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DETERMINATION OF ZIRCONIUM IN MAGNESIUM ALLOYS BY THE METHOD OF DOCUMENT ISO/TC 79/SC-1 - 248, AND COMMENTS ON THE METHOD

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SUMMARY OF RESULTS

"Soluble" and "insoluble" zirconium were determined in a series of magnesium alloys prepared and distributed by Magnesium-Electron Limited, England. These alloys were used to test the accuracy, precision and applicability of a method proposed by ISO Technical Committee 79 - Subcommittee 1 in Document No. 248.

It is considered that the method was, generally, good but modifications are offered with respect to the method of handling the insoluble fraction and the optimum wavelength for the spectrophotometry.

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INTRODUCTION

Britain and France, jointly, submitted a proposed method for the determination of "soluble" and "insoluble" zirconium in magnesium alloys to the Seventh Meeting of ISO/TC-79/SC-1 in Madrid on October 22, 1964. This was coded as Document 240. Subsequently the method was modified slightly and re-issued as Document 248. Participating countries were asked to test the method on samples supplied by Magnesium-Electron Ltd. (MEL).

This report presents the results obtained on MEL samples 13 to 19 and 21, and also on BCS standard 307 and on a standard Dow sample, by the proposed method. For comparison purposes, "soluble" and "insoluble" zirconium was determined on MEL samples 13, 15, and 21 and BCS 307 by a modified Dow (Alizarin) method currently used in this laboratory.

The method is discussed briefly from the point of view of optimum wavelength for the spectrophotometric measurement, and the decomposition of the "insoluble" fraction.

EXPERIMENTAL

Results on MEL Samples

Except where noted that a slight modification was used, the procedure as detailed in Document ISO/TC 79/SC-1 (UK-21) 248 was followed for all determinations on the MEL samples 13 to 18 and 21.

The samples were analysed on 4 separate days, giving a total of 8 (in some cases 9) replications. The results are presented in Table 1. For all samples the attack was with 4 N hydrochloric acid. As a check on the precision, 2 standards were run concurrently with some of the MEL samples. These were BCS 307 (0.56% Sol. Zr) and a Dow "unofficial" standard (0.54% Sol. Zr).

The determination of "soluble" zirconium in the silver-bearing alloy MEL 19 was performed following the procedure given in Document 248. The 3 samples MEL 19-1, 19-2 and 19-3 were analysed in duplicate on 2 separate days. Standard samples were carried through the procedure at the same time. The results are presented in Table 2.

TABLE 1

"Soluble" and "Insoluble" Zirconium in MEL Alloys

by Method of Document ISO/TC 79/SC-1 - 248

Sample No.		Replicate Values (% Zr)	Mean
MEL 13	Sol. Zr	0.712, 0.687, 0.687, 0.694, 0.694, 0.688, 0.688, 0.688, 0.688	0.692
	Insol. Zr	0.128, 0.130, 0.114, 0.121, 0.121, 0.120, 0.128[a], 0.120[a]	0.123
MEL 14	Sol. Zr	0.931, 0.919, 0.875, 0.850, 0.867[b], 0.882[b], 0.875[b], 0.917[b]	0.890
	Insol. Zr	0.130, 0.130, 0.125, 0.125, 0.126, 0.108, 0.133[a], 0.133[a]	0.126
MEL 15	Sol. Zr	0.825, 0.800, 0.819, 0.800, 0.819, 0.838, 0.813, 0.831	0.818
	Insol. Zr	0.143, 0.143, 0.123, 0.120, 0.138, 0.137, 0.140[a], 0.125[a]	0.134
MEL 16	Sol. Zr	0.706, 0.719, 0.713, 0.719, 0.706, 0.700, 0.700, 0.713, 0.713	0.710
	Insol. Zr	0.126, 0.125, 0.110, 0.110, 0.122, 0.122, 0.118[a], 0.112[a]	0.118
MEL 17	Sol. Zr	0.342, 0.342, 0.338, 0.342, 0.342, 0.337, 0.341, 0.342, 0.342	0.341
	Insol. Zr	0.020, 0.020, 0.022, 0.022, 0.023, 0.022, 0.022[a], 0.022[a]	0.022
MEL 18	Sol. Zr	0.133, 0.142, 0.141, 0.133, 0.137, 0.138, 0.150, 0.133	0.138
	Insol. Zr	0.032, 0.032, 0.036, 0.036, 0.038, 0.038, 0.037[a], 0.036[a]	0.036
MEL 21	Sol. Zr	0.158, 0.158, 0.154, 0.158, 0.158, 0.158, 0.158, 0.158, 0.158	0.158
	Insol. Zr	0.039, 0.040, 0.039, 0.038, 0.042, 0.041, 0.041[a], 0.042[a]	0.040
BCS 307 0.56% Sol. Zr	Sol. Zr	0.550, 0.550, 0.556, 0.563, 0.544, 0.550	0.552
	Insol. Zr	0.021, 0.023, 0.025, 0.025	0.024
Dow Std. 0.54% Sol. Zr	Sol. Zr	0.537, 0.530	0.534
	Insol. Zr	0.031, 0.032	0.032

a - Results obtained by determining the insoluble zirconium by the method detailed in the Appendix (method used in Mineral Sciences Laboratories of the Mines Branch).

b - Results obtained using 3 g sample in order to read optical density at a lower absorbance level.

Comparison of Results by Method of Document 248 and by Mineral Sciences Method (Appendix)

The method used in the Mineral Sciences analytical laboratories is given in detail in the Appendix to this report. To compare results obtainable by the two methods, a different, but very experienced, analyst determined the "soluble" and "insoluble" zirconium in MEL samples 13, 15 and 21, and also in BCS 307 by the method detailed in the Appendix. The results are given in Table 3.

Optimum Wavelength for the Spectrophotometry

Mayer and Bradshaw (1) recommended a wavelength of 550 nm for reading the absorbance of the Zr-Alizarin red S complex vs a blank. Wengert (2), on the other hand, used 510 nm and this latter wavelength is, in fact, specified in the latest ASTM (3) method for the determination of Zr by Alizarin red S.

The absorbance of the Zr Alizarin red S complex vs a dye blank vs wavelength was run on a Beckman DK 2A recording spectrophotometer for several concentrations of Zr. (Figure 1). The absorbance of the dye vs water was run similarly (Figure 2). Two concentrations of dye were used, the "strong" as recommended by Mayer and Bradshaw, Document 248, and the "weak" as specified by Wengert and ASTM.

Study of these two figures will disclose the reasons for the differences between wavelength suggested by the authors quoted above. Apparently Mayer and Bradshaw chose a wavelength where the blank was essentially negligible. Wengert, on the other hand, preferred the point of greatest absorbance of complex vs blank. However, it will be noted from Figure 1 that the point of greatest absorbance vs blank shifts to higher wavelength with increasing concentration of Zr. This effect can be seen also in Wengert's paper. Wengert apparently chose the maximum absorption for low concentration of zirconium; his data do not include such high concentrations as are presented here.

Colour was developed in a blank solution and in a standard solution containing 0.6 mg of Zr, according to the instructions given in Document 248. Absorbance of Zr complex vs blank was plotted for various wavelengths using a Beckman B spectrophotometer. The results are presented in Table 4. It is obvious that the greatest absorbance is in the region of 525 - 535 nm.

From Figure 1 and Table 4 it will be seen that the maximum absorbance vs. blank varies from about 510 nm at 0.1 mg of Zr to about 530 nm at 0.6 mg of Zr. From the shapes of the curves it is obvious that

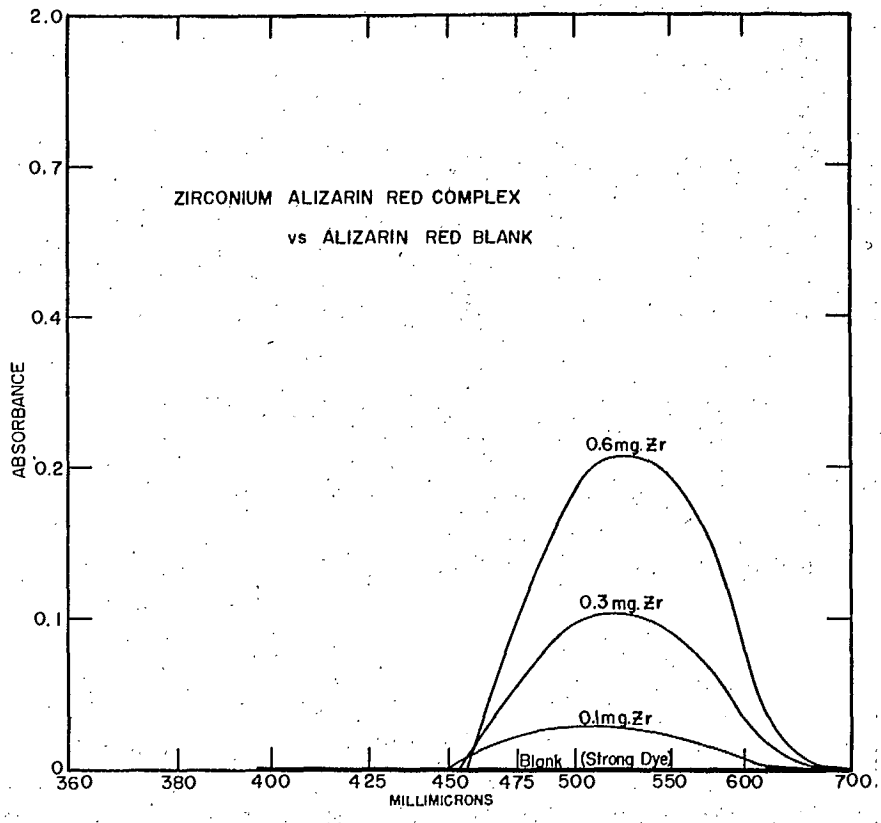

Figure 1

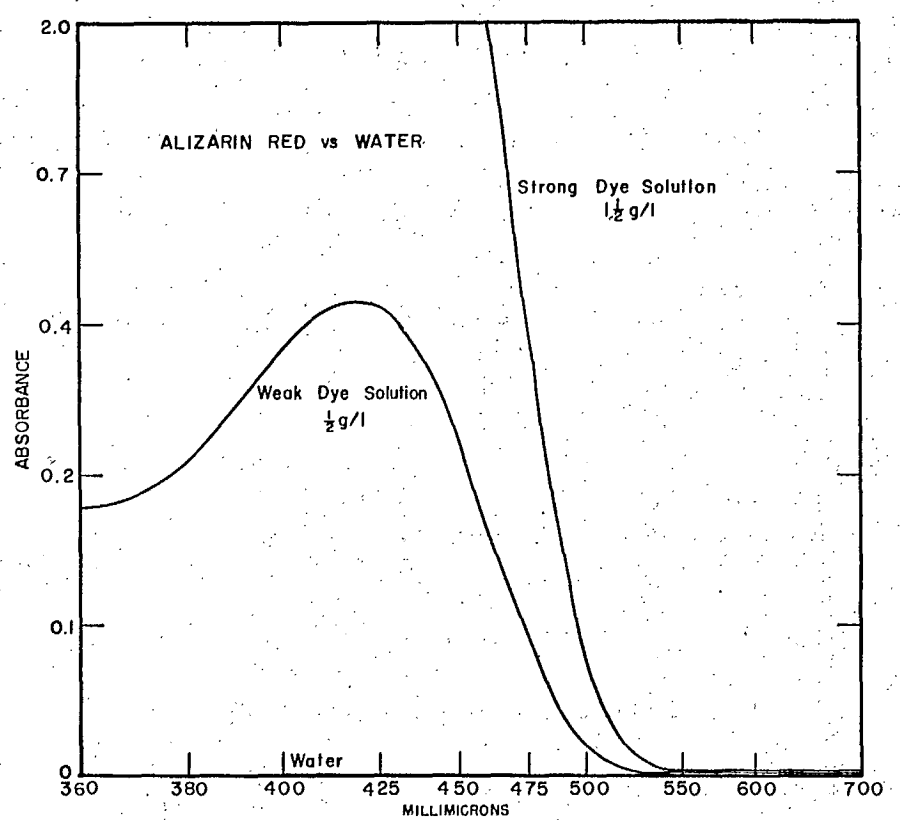

Figure 2

TABLE 2

"Soluble" Zirconium Content of Silver-Bearing

Magnesium Alloy – MEL 19

Sample No.	Sol. Zr %			
	1st Determination		2nd Determination	
MEL 19-1	0.513	0.513	0.519	0.531
MEL 19-2	0.513	0.513	0.525	0.525
MEL 19-3	0.513	0.513	0.525	0.525
BCS 307 Certified 0.56% Sol. Zr	0.550	0.550	0.550	0.550
Dow (unofficial standard) 0.54% Sol. Zr	0.531	0.531		

TABLE 3

Comparison of Results – Method of Doc. 248 and

Mineral Sciences' Method

Sample No.	Sol. Zr % (Average)		Insol. Zr % (Average)	
	Doc. 248	Min. Sci.	Doc. 248	Min. Sci.
MEL 13	0.692	0.65	0.128	0.13
MEL 15	0.818	0.81	0.134	0.15
MEL 21	0.158	0.15	0.040	0.04
BCS 307 (0.56% Sol. Zr)	0.552	0.52	0.024	0.03

Considering that the figures were obtained by different analysts the results are acceptable as checks.

TABLE 4

Optical Density of Zr-Alizarin Complex

vs a Reagent Blank

	Wavelength (nm)						
	500	520	525	530	535	545	555
Optical density	0.35	0.41	0.41	0.41	0.40	0.38	0.35

while there is relatively little loss in sensitivity if the 0.1 mg level of Zr is read at 525 nm, there is considerable loss at the 0.6 mg level read at 510 nm.

Therefore, the results in this report are based on the absorbance being read at 525 nm.

The method presented in the Appendix calls for the absorbance to be read at 510 nm. This is because the method was adopted from Wengert's work and the ASTM procedure. In the light of the present report however it would seem preferable to use 525 nm.

COMMENTS

1. It is considered that the method can yield accurate and precise results, and is generally satisfactory.

2. It is suggested that the procedure for decomposing the "insoluble" fraction is tedious and unduly complicated. It is requested that the procedure outlined in the Mineral Sciences' method (Appendix) be considered as an alternative.

3. The optimum wavelength for the spectrophotometry is 525 nm.

REFERENCES

1. Mayer, A., and Bradshaw, G., Analyst, 77, 476-483 (1952).

2. Wengert, Glenn B. Anal. Chem., 24, 1449-1451 (1952)

3. ASTM Standards. Part 32. Chemical Analysis of Metals, Sampling and Analysis of Metal Bearing Ores. American Society for Testing and Materials. (1965)

APPENDIX

DETERMINATION OF ZIRCONIUM IN MAGNESIUM-BASED ALLOYS ("SOLUBLE" AND "INSOLUBLE") ZIRCONIUM ALIZARIN-SPECTROPHOTOMETRIC METHOD

This method is based largely on the publications of Mayer and Bradshaw (1) and Wengert (2).

PRINCIPLE

The sample is dissolved in 4 N HCl. The solution is filtered, and "soluble" zirconium is determined spectrophotometrically in the filtrate as the alizarin complex. The insoluble residue is dissolved in an acid mixture (HNO_3 + $HClO_4$ + H_2SO_4) and the "insoluble" zirconium determined by the same spectrophotometric procedure as used for the "soluble".

APPARATUS

Spectrophotometer: Beckman B or DU, or an instrument of similar capability.

REAGENTS

HCl: 1:9 with distilled water.
HCl: 1:1 with distilled water.
HCl: Concentrated, ACS Specification.
HNO_3: Concentrated, ACS Specification.
$HClO_4$: Concentrated, ACS Specification.
H_2SO_4: Concentrated, ACS Specification.
H_2SO_4: 1:1.

Alizarin Red S: As free from sulphate as possible (1, 2).

Standard $ZrCl_2.8H_2O$ Solution: Do not dry this reagent. Dissolve 0.712 g $ZrClO_2.8H_2O$ in a 2000 ml volumetric flask with 200 ml of concentrated HCl; dilute to the mark with water and mix well. This should contain approximately 0.1 mg of Zr per ml. Standardize this solution by determining the Zr in 100 ml, using the phosphate method.

STANDARD CALIBRATION GRAPH

Prepare the graph as follows. Dilute 10 ml of the standard zirconium to 100 ml (1ml of resultant solution = 0.01 mg Zr). To five 100 ml volumetric flasks add:

5 ml Zr solution (1 ml = 0.01 mg Zr) + 14 ml 1:9 HCl
10 ml Zr solution (1 ml = 0.01 mg Zr) + 13 ml 1:9 HCl
15 ml Zr solution (1 ml = 0.01 mg Zr) + 12 ml 1:9 HCl
20 ml Zr solution (1 ml = 0.01 mg Zr) + 11 ml 1:9 HCl
0 ml Zr solution (1 ml = 0.01 mg Zr) + 15 ml 1:9 HCl (blank)

to each flask, now add 5.0 ml of 0.05% alizarin red S solution. Dilute to the mark with distilled water and mix by inversion. After 15 minutes, read absorbance at 510 mμ in a spectrophotometer against the "blank". From readings of the absorbance of the solutions containing the zirconium draw a calibration curve. The curve should be checked with each lot of samples (Note 2).

PROCEDURE

Weigh a 1.000 g sample into a 400 ml beaker, cover it with a watch glass and add 25 ml of water and, cautiously, 50 ml of 1:1 HCl. Wash down the sides of the beaker with 2 or 3 ml of water, delivered from a fine jet of a wash bottle. After the contents of the beaker have been brought just to a boil remove the beaker from the hot plate and filter its contents through an 11 cm No. 40 Whatman paper into a 250 ml flask, wash with water and make contents of flask up to volume and mix well. Reserve this solution for the determination of "soluble" zirconium.

Place the paper containing the insoluble residue back into the original beaker and add 15 ml of HNO_3, 10 ml of $HClO_4$ and 5 ml of 1:1 H_2SO_4. Heat to fumes of H_2SO_4, then, cautiously bring to dryness. Cool, wash down sides of the beaker and again bring to dryness (to expel H_2SO_4 which must be reduced to a minimum). Add 15 ml of concentrated HCl, cover and heat gently to dissolve salts. Cool, add about 50 ml of water and transfer to a 250 ml volumetric flask. Make to volume with water, mix well, and reserve for "insoluble" zirconium.

"SOLUBLE" ZIRCONIUM

Pipette an aliquot into a 100 ml volumetric flask. The aliquot will depend on the expected amount of zirconium and the acidity should be adjusted so that the flask finally contains HCl equal to 1.5 ml of concentrated HCl. Therefore use aliquots and additions of 10% HCl as given below:

% Zr Expected	Aliquot	Add 1:9 HCl
0.01 - 0.2	15 ml	0
0.2 - 0.4	10 ml	5 ml
0.4 - 1.0	5 ml	10 ml
More than 1.0	2 ml	13 ml

Proceed as outlined under construction of calibration graph and determine the Zr concentration from the graph. Read against a reagent blank.

"INSOLUBLE" ZIRCONIUM

Pipette a 25 ml aliquot into a 100 ml volumetric flask. This aliquot will give an optimal absorbance range for the 0.01% to 0.20% zirconium range; most of the insoluble zirconium determinations lie within this range. Add 5 ml of 0.05% Alizarin red S and proceed as outlined under the calibration graph. Read against a reagent blank and determine Zr content from the calibration graph. If insoluble Zr is greater than 0.20% use a smaller aliquot and add 1:9 HCl to bring the total HCl acidity up to 1.5 ml/100 ml. After 15 minutes the colour remains stable for at least 24 hours.

INTERFERING IONS

The following ions are permissible up to the stipulated concentrations:

Ion	Mg/100 cc	Ion	Mg/100 cc
Al	4	Mn	5
Cu	4	Ni	12
Fe	4	rare earths	9
Pb	10	Th	40
Mg	500	Zn	18
		F	0.01

Sulphate and phosphate interfere.

Note 1

In the case of magnesium alloys containing silver, the precipitated metallic silver is filtered off with the insoluble zirconium. The paper containing the insoluble zirconium is decomposed as in the regular

method. The residue in the beaker is dissolved with 15 ml HCl, heated 1 min, diluted to 100 ml and boiled for a few minutes to coagulate the silver chloride. The solution is then filtered into a 250 ml volumetric flask and the determination proceeded with as in the usual method. In the case of silver alloys containing zinc which exceeds 6%, the insoluble zirconium may exceed 0.20%. If insoluble Zr is greater than 0.20% use a smaller aliquot and add 1:9 HCl to bring the total HCl acidity up to 1.5 ml/100 ml.

Note 2

The standard curve should be checked by means of standards for each set of determinations as small variations may occur in the slope of the curve from time to time.