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POLAROGRAPHIC DETERMINATION OF ZINC IN MAGNESIUM AND MAGNESIUM ALLOYS

(INVESTIGATION OF METHOD ISO/TC-79/SC-1-145)

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MINERAL SCIENCES DIVISION

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Marilyne Spotswood* and C.H. McMaster**

SUMMARY OF RESULTS

A polarographic method for the determination of zinc in magnesium and magnesium alloys, as described in Document 145 of Technical Committee 79 of the International Standards Organization (ISO/TC-79/SC-1-145), has been evaluated. The method employs an ammoniacal-citrate solution as the supporting electrolyte.

The method is suitable for zinc contents ranging from 0.1-4%, as recommended in Document 145, provided that the amounts of other constituents in the alloy are known beforehand.

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INTRODUCTION

The work presented in this report was undertaken in order to evaluate a polarographic method for the determination of zinc in magnesium and magnesium alloys as described in Document 145 of Technical Committee 79 of the International Standards Organization (ISO/TC-79/SC-1-145). The proposed method uses an ammoniacal-citrate supporting electrolyte that allows zinc to be determined in an alkaline solution while preventing the precipitation of aluminium hydroxide. The method is recommended for the determination of zinc in the range 0.1 - 4%.

Evaluation has been made by applying the method to the analysis of magnesium alloys containing various amounts of zinc and aluminium, and by noting the effects of other metal ions on the zinc polarogram.

EXPERIMENTAL

Apparatus

Polarograph: Leeds and Northrup Electrochemograph, Type E.

Polarographic Cells: Most of the work was performed with a single compartment cell employing a pool of mercury as the anode and a dropping mercury electrode as the indicating electrode.

For the measurement of half-wave potentials an H-type of cell was used with a saturated calomel electrode (S.C.E.) serving as the reference electrode.

All polarographic measurements were made at 25 $\pm$0.1°C.

Reagents

Hydrochloric acid: C P grade, sp gr 1.19.
Citric acid: 40% (w/v) aqueous solution.
Ammonium chloride: C P grade.
Ammonium hydroxide: C P grade, sp gr 0.90.
Sodium sulphite: 20% (w/v) aqueous solution (freshly prepared).
Triton X-100: 0.1% (v/v) aqueous solution.
Standard zinc solution: 0.2% (w/v) solution.

Dissolve 2 g pure zinc in 60 ml 1:1 hydrochloric acid. Transfer to a 1000 ml volumetric flask and dilute to volume with water.

0.05% (w/v) solution.

Transfer 50 ml of 0.2% zinc solution to a 200 ml volumetric flask and dilute to volume with water.

Procedure

In the procedure outlined below for the preparation of the calibration graph and the sample solution, Triton X-100 is substituted for gum arabic, or tylose, as the maximum suppressor. Otherwise the procedure is identical to that outlined in Document 145.

1. Preparation of Calibration Graph

Into each of a series of seven beakers place 1.000 g of pure magnesium. Dissolve in 10 ml of water and 8 ml of hydrochloric acid. After complete dissolution, boil for a few minutes and transfer to 100 ml volumetric flasks.

To the flasks transfer aliquots of the standard zinc solutions corresponding to 0 (blank), 2.5, 5.0, 7.5, 10, 15, and 20 mg zinc.

To each flask add reagents in the following order with mixing between additions:

20 ml citric acid solution
5 g ammonium chloride
13 ml ammonium hydroxide
4 ml sodium sulphite solution
1 ml Triton X-100 solution

Cool the solution to room temperature, make up to volume with water, and mix well.

Transfer a portion of the solution to a polarographic cell, allow it to stand in the bath for a few minutes to reach constant temperature, and record the polarogram. Construct a plot of wave-height versus concentration of zinc.

2. Preparation of Sample

Place a sample of appropriate size (1.000 g alloy for Zn < 2%; 0.500 g of alloy + 0.5 g of pure magnesium for Zn > 2%) in a beaker, and dissolve it in 10 ml of water and 8 ml of hydrochloric acid. After the reaction has ceased, boil the solution for a few minutes and filter it catching the filtrate in a <u>100</u> ml volumetric flask. Wash the filter paper with water.

To the flask add the supporting electrolyte reagents, sodium sulphite solution, and the maximum suppressor in the same quantities, and in the same order, as shown in the preparation of solutions for calibration. Dilute to volume and record the polarogram.

Measure the wave-height and determine the amount of zinc present in the sample by reference to the calibration graph.

RESULTS AND DISCUSSION

Half-Wave Potential

The half-wave potential of zinc, in the ammoniacal-citrate solution used in the prescribed procedure, is - 1.35 volts vs S.C.E. The solution attains a pH of 8.5 ± 0.1.

Dissolution of the Sample

Magnesium-aluminium alloys dissolve readily in dilute hydrochloric acid. Oxidizing agents, such as potassium chlorate or hydrogen peroxide, can be added to dissolve any residue remaining after the acid treatment; however, in most cases the residue is small enough to be disregarded.

Interferences

Metal ions that are reduced at more positive potentials than, or in the vicinity of, the half-wave potential of zinc can interfere with the zinc reduction step. Copper, cadmium, nickel, iron, and cobalt are possible interfering elements.

Copper and cadmium ions are reduced at more positive potentials than zinc, and interfere only when present in larger amounts than the zinc. Using the present procedure for dissolution of the alloy, most of the copper remains in the residue.

Nickel ions are reduced just prior to the zinc reduction step and amounts equal to or less than the zinc concentration can be tolerated. With larger amounts of nickel the zinc wave is difficult to measure accurately.

Ferric ions are reduced at about the same potential as zinc in this medium. Usually iron occurs only in trace amounts ($\leq 0.005\%$) in magnesium-aluminium alloys, but occasionally may be as high as 0.05%. Tests show that ferric ions interfere when the ratio Fe:Zn is greater than 1:25. Thus, the amount of iron in the alloy must be known prior to the polarographic determination of zinc.

Cobaltous ions are also reduced at the same potential as zinc but do not appear to be present in magnesium-aluminium alloys.

Application to Magnesium Alloys

The results obtained with various magnesium alloys are shown in Table 1. These alloys, with the exception of BCS 307 (British Chemical standards sample No. 307), contained aluminium in the range from 3 - 8%. BCS 307 was reported to contain 2.84% of rare earths.

The polarographic method is applicable to the determination of zinc in the concentration range recommended in Document 145. However, due to the interferences described above, it is essential to know the amounts of such elements in the magnesium alloy.

MS:C.H.McM/af

TABLE 1

Determination of Zinc in Magnesium Alloys by Method

ISO/TC-79/SC-1-145

Magnesium Alloy	NBS 171 (Zn = 1.05%)	BCS 307 (Zn = 2.08%)	ATESIA 1	ATESIA 2	ATESIA 4	ATESIA 8	DOMAL 12
Zinc Found (%)	1.03	2.11	0.502	0.925	0.477	3.12	0.699
	1.03	2.12	0.500	0.912	0.476	3.10	0.702
	1.03	2.10	0.500	0.920	0.480	3.09	0.701
	1.03	2.10	0.507	0.920	0.477	3.06	0.702
	1.03	2.11	0.502	0.921	0.470	3.00	0.698
		2.11	0.501	0.922	0.472	3.04	
		2.11		0.918	0.475	3.05	
		2.11		0.915			
		2.10		0.908			
		2.13					
		2.10					
Mean	1.03	2.11	0.502	0.918	0.475	3.07	0.700
Std Dev	--	0.009	0.0026	0.0053	0.0034	0.041	0.0019