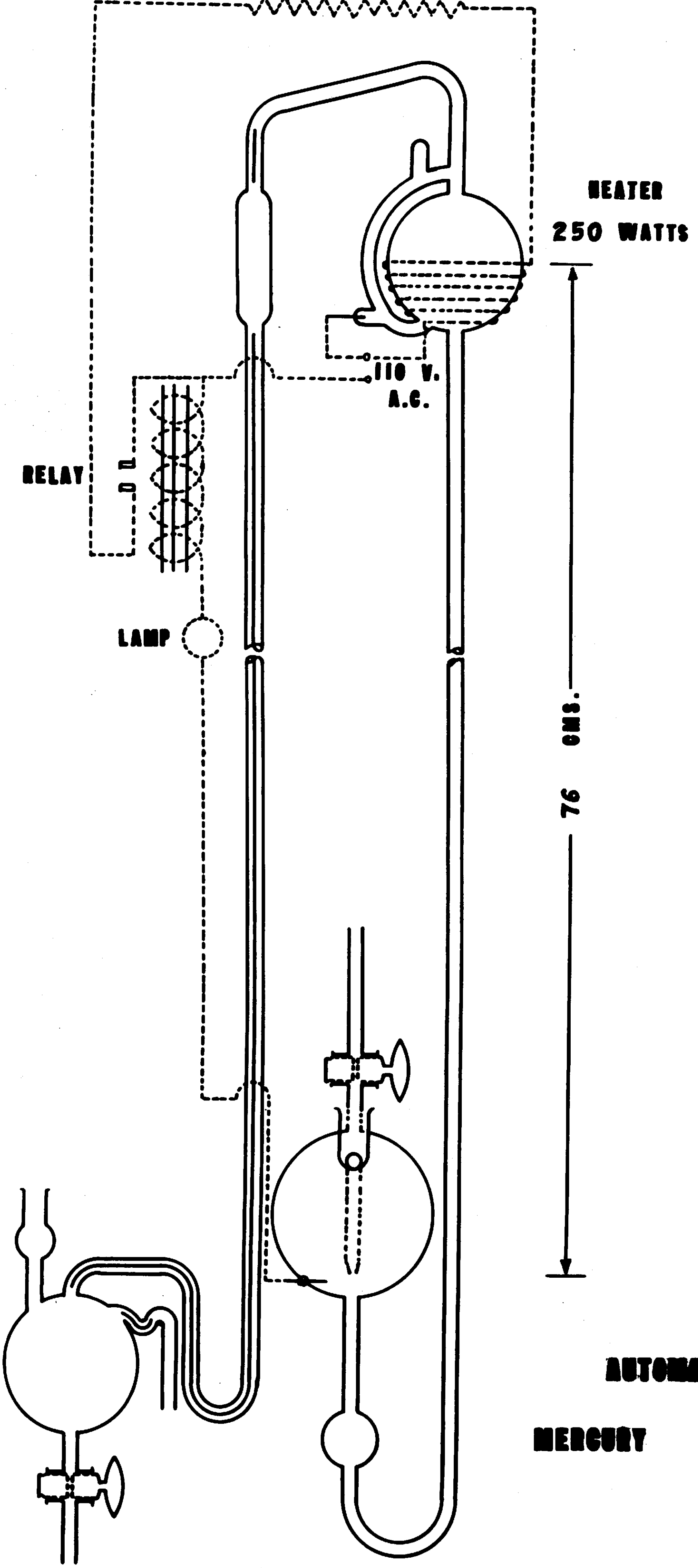
[†] At one time, the capillary became plugged so tightly that it was necessary to remove the obstruction. The obstruction was found to be a piece of rubber from the connector. This was because a soft type of artificial rubber was used which chipped easily.

of Hg for periods of not less than forty-five minutes. An ordinary electrolysis cell with an internal anode was used throughout these experiments. (~~Fig. 2~~). A supply of pure mercury was kept constantly on hand by an automatic Hg still of the author's design. (Fig. 4). The wave heights were measured by the slope intercept method, i.e. straight lines were drawn along the principal slopes of the wave, and the vertical distance between the points of intersection of the projections of these lines was measured with a millimetre scale. (Fig. 1). All the work was carried out at 25±0.5 °C.

Most commercial reagents contain traces of various elements as impurities and as a result it was found necessary to check the purity of the reagents used under the conditions existing in the procedure outlined below. It was not possible to procure zinc metal of such purity that no waves were obtained under the operating conditions. The checks were, therefore, carried out in the following manner:

A sample of zinc was made uniform by reducing the sample to shavings and mixing. A portion of this sample was analysed polarographically using the procedure outlined, without additions of metal ions. This gave the residual current for the ensuing determinations.

> Conc. HCl (Sp. Gr. 1.19) 100 ml. of conc. HCl were evaporated almost to dryness in a 125 ml. pyrex beaker. An 8 gram sample of the above zinc was then added to this residual liquid and the whole carried through the procedure for analysis. After subtracting the residual current due to the zinc, it was found that for the 32 ml. of HCl required, a correction of 5×10^{-5} % of Cd and 5×10^{-5} % of Cu would have to be applied. No trace of lead was found. (110 ml. HCl gave 0.0091 uA for Cu and 0.0075 uA for Cd).
>
> Conc. HNO_3 (Sp. Gr. 1.42) 100 ml. of conc. HNO_3 were treated in a manner similar to that used for the HC. No traces of Cu or Pb were found but Cd corresponding to 0.00015 % on gram zinc sample was detected. Inasmuch as the amounts of HNO_3 used were seldom in excess of 10 ml., this amount of Cd was considered to be negligible for the present purpose.



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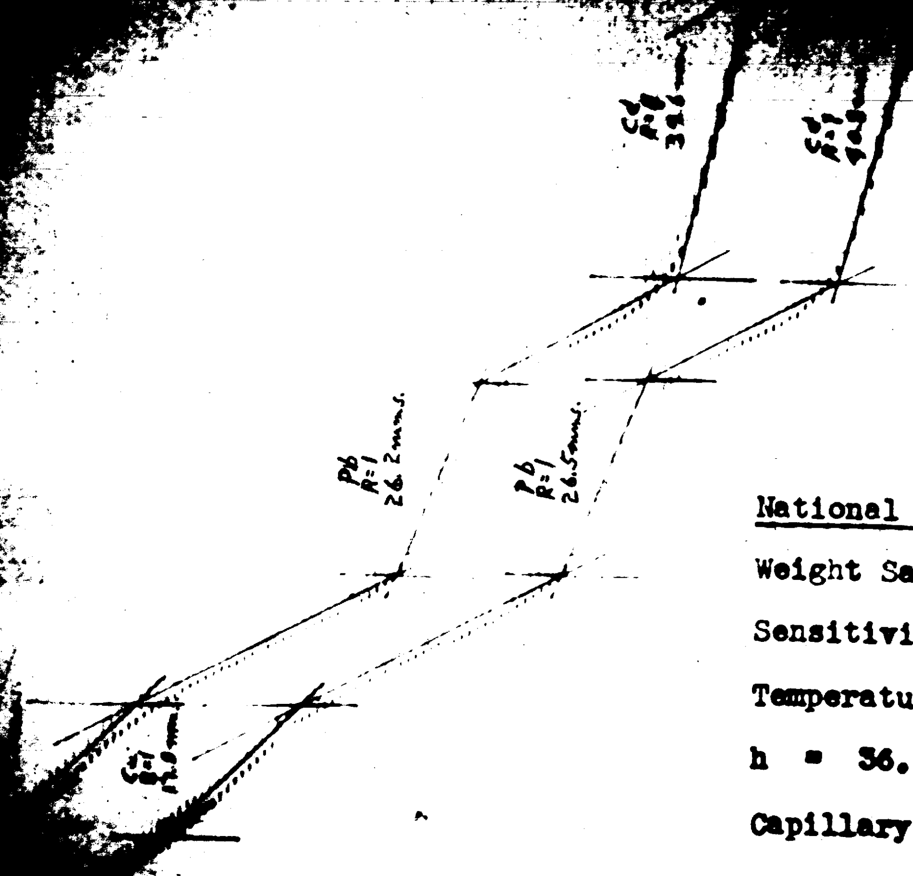

National Bureau Stds. Sample 109

Weight Sample = 8.0003 g.

Sensitivity = 1/1

Temperature = 25.0 ± 0.5 °C.

h = 36.5 cms. Hg. t = 3.3 secs.

Capillary Constant = 1.37 mg.$^{2/3}$ sec.$^{-\frac{1}{2}}$

Fig. 2

Hydroxylamine Hydrochloride (2N) 10 ml. of 2N NH_2OH HCl were evaporated almost to dryness and treated as was the HCl. (Caution--- violent action when zinc added). No traces of Cu, Pb, or Cd were found.

Gelatin Soln. (0.2% aqueous) 1 gram of gelatin was ashed in a porcelain crucible and the residue taken up in a few mls. of conc. HCl. The contents of the crucible were then added to a zinc sample as for HCl. Cu corresponding to 3 x 10 % and Cd to 1 x 10 % in an 8 gram zinc sample were found. Since only 2.5 ml. of the 0.2% solution are used in an analysis, these impurities were considered to be negligible.

Distilled Water 500 ml. of water were evaporated to dryness and treated as for HCl. No detectable amounts of Cu, Pb, or Cd were found.

Using the procedure to be described below, it was found that the overall effect of impurities in the reagent amounts to Cu=0.00005%, Pb=0.00000%, Cd=0.00005%. These amounts may be neglected for most purposes.

The standard solution of copper, lead and cadmium required for the calibration of the capillary were prepared by diluting stock solutions.

Std. Stock Soln. For Copper A 0.2 M solution of $Cu(NO_3)_2$ was prepared by dissolving 12.714 grams of electrolytic copper in dilute nitric acid and diluting 1 liter. This solution was analysed by slow electrical deposition with the following results.

Detn. No.	Volume Stock Soln. (ml.)	Weight Cu. (gms.)	Deviation (gms.)
1	25.00	0.3152	+0.0003
2	25.00	0.3146	-0.0003
3	25.00	0.3148	-0.0001
4	25.00	0.3149	±0.0000
	Average	0.3149	±0.0002 gm/25 ml

Molarity-0.1982 ±0.0002M.

Std. Stock Soln. For Cadmium A 0.2 M solution of $Cd(NO_3)_2$ was prepared by dissolving 22.496 grams of C.P. cadmium in dilute nitric acid and diluting to 1 liter. This solution was analysed by electro-deposition according to the

A.S.T.M. method. The stock solution was diluted 1:5 with distilled water in order to obtain a satisfactory volume to measure out the Cd. Volumes below are for diluted solutions.

Detn. No.	Vol. 1:5 Stock Soln. (ml.)	Weight Cd (gms.)	Deviation (gms.)
1	25.00	0.1120	-0.0002
2	25.00	0.1144[*]	+0.0022
3	25.00	0.1125	+0.0003
4	25.00	0.1122	0.0000
	Average[*]	0.1122	±0.0002 gram

Molarity- 0.1996 ±0.0004 M.

Std. Stock Soln. For Lead A 0.2 M solution of Pb(NO$_3$)$_2$ was prepared by dissolving 41.458 grams of C.P. lead in dilute nitric acid and diluting to 1 liter. This solution was analysed (1) by electrodeposition and (2) by the lead acid method with the following results. Stock solution was diluted 1:10 for these tests.

(i)

Detn. No.	Vol. 1:10 Stock Soln. (ml.)	Weight PbO$_2$ (gms.)	Weight Pb gm/25 ml.	Deviation gm./25 ml.
1	25.00	0.1173	0.1014	+0.0001
2	25.00	0.1167	0.1009	-0.0004
3	25.00	0.1194	0.1024	+0.0011
4	19.00	0.0884	0.1005	-0.0008
		Average	0.1013	±0.0006

Molarity[†] - 0.1956 ±0.0012 M.

[†] Results suspected low because of poor adherence of PbO$_2$ to electrode.

[*] The electrode here was dried by igniting the residual alcohol. Dark spots developed. Possible CdO. Not included in average.

(ii)

Detn. No.	Vol. 1:10 Stock Soln. (ml.)	Weight $PbSO_4$ grams	Weight Pb grams/25ml.	Deviation grams Pb/25 ml.
1	25.00	0.1498	0.1024	-0.0002
2	25.00	0.1504	0.1028	+0.0002
3	50.00	0.3004	0.1027	+0.0001
4	50.00	0.3002	0.1026	±0.0000
		Average	0.1026	±0.0001

Molarity = 0.1981 ±0.0002 M (accepted)

Procedure

After a few experiments as to sample size and other details, such as the amount of acid necessary, bubbling time, etc., the following procedure was adopted as satisfactory.

To 8 grams of turnings in a 125 ml. pyrex beaker, add slowly 25 ml. of conc. HCl. After the first violent reaction has subsided, add cautiously a few ml. of conc. HNO_3, and warm to effect solution. When solution is complete, add sufficient HNO_3 to make the volume of added HNO_3 5 ml. Evaporate on a hot sand bath until salts crystallize out, and the mixture boils like a thick syrup. If desired, the evaporation may be hastened somewhat by careful heating on a wire gauze. Allow the mixture to cool for a short time, or until solid. Wash down with distilled water until about ten ml. of water have been added. Add seven ml. of conc. HCl and heat on a sand bath until any hydrolysed aluminum is redissolved. This may require 10-15 minutes. Transfer to a 50 ml. volumetric flask with the minimum of distilled water. Add 2.5 ml. of 0.2% gelatin solution and 0.1 ml. of 2N NH_2OH HCl. Shake and heat until the solution becomes colourless. If necessary, add a second portion of NH_2OH HCl. Dilute with freshly boiled distilled water, cool, and dilute to volume. Bubble with nitrogen in the electrolysi cell for 15-20 minutes to remove dissolved oxygen, and electrolyse from -0.04v to the discharge potential of the supporting electrolyte (approx. -0.8v) using a bridge potential of 1v. The sensitivity should be adjusted to give the largest possible steps in the curves.

Occasionally a solution may remain coloured in spite of a large excess of hydroxylamine. If the excess corresponds to 100-200 times the amount of iron present, this colour can usually be ignored.

The ferric iron is readily reduced to the ferrous state by treating the warm hydrochloric acid solution with hydroxylamine.[4] In this state, the iron will not interfere with the determination of the copper, lead, and cadmium. Strubl also made use of this reagent in the analysis of zinc-blende, which was high in iro

The time required for a determination of copper, lead, and cadmium in a zinc-base alloy using the above procedure is about three hours. However, a large number of samples may be run at the same time as only ten minutes are required for a polarogram after the sample is prepared.

In the event that copper is present in the alloy in excess of 0.1%, it is advisable to remove the copper by electro-deposition from HNO_3 solution as follows:

To 8 grams of zinc in a tall form 250 ml. beaker add 50 ml. H_2O and then add 23 ml. HNO_3 in small portions. When all the acid has been added, boil to complete solution, dilute to 100 ml. (or sufficient volume to cover the electrode) and electrolyze at 4 amps. and 3 to 4 volts for 1 hour with a rotating gauze anode and a gauze cathode. At the end of this time, wash down the cover glass and beaker and continue for another five minutes. Carefully remove the cathode while washing with a heavy stream of water. Under no circumstances should the circuit be broken before the electrode is completely free of acid. Rinse the electrode several times in 95% alcohol, shake free of excess alcohol and dry be revolving rapidly over a bunsen flame after igniting the film of alcohol. Weigh as pure Cu. The anode, which may have PbO_2 deposited, is replaced in the electrolyte and the whole heated to boiling. The electrode is then washed and removed and the solution boiled down to incipient crystallization. HCl is then added and the procedure carried out as for zinc which is low in copper. Care must be taken to remove the large excess of HNO_3. To do this, an extra evaporation with 10 ml. of HCl is recommended before the addition of the 7 ml. of HCl and 10 ml. of H_2O to redissolve the hydrolyzed aluminum.

The above modification increases the total time required for an analysis, but when a large number of samples are to be run, this increase is considerably lessened. The results obtained for the Cu by this method are usually slightly high (0.03% high for 3% Cu). No traces of Cd or Zn were found in the deposit when the deposit had been redissolved, deposited, and the electrolyte examined polarographically.

Results and Discussion

The Capillary used was first calibrated in $ZnCl_2$ with the following results.*

Capillary No. 1

Pressure--36.5 cms. Hg.   Medium--2.4 M $ZnCl_2$

Appl. Pot. (Volts) S.C.E.	Time for 50 drops (secs.)	Wt. Hg. for 50 drops (in mgs.)	Rate of flow Hg. (mg. sec.-1)	t Drop Time (secs.)	$m^{2/3}\ t^{1/6}$ mg.$^{2/3}$ sec.$^{-1/2}$	Temp.° C Before	Temp.° C After	Av. Temp.° C
0	163.7	194.2	1.1863	3.274	1.366	25.0	24.5	24.75
-0.2	164.0	195.2	1.1903	3.280	1.369	24.8	24.8	24.80
-0.4	173.2	208.2	1.1938	3.464	1.391	25.0	25.0	25.00
-0.6	180.5	216.0	1.1962	3.610	1.396	25.0	25.0	25.00
-0.8	178.0	213.2	1.1978	3.560	1.394	25.0	25.0	25.00
-1.0	167.0	199.0	1.1916	3.340	1.374	25.0	25.0	25.00
-1.2	163.2	195.6	1.1986	3.264	1.374	24.8	25.0	24.90
-1.4	163.8	196.6	1.2002	3.276	1.376	25.0	25.1	25.05
-1.6	162.6	194.6	1.1968	3.252	1.3720	25.0	25.0	25.00
-1.8	171.2	204.6	1.1951	3.424	1.383	25.0	25.0	25.20
	163.6	194.2	1.1870	3.272	1.366	25.2	25.0	25.10
-2.0	160.8	192.7	1.1983	3.216	1.371	25.0	25.0	25.00

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*Results obtained in conjunction with Mr. D. H. Simpson, B. Sc. '43

In this manner, data was obtained which would make possible the conversion of any results obtained on Capillary No. 1 to any other capillary should the necessity arise. This is because the diffusion currents for any two capillary are proportional within plus or minus three per cent to the ratio of their capillary constants, (i.e. $m^{2/3}$ $t^{1/6}$).

The next calibration to be undertaken was the calibration of the capillary for the diffusion currents of copper, lead, and cadmium, under the actual conditions of the procedure. This was done by making additions of copper, lead and cadmium from the diluted stock solutions to a sample of a known zinc, in a manner similar to that employed for testing the impurity content of the reagents.

The calibration was carried out on both the Leeds and Northrup and the Sargent Polarographs. The wave-heights were obtained by difference from the residual current of the zinc used as a supporting electrolyte, and those produced by the zinc plus added ions. In the lower concentration range, (1×10^{-6} to 5×10^{-6} M), this residual current amounted to from ten to twenty times the increase in current due to the added ions, and, accordingly, a large error was introduced. This error was more significant when using the Leeds and Northrup instrument than when employing the Sargent apparatus. The fact that the latter has about twice the maximum sensitivity of the former would account in part for this difference in the results.

Calibration--(1)

Copper

Conc. of element (moles/liter)	per cent on basis 8 grams in 50 ml.	L and N			Sargent		
		microamp.			microamp.		
		Observed	Corrected	Factor % A	Observed	Corrected	Factor % A
NONE	--------	0.106	--------	------	0.0832	-------	------
1×10^{-6}	0.00004	0.104	--------	------	0.0757	--------	-------
5×10^{-6}	0.0002	0.137	0.031	0.00645	0.0902	0.0070	0.02860
2.5×10^{-5}	0.000993	0.150	0.044	0.02250	0.125	0.042	0.02365
1.25×10^{-4}	0.00496	0.332	0.226	0.02195	0.322	0.239	0.02075
6.25×10^{-4}	0.0248	1.42	1.31	0.01895	1.23	1.15	0.02155
3.13×10^{-4}	0.124	6.86	6.75	0.01838	6.42	6.34	0.01960
		Average		0.02045		Average	0.02063

Lead

Conc. of element (moles/liter)	per cent on basis 8 grams in 50 ml.	L and N			Sargent		
		microamp.			microamp.		
		Observed	Corrected	Factor % A	Observed	Corrected	Factor % A
NONE	0	0.480	---------	-------	0.384	-------	--------
1×10^{-6}	0.00013	0.480	0	-------	0.386	0.002	0.0650
5×10^{-6}	0.00065	0.500	0.020	0.03245	0.403	0.019	0.03423
2.5×10^{-5}	0.00323	0.587	0.107	0.03015	0.489	0.105	0.03078
1.25×10^{-4}	0.0162	1.02	0.54	0.03005	0.842	0.458	0.03538
6.25×10^{-4}	0.0810	3.14	2.66	0.03045	2.75	2.37	0.03420
3.13×10^{-4}	0.4051	14.00	13.50	0.03002	12.55	12.17	0.03330
		Average		0.03019	Average		0.03428

Cadmium

Conc. of element (moles/liter)	per cent on basis 8 grams in 50 ml.	L and N			Sargent		
		microamp.			microamp.		
		Observed	Corrected	Factor % A	Observed	Corrected	Factor % A
NONE	----------	0.330	----------	--------	0.226	----------	--------
1×10^{-6}	0.00077	0.346	0.016	0.00438	0.242	0.016	0.00438
5×10^{-6}	0.00035	0.382	0.052	0.00673	0.251	0.025	0.01400
2.5×10^{-5}	0.00176	0.442	0.112	0.01570	0.334	0.108	0.01630
1.25×10^{-4}	0.0088	0.76	0.430	0.02048	0.693	0.467	0.01885
6.25×10^{-4}	0.0440	2.84	2.51	0.01750	2.54	2.31	0.01905
3.13×10^{-4}	0.2205	12.50	12.17	0.01813	-------	-------	--------
		Average		0.01795	Average		0.01895

Calibration--(2)

Copper

Conc. of element (moles/liter)	per cent on basis 8 grams in 50 ml.	L and N			Sargent		
		microamp.			microamp.		
		Observed	Corrected	Factor % A	Observed	Corrected	Factor % A
None	----------	0.076	---------	--------	0.0510	---------	----------
1×10^{-6}	0.00004	0.074	---------	--------	0.0611	0.0101	0.004
5×10^{-6}	0.0002	0.097	0.021	0.00953	0.0708	0.0198	0.01010
2.5×10^{-5}	0.000993	0.134	0.058	0.01713	0.1058	0.0548	0.01825
1.25×10^{-4}	0.00496	0.328	0.252	0.01968	0.2895	0.2385	0.02078
6.25×10^{-4}	0.0248	1.473	1.399	0.01775	1.313	1.262	0.01965
3.13×10^{-3}	0.124	7.05	6.97	0.01780	6.04	5.99	0.02070
		Average		0.01759	Average		0.02038

Lead

Conc. of element (moles/liter)	per cent on basis 8 grams in 50 ml.	L and N			Sargent		
		microamp.			microamp.		
		Observed	Corrected	Factor % A	Observed	Corrected	Factor % A
NONE	---------	0.141	--------	--------	0.1130	--------	--------
1×10^{-6}	0.00013	0.137	--------	--------	0.1181	0.0051	0.02550
5×10^{-6}	0.00065	0.167	0.026	0.02502	0.1322	0.0192	0.03388
2.5×10^{-5}	0.00323	0.257	0.116	0.02785	0.2148	0.1018	0.03175
1.25×10^{-4}	0.0162	0.722	0.581	0.02793	0.6120	0.4990	0.03250
6.25×10^{-4}	0.0810	2.85	2.71	0.02990	2.520	2.407	0.03364
3.13×10^{-3}	0.4051	13.80	13.66	0.02971	12.26	12.15	0.03339
		Average		0.02885	Average		0.03364

Cadmium

Conc. of element (moles/liter)	per cent on basis 8 grams in 50 ml.	L and N			Sargent		
		microampere			microampere		
		Observed	Corrected	Factor % A	Observed	Corrected	Factor % A
NONE	----------	0.149	---------	-------	0.1117	--------	--------
1×10^{-6}	0.00007	0.140	---------	-------	0.1201	0.0084	0.00834
5×10^{-6}	0.00035	0.165	0.016	0.02190	0.1342	0.0225	0.01557
2.5×10^{-5}	0.00176	0.240	0.091	0.01935	0.2169	0.1052	0.01672
1.25×10^{-4}	0.0088	0.632	0.483	0.01822	0.5875	0.4758	0.01850
6.25×10^{-4}	0.0440	2.50	2.35	0.01873	2.971	2.359	0.01874
3.13×10^{-3}	0.2205	12.15	12.00	0.01838	11.70	11.59	0.01905
		Average--		0.01844	Average--		0.01876

Averaging these values we get:

	L and N	Sargent
Cu	0.01902 per cent/uA	0.02051 per cent/uA
Pb	0.02952 per cent/uA	0.03396 per cent/uA
Cd	0.01820 per cent/uA	0.01886 per cent/uA

The factors were obtained in terms of per cent for microampere for the sake of convenience in calculating the values from the wave-heights. The basis for the calculation is an 8 gram sample in a 50 ml. solution.

It is to be noted that the calibration factors obtained with the Sargent instrument are more consistent that those obtained with the L & N apparatus. It might be mentioned that, although the L & N for an instrument requires smaller factors than the Sargent instrument, the latter gives larger wave-heights for a given percentage. The maximum sensitivity of the Sargent instrument is 0.0027 uA/min., and for the L & N 0.0080 uA/min. The reason for the difference in the factors has not as yet been explained. There is no percentage relationship which might indicate an error in the recorded sensitivity. This, however, is of no concern, provided the instrument used is calibrated against known standards.

In order to determine the precision of the method and expose any possible source of error in the procedure, four series of determinations were carried out using the Sargent instrument.

(a) Precision of repeated determinations on the same cell.

(b) Precision of repeated determinations on different aliquots of the same solution.

(c) Precision of repeated determinations on different samples of the same alloy.

(d) Precision of repeated measurements of the same waves by

- (1) different individuals
- (2) same individual.

Precision of Polarographic Procedure

	Copper		Lead		Cadmium	
Series	Average %	Deviation %(±a.d.)*	Average %	Deviation %(±a.d.)	Average %	Deviation %(±a.d.)
(a)	0.0018_1	0.00006	0.0057_9	0.00008	0.0005_6	0.00004
(b)	0.0018_1	0.00003	0.0058_7	0.00003	0.0006_2	0.00005
(c)	0.0018_5	0.00011	0.0056_0	0.00008	0.0006_2	0.00005
(d)	0.0010_4[a]	0.00003	0.0017_1	0.00004	0.0009_5	0.00002
	0.0010_2[b]	0.00003	0.0016_7	0.00005	0.0009_3	0.00003

The above results indicate that the mean deviation of measurements in all cases is approx. one half of the total mean deviation of the procedure. The deviation is not significant, however, in that it barely affects the fourth place of decimals. The overall precision would indicate that it is possible to determine copper, lead, and cadmium to within 1×10^{-4} % for the range of concentrations encountered in high purity zinc alloys of the "Mazak" type.

The accuracy of the method was determined by the analysis of a number of standard samples from the National Bureau of Standards, as well as some samples analysed by other independent laboratories. The results of these determinations are given in Table V.

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* ±a.d. is the "average deviation from the arithmetical mean."

[a] a.--mean personal error of nine different individuals measuring a wave of 18.7 mm.

[b] b.--mean personal error of same individual measuring an 18.3 mm. wave ten times.

Table V

Analysis of Bureau of Standards Zincs

Sample No.	Value	Copper Average %	Copper Deviation %(-a.d.)	Lead Average %	Lead Deviation %(-a.d.)	Cadmium Average %	Cadmium Deviati %(-a.d.
108	Experimental	0.0004	±0.0001	0.0505	±0.0002	0.0960	±0.0007
	Certificate	0.0004		0.047		0.092	
	Difference			+0.0035		+0.0040	
109	Experimental	0.0007	±0.0001	0.0025	±0.0001	0.0019	±0.0001
	Certificate	0.0005		0.0020		0.0018	
	Difference	+0.0002		+0.0005		+0.0001	
110	Experimental	0.0073	±0.0005	0.571	±0.001	0.600	±0.017
	Certificate	0.0031		0.53		0.56	
	Difference	+0.0042		+0.041		0.040	
94	Experimental	2.83	±0.01*	0.0318	±0.0002	0.0025	±0.0001
	Certificate	2.82		0.031		0.004	
	Difference	+0.01		+0.0008		-0.0015	±0.0001

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* By electro-deposition

Table VI

Analysis of Samples from Anaconda Zinc Co.

		Copper		Lead		Cadmium	
Sample No.	Value	Average %	Deviation %(-a.d.)	Average %	Deviation %(-a.d.)	Average %	Deviation %(-a.d.)
A-58219	Ex.	0.0016	±0.0001	0.0163	±0.0009	0.0007	±0.0000
	Anac.	------		0.020		less than 0.01	
	Diff.	------		-0.0037	±0.0009	------	
A-59220	Ex.	0.0018	±0.0001	0.0227	±0.0008	0.0007	±0.0000
	Anac.	------		0.020		less than 0.01	
	Diff.	------		+0.0027	±0.0008	------	
A-58222	Ex.	0.0020	±0.0000	0.0158	±0.0019	0.0007	±0.0000
	Anac.	------		0.020		less than 0.01	
	Diff.	------		-0.0042	±0.0019	-------	
A-58835	Ex.	0.0017	±0.0001	0.0213	±0.0003	0.0006	±0.0000
	Anac.	------		0.021		less than 0.01	
	Diff.	------		+0.0003	±0.0003	------	
A-58836	Ex.	0.0016	±0.0001	0.0188	±0.0006	0.0006	±0.0000
	Anac.	------		0.014		less than 0.01	
	Diff.	------		+0.0048	±0.0006	------	

Table VII

Analysis of Samples from Canadian National Carbon Co.

Sample No.	Value	Copper		Lead		Cadmium	
		Average %	Deviation %(±a.d.)	Average %	Deviation %(±a.d.)	Average %	Deviation %(±a.d.)
T-11999	Ex.	0.0022	±0.0001	0.252	±0.007	0.184	±0.004
(CNC-1)	C.N.C.	0.0015		0.207		0.171	
	Diff.	+0.0007	±0.0001	+0.045	±0.007	+0.013	±0.004
T-5177	Ex.	0.0017	±0.0003	0.408	±0.002	0.308	±0.002
(CNC-2)	C.N.C.	0.0015		0.350		0.290	
	Diff.	+0.0002	±0.0003	+0.058	±0.002	+0.018	±0.002
T-16999	Ex.	0.0020	±0.0002	0.350	±0.000	0.278	±0.006
(CNC-3)	C.N.C.	0.0015		0.323		0.259	
	Diff.	+0.0005	±0.0002	+0.027	±0.000	+0.019	±0.006
T-?	Ex.	0.0022	±0.0001	0.365	±0.003	0.238	±0.002
(CNC-4)	C.N.C.	0.0015		0.320		0.205	
	Diff.	+0.0007	±0.0001	+0.045	±0.003	+0.033	±0.002
T-11288	Ex.	0.0022	±0.0001	0.286	±0.002	0.226	±0.001
(CNC-5)	C.N.C.	0.0015		0.268		0.201	
	Diff.	+0.0007	±0.0001	+0.018	±0.002	+0.025	±0.001
T-?	Ex.	0.0024	±0.0004	0.346	±0.001	0.218	±0.006
(CNC-6)	C.N.C.	0.0015		0.326		0.216	
	Diff.	+0.0009	±0.0004	+0.020	±0.001	+0.002	±0.006

Table VIII

Analysis of Samples from Burgess Battery Co.

		Copper		Lead		Cadmium	
Sample No.	Value	Average %	Deviation %(±a.d.)	Average %	Deviation %(±a.d.)	Average %	Deviation %(±a.d.)
B-32	Ex.	0.0020	±0.000	0.318	±0.002	0.208	±0.000
	B.B.	0.001		0.332		0.205	
	Diff.	+0.001	±0.000	-0.014	±0.002	+0.003	±0.000
B-33	Ex.	0.0021	±0.0000	0.107	±0.002	0.0018	±0.0002
	B.B.	0.0008		0.086		0.0025	
	Diff.	+0.0013	±0.0000	+0.021	±0.002	-0.0007	±0.0002

Table IX

Analysis of Samples from Schultz Metal Co.

		Copper		Lead		Cadmium	
Sample No.	Value	Average %	Deviation %(±a.d.)	Average %	Deviation %(±a.d.)	Average %	Deviation %(±a.d.)
1	Ex.	0.129	±0.001	0.0248	±0.0006	0.0018	±0.0001
	S.M.	0.14		0.003		nil.	
	Diff.	-0.011	±0.001	+0.0198	±0.0006	+ 0.0018	±0.0001
2	Ex.	0.130	±0.004*	0.0239	±0.0003	0.0017	±0.0001
	S.M.	0.14		0.003		nil.	
	Diff.	0.010	±0.001	+0.0209	±0.0003	+ 0.0018	±0.0001

* Electrodeposition

Table X

Interfering Elements *

There are some nineteen elements which may be found in zinc, either as impurities or as alloying elements. These are Cu, Pb, Cd, Ni, Co, Mn, Ag, As, Hg, Tl, Bi, Sb, Al, Fe, Ge, Ga, In, Mg, Sn.

ement Added	Concentration %	Analysis of zinc electrolyte		
		Copper %	Lead %	Cadmium %
Ag	0.05	0.0035	0.0044	0.0008
Al	none	0.0019	0.0137	0.0007
	1.00	0.0016	0.0136	0.0007
	2.00	0.0022	0.0136	0.0009
	4.00	0.0017	0.0141	0.0007
	8.00	0.0022	0.0119	0.0008
As	0.05	0.0035	0.0044	0.0008
Bi	0.002	0.0035	0.0049	0.0008
	0.01	0.0032	0.0047	0.0011
	0.05	0.0021	0.0048	0.0010
Cd	To be determined	Maximum amount determined using 8 gram sample approx. 0.5%		
Co	0.05	0.0035	0.0044	0.0008
Cu	To be determined	Large amounts (over 0.1%) removed by electrodeposition.		
	0.0034	0.0014	0.0046	0.0008
	3.00 (Cd added=none)	0.0276	0.0050	0.0010
	3.00 (Cd added=0.004)	0.0242	0.0048	0.0048
	3.00 (Cd added=0.009)	0.0198	0.0045	0.0094
	3.00 (Cd added=0.049)	0.0187	0.0040	0.0488
Fe	0.02	0.0037	0.0044	0.0009
	0.1	0.0045	0.0044	0.0012
	values not significant 0.5	0.0036	0.0058	0.0011
	values not significant 2.5	0.0039	0.0054	0.0014
Ga	not tested	-high discharge potential		
Ge	not tested	-chloride extremely volatile		
Hg	0.05	0.0034	0.0045	0.0008
In	0.002	0.0033	0.0042	0.0007
	0.01	0.0033	0.0041	0.0008
	0.05	0.0034	0.0044	0.0008
Mg	0.05	0.0034	0.0046	0.0009
	0.1	0.0034	0.0045	0.0008
	0.5	0.0032	0.0046	0.0009

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* "Interference" is intended to describe the preliminary or almost coincidental discharge of some undesired ion which either results in a masking of the wave desired or makes impossible the recording of the wave of the desired ion at maximum sensitivity.

‡ Special zinc used for Al additions.

Element Added	Concentration %	Analysis of zinc electrolyte		
		Copper %	Lead %	Cadmium %
Mn	0.05	0.0035	0.0044	0.0008
Ni	0.05	0.0035	0.0044	0.0008
Pb	To be determined			
Sb	0.002	0.0036	0.0046	0.0007
	0.01	0.0035	0.0046	0.0013
	0.05	0.0037	0.0086	0.00
Sn	0.001	0.0032	0.0046	0.0008
	0.002	0.0035	0.0047	0.0008
	0.004	0.0032	0.0056	0.0009
	0.008	0.0031	0.0078	0.0008
	0.016	(0.0029)	(0.0100)	0.0009
Tl	0.002	0.0035	0.0042	0.0007
	0.01	0.0035	0.0042	0.0010
	0.05	(0.0025)	------	------
	Normal zinc	0.0033	0.0047	------
	Normal zinc	0.0034	0.0047	0.0009

The only elements which are liable to cause interference as shown by the above table are, Bi which interferes when Cu wave when present in excess of 0.01%, Sn in excess of 0.0015% which interferes with the Pb wave, Sb in excess of 0.03% which interferes with Pb and Cd waves, and Tl in excess of 0.002% which interferes with the wave for Cd and eventually Pb(Tl = 0.05%). Cu interferes in excessive amounts (0.1%) but can be removed satisfactorily by electro-deposition as outlined.

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OBJECT AND AUTHORITY

The development of a polarographic method of analysis for trace elements in high purity zinc alloys.

This project was assigned to No.CE-138 in a letter dated October 24, 1942, and signed by O. Maass, Chairman Advisory Committee of Industrial Chemists, National Research Council.

A further grant was approved on April 8, 1943 to complete the project, the project number being changed from CE-138 to C-1000-42.

H. G. Thode

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THE POLAROGRAPHIC DETERMINATION OF TIN IN HIGH-PURITY ZINC AND ZINC DIE-CASTING ALLOYS.

ABSTRACT

The discovery that trace amounts of lead, cadmium and tin cause intergranular corrosion in zinc die-casting alloys, which results in a serious weakening of the alloy makes it important to have available a rapid and accurate method for determining trace amounts of these elements. The spectroscopic method has been applied with a fair degree of success, but the equipment necessary is expensive. A procedure has been developed for the determination of tin in high-purity zinc and zinc die-casting alloys present in amounts from 0.0001 to 0.2 per cent. The samples are dissolved in H_2SO_4, oxidized with H_2O_2, precipitated with cupferron, redissolved and reduced, and finally the tin determined with an accuracy of ±0.0001% when present in amounts less than 0.005%.

A method is now available for the routine polarographic determination of trace amounts of copper, lead, cadmium, and tin in high-purity zinc and zinc die-casting alloys with a high degree of accuracy and precision.

THE POLAROGRAPHIC DETERMINATION OF Sn IN HIGH PURITY ZINC ALLOYS

INTRODUCTION

The British Standard Specifications, B. S. S. 1003 and 1004 for Mazak or "Zamak," therein referred to as "High Purity Zinc and Zinc Alloys for Die-Casting" demands Tin 0.001 per cent max. for Ingot metal and Tin 0.002 per cent max. for the cast metal.

Present methods of analysis for tin are difficult to apply to trace amounts. The spectrochemical method has been reasonably successful to date, but the equipment necessary to obtain accurate results is expensive. At the suggestion of Mr. Scotland of the Metals Inspection Board, United Kingdom of Canada, an attempt was made to develop a polarographic method for the harmful metals, lead, tin, and cadmium, present as traces in High Purity Zinc and Zinc Alloys. A method was developed for the determination of copper, lead, and cadmium, but tin presented considerable difficulty. Application was, therefore, made for a grant to cover the expenses involved in developing a polarographic method for trace amounts of tin, in High Purity Zinc Die-Casting alloys, in order that a rapid and accurate method of analysis might be available for the determination of lead, cadmium, and tin by the Inspection Board.

Smrz[26] made a study of stannous tin and found that in a chloride solution (0.5 to 0.1 N HCl) the wave for tin almost coincides with that of lead, and that it was possible to determine tin to 10^{-6} mol./litre provided the stannous solutions were fresh, free from oxygen and acidic. He also observed an ageing effect for stannous tin in alkaline solutions which made the quantitative determination of tin in such a medium difficult. Kalovsek[9] studied the redox system of tin and found that stannic chloride is not reducible except in very strong chloride solutions (above 0.1 N) where its reduction appears inhibited. He also observed waves for stannous tin in alkali and citrate solutions. Strubl[27] investigated the anodic oxidation of the stannous tartrate complex. Lingane and Scott[13] were able to obtain waves for stannous tin in 2N perchloric acid and for stannic tin in 2N perchloric acid in the presence of at least 0.5 N chloride. Shokhov[25] determined stannous tin in potassium fluocolumbate and metallic columbium (niobium) using an alkaline citrate medium. Winkel and Proske[28] state that in acid and neutral solution, cobalt, lead, and tin (ous) come too close together to give separate waves. In alkaline solutions a good separation is obtained. Cozzi[4] determined tin in white metals by difference from the sum of the lead and tin (ous) waves. The lead alone was determined in alkali medium, and the sum of tin and lead by reduction in acid chloride medium. Seith and Esche[24] also used the method of measurement of difference for tin in Zinc. The lead wave alone is obtained by volatilizing the tin as stannic chloride from acid solution.

The work of the above authors indicates that the applications of the polarograph to the determination of tin are nearly always complicated by the fact that the tin (ous) wave is almost coincident with that of lead. The determination of tin by difference is inclined to be inaccurate when the lead concentration exceeds that of the tin by a factor of approx. five. Cozzi[4] partially surmounted this difficulty by making a preliminary separation of most of the lead, but this particular procedure is rather impractical for trace elements in zinc due to the difficulties of precipitation. The purpose of this investigation was, therefore, to develop an accurate method for the determination of trace amounts of tin (0.001 per cent or less) in high purity zinc die-casting alloys by as direct a method as possible.

Preliminary Investigations

Inasmuch as the determination of tin by difference from the lead is liable to be inaccurate, if not impossible under certain conditions, two possibilities were considered: one, the formation of a suitable complex to cause a shift in the half-wave potential of tin to such a value that it would no longer coincide with that of lead, two, the quantitative separation of tin and lead by chemical means. Inasmuch as the diffusion current for the stannic ion is not sufficiently great for the purpose at hand,[9] it was decided to confine experiments to the stannous ion.

In the attempts at complex formation, tartaric acid was tried but abandoned because of an apparently low diffusion coefficient for stannous tin in such a medium. A number of experiments were conducted using the oxalate ion, both as potassium oxalate and oxalic acid. It was found that in neutral oxalate solution, two waves were obtained for tin. This medium was abandoned for two reasons: first, in the reduction method of Cozzi[4] the reagents used tend to prevent the formation of an oxalate complex of tin, and second, in the Al reduction method the Al precipitates as oxalate causing erratic results. It was established, however, that K-oxalate is a more suitable medium for tin than oxalic acid. In the latter, the waves exhibit maxima and seem hindered. In K-oxalate, two cathodic waves were observed, whereas, in oxalic acid solution, only one cathodic wave was found. Increasing K-oxalate from 0.2 to 2 M caused a shift of -0.05 v in the $E_{\frac{1}{2}}$ for tin (ous) (to more negative values). On the other hand, the addition of HCl to K-oxalate tin solutions apparently destroys the complex and thereby rules out the Cozzi reduction method for tin in K-oxalate solutions. Above 0.1 M a heavy precipitate is formed.

Attempts were made to separate the tin by co-precipitation[3, 1] with the aluminum already present in the zinc die-casting alloy. It was found that the tin and lead were both precipitated and the method was slow and tedious, due to the large amount of aluminum present.

N. H. Law[12] reported that it was possible to separate tin in foods by distillation using the principle of Scherrer[21, 22]. The tin is estimated in the distillate by means of "Dithiol" (Toluene--3:4- disulphonic acid). Hoffman and Lundell[8] have also used this distillation method with success. With slight modifications of their apparatus (Fig. 1), it was found possible to distil tin from 10 g samples of Zn. So far, attempts at the determination of the tin, polarographically, in the distillate have been unsuccessful, possibly due to the presence of HBr in the distillate. Further, the reagent "Dithiol" used by Law for the colorimetric determination of tin in the distillate, was unavailable. The following results were obtained for the distillation of tin using solutions of $ZnCl_2$ and added tin.

Distillation of Tin

Procedure used

Ten mg. of tin as the chloride were introduced together with a chloride solution equivalent to 10 gms. of zinc. These solutions were washed down with a few ml. of water, and the whole heated to boiling using a bath of Wood's metal. If the flask is coated with carbon black prior to immersion in the bath, the metal will not adhere to the glass. 45 ml. of conc. sulphuric acid were placed in the funnel and run fairly rapidly into the solution, until the temperature reached 130-132 degrees C. at which point bumping almost invariably occurred. The remaining acid was then run in as rapidly as possible and the whole raised to 220 degrees C. Hydrobromic acid was then added dropwise over a predetermined perio of time. Dry carbon dioxide was bubbled into the system throughout the distillatio The distillate was collected in a series of 3-25 ml. receivers, each containing 5 ml. of water. The tin in the distillate was then reduced by the method of Scherrer[23] and Clarke et al[3], using stabilized starch indicator as described by Ehrlich[5]. The only modifications in the reduction apparatus were the use of a three-necked flask and introduction of the thermometer, through the air condenser, suspended by a wire.

The reducing flask was charged by the addition of the distillate, 75 ml. conc. HCl, 5 gm. of granulated test lead and 20 gm. pure NaCl. This was diluted to 300 m with H_2O and boiled for 1 hour in a stream of dry CO_2. After reduction, the flask was cooled to 10 degrees C., and 5 ml. KI (10%) and 5 ml. of starch solution added. The Sn^{+2} was titrated with 0.01 N iodine solution standardized against tin.

Results

The experimental work was designed to establish the relationship between amount of tin recovered and each of the following variables as a preliminary to the polarographic determination.

(a) time of distillation (constant--60 mins.)
(b) volume of hydrobromic acid used (constant--25 ml.)
(c) temperature of distillation (constant--220 degrees C)
(d) amount of tin present (constant--10 ml.)

The following points were established:-

(1) When HCl is substituted for HBr, only 6.6 per cent of tin is recovered under conditions which recover 98 per cent using HBr.

(2) The HCl distilled below 220 degrees C (produced by action of H_2SO_4 on $ZnCl_2$) contained 5.2 per cent of the tin.

(3) The average recovery of tin from Zn solutions is slightly lower than from pure tin solutions under the same conditions.

(4) Recovery of about 99 per cent of 10 mg. of added tin was made using 25 ml. HBr at 220 degrees C over a period of 60 mins.

(5) A steady state is almost reached, where no further tin is distilled, at 25 ml. of HBr and 60 mins. indicating that the optimum conditions would be at 35 ml. and 75 mins.

Cupferron

Cupferron has been successfully used as a precipitant for the separation of tin from many metals. Attempts to separate tin from lead in zinc alloys met with rapid success and resulted in the present successful method.

THE POLAROGRAPHIC DETERMINATION OF TIN IN HIGH PURITY ZINC AND ZINC ALLOYS USING CUPFERRON AS A PRECIPITANT

LITERATURE

Rothschild[20] used cupferron for the detn. of Cu and Fe in Zn metal and Zn dust. Kling and Lassieur[10] report a method for the separation of Sn and Sb with cupferron, but N. H. Furman[6] has criticized the procedure and offers a modification involving th use of H_2F_2 and H_3BO_3 as a precipitating medium, by means of which tin may be separated from Cu, Pb, As, Sb, Bi, Cd, Zn, Mn, Co, and Ni. In both cases, however, the tin is ignited to SnO_2 and weighed as such. Pinkus and Claessens[17] have modified the method of Furman and produced Zn, as well as Al, Mn, Co, Ni, Ag, Cd, and Hg^{+2}. Pinkus and Martin[18] claim practically complete precipitation of Hg^{+2}, Cu, Bi, Sb^{+3}, Sn^{+2}, Sn^{+4}, Fe^{+2}, Fe^{+3}, when in the presence of dil. strong acids. The solubilities of the various precipitates are also given.[19] Chervyakov and Ostroumov[2] have modifie the procedure of Pinkus and Claessens to allow for the presence of thio salts for the determination of Sn in the presence of Sb and As. Mack and Hecht[16] report a microgravimetric method for separation of Sn and Sb but claim that the Sn must be present in the Sn^{+4} state. ¶ Lundell and Knowles[15] have surveyed the uses of cupferron as a reagent in quantitative analysis, but make no mention of the determination of tin. The most complete survey of the uses of cupferron in quantitative analysis, is presented by Lundell and Hoffman[14] who list in a table the effect of cupferron on the elements of the periodic system when used in 1:9 H_2SO_4 or HCl. According to this table, cupferron can be used to separate tin and lead in the presence of zinc, magnesium and aluminum, found in zinc die-casting alloys. However, no mention has been made of the use of cupferron for the separation of micro quantities of tin, of the order of 10γ, particularly in the presence of a large excess of other metal ions such as are found in zinc and zinc die-casting alloys.

APPARATUS AND REAGENTS

This work was carried out exclusively on the Heyrovsky Model XI Polarograph (E. H. Sargent and Co.) which has a galvanometer sensitivity of 0.0027 uA/mm. The same capillary was used as in the work on copper and lead and cadmium, and the precautions observed were the same. The electrolysis cell with an external anode was of a design similar to that of Lingane and Laitinen[11] (Fig. 2). The solution of the samples was carried out in 150 ml. beakers which were cooled in a bath of running water prior to precipitation. Filtrations were made with Jena No. 3 sintered glass crucibles and the precipitate dissolved in the apparatus shown in Fig. 3. Reductions were carried out in a 50 ml. flask (Fig. 4.), through which a steady stream of CO_2 was passing. After reduction, the flask was cooled to 25 degrees C and finally after proper dilution, a portion of the solution was transferred to the electrolysis cell as shown in the diagram (Fig. 2). A stream of CO_2 or N_2 was maintained through the solution in the electrolysis cell during the transfer, and over the solution when ready to record.

The reagents outlined were tested for tin content by the method of difference. After proper treatment, the residue in each case was added to ten grams of analyzed zinc and the whole carried through the procedure for tin. After subtracting the residual current for the tin in the zinc and reagents, the correction for the tin in the reagent tested was obtained.

Distilled Water:-

Duplicate samples of 1 litre of distilled water were evaporated with 4 mls. of conc. H_2SO_4 until fumes of SO_3 appeared. The zinc was then added and the procedure followed. The correction for the 200 ml. of H_2O used in the procedure amounted to 7×10^{-5} per cent of Sn. As noted below, no correction is necessary for the 4 ml. of H_2SO_4 in excess of normal.

Example:-

Average height of tin wave in sample--19.8 mm.
Height of tin wave in analyzed zinc---12.9 mm.
Height due to 1000 ml. H_2O 6.9 mm.

Now, 6.9 is equivalent to 0.0186 uA.
By calibration, the tin in a 10 gm. zinc sample in 50 ml.
is 0.0147 per cent/uA.
Therefore, we have in 1 litre of water what would correspond to
0.0003 per cent Sn for 10 gm. Zn in 50 ml.
Hence, the 200 ml. of water used in the procedure requires a
correction of 7 x 10^{-5} per cent Sn on each zinc sample.

Conc. H_2SO_4 (Sp. Gr. 1.83):-

Duplicate samples of 200 ml. of conc. H_2SO_4 were evaporated to approx. 4 ml. and ten grams of zinc added. After following the procedure for tin, the correction for the 200 ml. of H_2SO_4 required in the procedure amounted to 6.9 x 10^{-6} per cent of Sn/ 10 gm. Zn in 50 ml. That is, the H_2SO_4 contained 6 γ or 1.89 x 10 per cent Sn.

H_2O_2 (30 per cent):-

Duplicate samples of 100 ml. of 30 per cent H_2O_2 were evaporated to fumes with 4 ml. of H_2SO_4 and ten grams of analyzed zinc added. After treatment, no traces of tin in excess of that due to the zinc were found. Thus, no correction was necessary.

Conc. HCl (Sp. Gr. 119):-

Duplicate samples of 200 ml. of HCl were evaporated slowly to fumes of SO_3 with 4 ml. of H_2SO_4 and treated as outlined above. No traces of tin were found and hence no correction was necessary. The possibility that the tin may be lost by volatilization as $SnCl_4$ was considered, but on the basis of experiments conducted in the preliminary investigations whereby attempts were made to determine tin by first recording the Pb Sn and then volatilizing the $SnCl_4$ this possibility was eliminated.

Conc. HNO_3 (Sp. Gr. 1.42):-

Duplicate samples of 200 ml. of conc. HNO_3 were evaporated to fumes with 4 ml. of conc. H_2SO_4. After treatment, no traces of tin were found and consequently no correction was necessary.

Al-foil (approx. 0.015"):-

Ten grams of zinc were added to 5 g of Al-foil, in duplicate, and the whole carried through the procedure for tin. Precipitations were made from a 250 ml. beaker and a volume of 150-175 mls. of solution. 27 mls. of H_2SO_4 in excess of that normally required for Zn, were necessary for solution. Tin corresponding to 127 γ was found, equivalent to 0.0012 per cent/10 gm. Zn in 50 ml. Correcting for the excess of H_2SO_4 added, we have (127-0.8) or 126 γ in 5 grams of Al. Therefore, correction for 0.1 gm. of Al used in the reduction of the tin was 0.00000252 gm. or 2.5 x 10^{-5} per cent Sn/10 gm. Zn in 50 ml.

Phenacetin:-

Duplicate samples of 1 g. of phenacetin were ignited until free from organic matter (20 min.) and the residue fumed with 4 ml. of H_2SO_4. A few drops of HNO_3 were added after cooling and the whole again brought to a boil. The contents of the crucible were then transferred to a 150 ml. beaker and treated as usual. A wave-height equivalent to 5.5 mm. or 0.0002 per cent/10 gm. Zn in 50 ml was observed. Hence, there was no appreciable correction necessary for the 0.0075 g phenacetin used to stabilize the cupferron used in the precipitation.

Gelatin (0.2 per cent aqueous):-

Duplicate samples of 1 g. of gelatin were ashed for 20 min. The ash was treated with 2 ml. H_2SO_4 and a few drops of HNO_3 and warmed. The whole was then transferred to a 150 ml. beaker and treated as usual. A wave-height equivalent to 3.2 mm. or 0.0001 per cent Sn for 10 gm. Zn in 50 ml. was found. The correction for the 1.25 ml. of 0.2 per cent gelatin solution was negligible.

Cupferron (5 per cent aqueous):-

Duplicate samples of 2.5 g. of cupferron were ignited, the residue treated with 2-5 ml. portion of H_2SO_4 and the whole transferred to a 150 ml. beaker and treated as usual. A wave-height equivalent to 4.3 mm. or 0.0001 per cent Sn/10 gm. Zn in 50 ml. was found. The correction for the 3 ml. of 5 per cent solution of cupferron used in the procedure was 6.8×10^{-6} per cent.

Filter-Aid (Celite, Analytical):-

A diatomaceous earth especially purified for analytical use. This material is supplied by The Johns-Manville Co. No traces of tin were found within the limit of detection of the instrument.

The overall effect of impurities amounted to Sn--0.00011 per cent.

Standard Stock Solution for Tin:-

23.7521 gms. of Sn (containing 0.05 per cent foreign metals) dissolved in 1:1 HCl and diluted to 1 litre with 1:1 HCl to give a 0.200 M solution.

PROCEDURE

To 10 gms. of zinc in a 150 ml. pyrex beaker add 50 ml. of distilled water and 15 ml. of conc. H_2SO_4 (Sp. Gr. 1.84). When the reaction has subsided, warm on a sand bath to complete the solution of the zinc. Wash down with distilled water, dilute to 100 ml. and add 5 ml. of 30 per cent H_2O_2. Boil until solution is complete and all H O is decomposed*. Dilute again to 100 ml., add 5 ml. conc. HCl (Sp. Gr. 1.19) and cool in running water (15 degrees C. or less)†. Add about 3 ml. of a 5 per cent solution of cupferron (stabilized with phenacetin**) drop by drop with constant stirring. Stir until the precipitate coagulates***. Stir in approx. 0.1 g. of Analytical Filter-Aid (Johns-Manville Co.) and filter within half an hour (keep solution cool if allowed to stand with precipitate) using moderate suction on a Jena No. 3 sintered glass filtering crucible. Wash beaker and precipitate with 20 ml. of 0.05 per cent cupferron solution, containing 1:50 H_2SO_4. Dissolve precipitate in the filtering crucible with 10 ml. conc. HNO_3 (used in small portions e.g. 5+5 or 3+3+4) and wash with water, collecting the filtrate in the original beaker. Add 4 ml. conc. H_2SO_4 and evaporate to fumes. Cool, add 5 ml. HNO_3 and evaporate again to fumes. Wash down with 10 mls. of water and warm to dissolve salts. Transfer to a 50 ml. reduction flask, using a rubber policeman to ensure complete transfer. Add 4 ml. conc. HCl and 0.1 gm. pure Al-foil. Heat gently in a stream of CO_2 until clear and then for 15-30 mins. longer to ensure complete solution of the tin. Cool, add 1.25 ml. of fresh 0.1 per cent gelatin solution and dilute to volume, with freshly boiled distilled water. Cool to 25 degrees C., adjust volume, transfer to electrolysis cell, through which a stream of N_2 is passing, and electrolyze immediately from -0.3 to -0.7 v, using a saturated calomel reference electrode. Record polarogram at greatest sensitivity possible.

*If solution is not complete add a second portion of H_2O_2. The absence of H_2O_2 is indicated by the absence of small bubbles at the surface of the boiling solution. Add extra water if necessary to keep salts in solution.

†cf. Section on interference of lead.

**5 per cent cupferron (5 gm. B.D.H. cupferron) Dilute to
(0.25 ms. Acetophenetidine (Phenacetin) 100 ml.

***Sometimes, in the presence of certain quantities of elements, such as Pb, As, Sb, or for unknown reasons, the precipitate will not coagulate. In such an event, filter after 10 min. stirring.

Results and Discussion

The electrocapillary curve and capillary constant in the medium in which the tin is determined were measured for the purpose of refering results to other capillaries. The temperature of measurement was 25.0 degrees C. and h = 36.5 cms. Hg.

Table 1

Electrocapillary Curve

Potential (volts)	0v cell disconnected	0v cell connected	-0.3v	-0.5	-0.7
Time (25 drops)	78.75 81.40 79.60	80.10 80.30	80.6 80.5	84.1 84.3	84.15 84.25
Drop Time	3.20 secs.	3.21 secs.	3.22	3.36	3.36

Table 2

Capillary Constant

Applied Pot. (S.C.E.)	Temp.	No. drops	Time	Weight(mgs.)	$m^{2/3}t^{1/6}$
-0.5	24.8 degrees C	50	168.4	211.7	1.43
-0.5	24.8 degrees C	50	169.2	213.7	1.43

The capillary was next calibrated for tin by making additions of tin from the diluted stock solution. The calibrations were carried out over a concentration range of 10^{-6} M to 3×10^{-3} M and the step-heights obtained by difference from the residual current of the tin present in the zinc used as a base. The calibration constants for three successive calibrations are given in Table 3.

Table 3

Calibration constants for tin in zinc.

Added conc. Sn moles/ litre	Per cent added Sn (10 g Zn in 50 ml.)	(1) Factor %/uA	(2) Factor %/uA	(3) Factor %/uA	Av Factor %/uA
1×10^{-6}	0.00006	0.00375	0.01362	0.02500	0.0141
5×10^{-6}	0.0003_0	0.01428	0.01605	0.01356	0.0146
2.5×10^{-5}	0.0014_8	0.01558	0.01586	0.01756	0.0163
1.25×10^{-4}	0.0074_2	0.01418	0.01645	0.01432	0.0148
6.25×10^{-4}	0.0371	0.01322	0.01347	0.01336	0.0134
3.13×10^{-3}	0.1855	----------	0.01264	0.01735	0.0151
			Average Factor--		0.0147

The factors were obtained in terms of per cent of the metal per microampere of diffusion current for a 10 gm. sample of zinc in 50 ml. of solution for the sake of convenience in calculating the results of analyses.

In order to determine the precision of the method, and to discover the greatest source of error in the procedure, four series of determinations were carried out.

(a) Precision of repeated determinations on the same cell.

(b) Precision of repeated determinations on different aliquots of the same solution.

(c) Precision of repeated determinations on different samples of the same alloy.

(d) Precision of repeated measurements on same curves by

    (1) different individuals

    (2) the same individual

Table 4

Precision of polarographic procedure.

Tin

Series		Average %	Deviation % (±a.d.)	Method
(a)		0.0020_9	±0.00004	Av. Deviation from mean of eight runs.
(b)		0.0019_0	±0.00003	Av. Deviation from mean of five runs in duplicate.
(c)		0.0021_0	±0.00008	Av. Deviation from mean of seven samples (duplicate runs)
(d)	(1)	0.0007_4	±0.00002	Av. Deviation from mean of two observations on each of six different curves for nine individua
	(2)	0.0007_3	±0.00002	Av. Deviation from mean of ten observations on each of six different curves by the same individual.

It is apparent that the error of reproduction of the curves by the instrument is very small, and that the error is almost entirely that of measurement of curve heights in this case. The error of repeated determinations on different samples is of the same order as the error of measurement of curve heights.

The accuracy of the procedure was determined by the analysis of a series of samples from the National Bureau of Standards, Washington, D. C. The results are shown in Table 5.

Table 5

Accuracy of Method
Experimental Values
(% Sn/10 gm. Zn in 50 ml.)

Sample No.	(1)	(2)	Av	Corrected	Certificate
#108 Spelter	0.0008_3	0.0007_1	0.00077	0.0007±0.0001	0.0008
#109 Spelter	0.0004_2	0.0004_3	0.00043	0.0003±0.0001	0.0002
#110 Spelter	0.0005_4	0.0005_7	0.00056	0.0005±0.0001	0.0005
#94 Al, Mg, Cu, Die-Casting Alloy	0.0007_2	0.0009_2	0.00082	0.0007±0.0001	$<$0.0005

The above table indicates that within the limit of the precision, the method is accurate to 1×10^{-4} %, except in the case of the die-casting alloy, where the error is 2×10^{-4} %. No explanation is available for the greater error in this case.

Al-reduction

The reduction process used in the procedure for tin was developed in our own laboratory for the purpose on hand, and as a result, a few essential facts about its manipulation will be given. The process is based upon the fact that metallic aluminum reduces tin to the metallic state quantitatively, and the resulting tin redissolves in HCl to the stannous state in an inert atmosphere.

Experiments have indicated that from 1 to 10 ml. of conc. HCl are quite satisfactory for amounts of tin up to 0.002 per cent but 4-5 ml. is recommended as ideal, in that the process is neither too slow nor rapid enough to be violent. In the event that the tin content is in excess of 0.007 per cent, an increase in the amount of HCl added is adviseable. Add 6 ml. HCl when Sn content is 0.04 per cent and 8 ml. HCl when Sn content is 0.2 per cent. By this means the reduction proceeds in a reasonable length of time. Additions of Al-foil from 0.025 to .05 gram were tried and were equally successful in the presence of 0.002 per cent Sn but 0.5 gram of Al caused a violent action. Al of approx. 0.1 gram is recommended. Studies of the time of digestion after the solution has lost its turbid appearance indicate that from 15-30 mins. is the best time. A longer digestion is wasteful of time. The ideal time is about 20 mins.

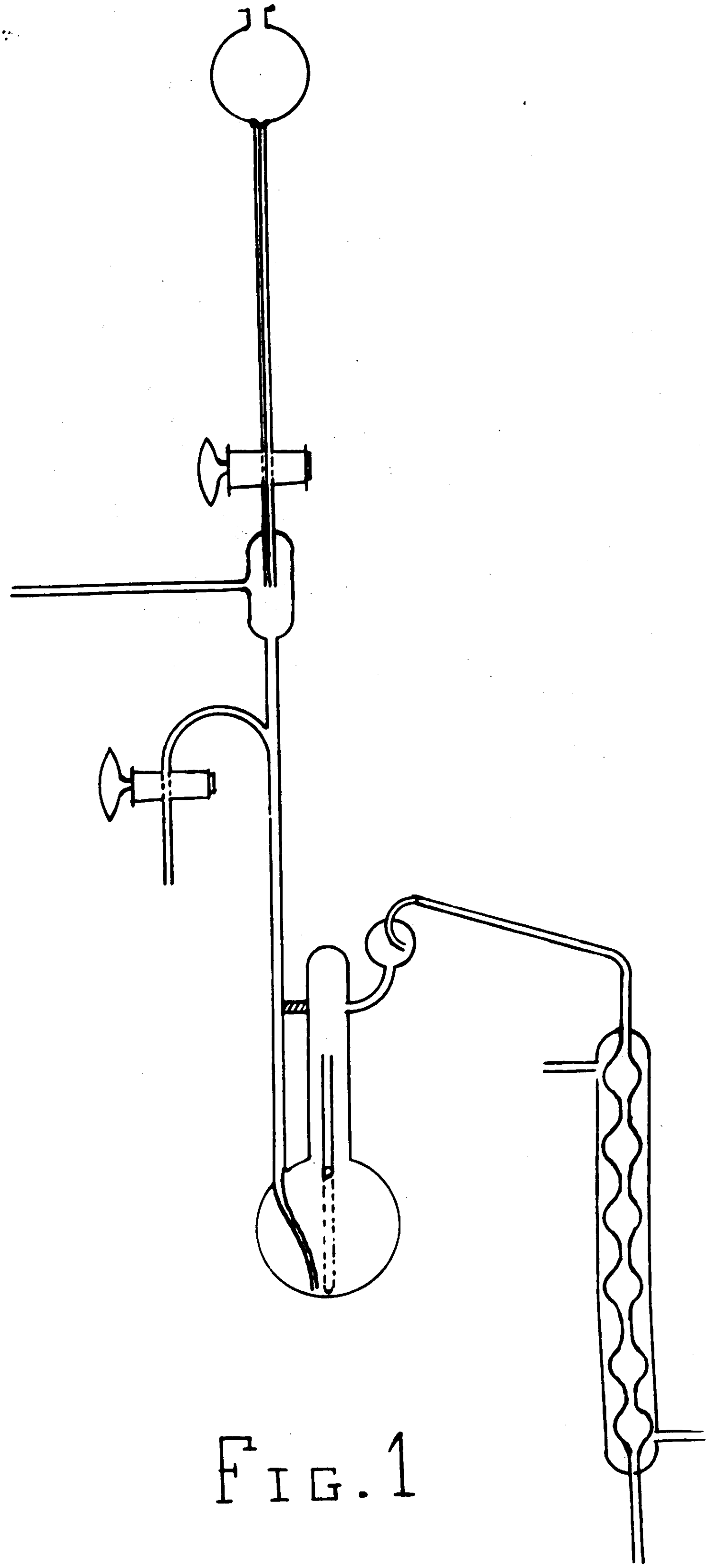
With these refinements, the procedure is satisfactory for tin concentrations up to 0.2 per cent. Larger amounts have not been tried although they should not be impossible. In such a case, however, it would be preferable to use a smaller sample.

Interfering Elements

The interference of some nineteen elements which may be found in zinc, either as alloying elements, or as impurities, has been considered. They are listed as follows:- Sn, Sb, As, Pb, Bi, Cu, Cd, Fe, Ni, Co, Mn, Al, Tl, In, Ag, Hg, Ge, Ga, and Mg.

Of these, Sn is to be determined. According to Lundell and Hoffman [14] Cupferron in diluted 1:9 HCl or H_2SO_4 will precipitate Sn, Bi, Sb, Ga, Fe, completely, Cu, and Tl incompletely. Furthermore, no precipitation of Sb as Sb^{+5} will occur. This leaves only Bi, Ga, Fe, Cu, and Tl as possible interfering elements. In a reduced chloride medium Ga and Fe^{+2} would not be expected to interfere because their discharge potentials are above that of Sn^{+2}. This leaves only Bi, Cu, and Tl as interfering elements from a polarographic point of view, and two of these, Cu and Tl are known to be incompletely precipitated.

Extensive experiments have shown that there is absolutely no interference from Co, Hg, Mn, Ni, Ag, Fe, Tl, Sb, when these elements are present in amounts of 0.05 per cent. In every case this is more than would normally be expected in high purity zinc or zinc die-casting alloy. The Fe may possibly be an exception to this, but as pointed out above, the Fe^{+2} has a discharge potential well above that of Sn^{+2}. Cd up to one per cent has no detectable effect on the determination of Sn. Bi was tried at the level of 0.05 per cent, and although a black residue appeared in the reduction flask (Bi) the wave for tin was quite normal. Al and Mg were already present in the metal used for the development work in amounts of approx. 4 per cent and 0.1 per cent respectively. That there is no interference from these elements is born out by the fact that the calibrations for Sn were made in their presence and the procedure applied with equal success to spelters (cf. B. Stds. NO. 108 No. 109, No. 110). In, Ge, and Ga were not tried, partially because of the difficulty in procuring the respective salts and partially on the basis of the confirmation of Lundell and Hoffman's work, on elements precipitated by Cupferron by the writers. Of the other three, only one, Ga, is expected to precipitate



Scale = 1/4

FIG. 1

Sn-Distillation Apparatus.

R.C.

and this has a higher discharge potential than Sn. As is not expected to precipitate, and tests with As = 0.05 per cent show no interference from this source.

The two remaining elements, Pb and Cu were found to give difficulty. The Pb is not precipitated by the cupferron, but is separated with the cupferron precipitate of Sn as $PbSO_4$ which later dissolves in the HNO_3 to appear as Pb^{+2} in the final solution. Cu is incompletely precipitated and appears in the final solution in the extent to which it is precipitated.

It was found, however, that by the addition of 5 ml. conc. HCl to the solution prior to cupferron precipitation, that Pb up to 0.01 per cent can be present without precipitation of $PbSO_4$. For the determination of Sn in the presence of larger amounts of Pb (up to 1.3 per cent tried) the Pb can be removed by suction filtration on a sintered glass crucible of the oxidized sulphuric acid solution to remove $PbSO_4$, followed by the addition of 5 ml. HCl and the precipitation of the Sn with cupferron. The use of larger amounts of HCl is not sufficiently effectiv to warrant its use.

The interference of Cu presented a more difficult problem. Copper up to 0.04 per cent can be tolerated by the procedure, and even amounts of 0.25 per cent are not impossible, although in this extreme case the limit of detection drops because of the necessity for using a lower galvanometer sensitivity to compensate for the Cu. It was found, however, that by a rapid 30 min. deposition of the Cu from the sulphuric acid solution using 2 amps at 5 V and a rotating gauze anode, that 3 per cent of Cu can be removed to such an extent that no interference is found. Experiments indicate Cu from 0.05 per cent to 3 per cent are easily deposited. The deposition is practically quantitative giving slightly high results for copper due to contamination of the deposit. The deposition is not affected by the presence of as much as 0.2 per cent tin which is quantitatively determined in the electrolyte by the usual procedure. Deposition times from 15 to 60 mins. were tried and deposition was found to be sufficiently complete in 30 mins. for the purpose on hand.

CONCLUSIONS

A procedure has been developed for the polarographic determination of tin in high purity zinc and zinc die-casting alloys which with suitable application of the procedure outlined, is accurate and precise in the presence of nineteen elements, which are liable to be present in varying amounts for tin contents rangeing from 0.001 per cent to 0.2 per cent. Furthermore, because of the nature of the procedure, it has application, with suitable modifications, for the micro-determination of tin in numerous other materials without recalibration of the capillary.

It is possible that with further work, the distillation procedure may be developed into a procedure for the micro-determination of tin polarographically, which would be far shorter than the present successful procedure. Recently, a modification had suggested itself, which should be an improvement, namely, the elimination of HCl from the procedure, by the use of H_2SO_4 only and such HNO_3 as may be necessary. In this way there would be no distillation of tin before the addition of the HBr. This would mean that the volume of distillate which it was necessary to retain would be considerably lessened.

It should also be pointed out that although the procedure for tin was developed using a 10 gram sample of zinc, there is no reason why a larger or smaller sample could not be used. If for example, a 100 gram sample is used, it should be possible to detect 1×10^{-5} % of tin following the procedure (with suitable modifications).

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