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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 60-116

**EXAMINATION OF A SPECTROGRAPHIC METHOD  
FOR THE ESTIMATION OF BERYLLIUM IN  
MAGNESIUM ALLOYS SUBMITTED BY  
DOMINION MAGNESIUM LIMITED,  
HALEY, ONTARIO, MARCH 1960**

by

ARCHIBALD H. C. P. GILLIESON

MINERAL SCIENCES DIVISION

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SUMMARY OF RESULTS

Five magnesium alloy samples supplied by Dominion Magnesium Limited were examined for their beryllium content by a semi-quantitative D.C. Arc Method, which employed alumina as a carrier and aluminum as the internal standard. Comparative analyses were also made by the Mines Branch, Stallwood semi-quantitative D.C. Arc Method with external beryllium standards, and by the Dow Chemical Company, Solution-A.C. Spark Method, with magnesium as the internal standard.

The Stallwood technique applied directly on the metal was both the simplest and most rapid method and gave results nearest the nominal beryllium content.

The Dow Solution-Spark technique appeared to be the more rapid and direct of the methods using internal standards.

The Domag technique was lengthy and had the disadvantage that the intensities of the aluminum lines used as internal standards were markedly dependent on the temperature of ignition of the alumina carrier precipitate.

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## INTRODUCTION

A method, entitled "Magnesium Beryllium Low", for the spectrographic estimation of small amounts of beryllium in magnesium alloys, and appearing in the 4th Edition of their "Chemical Laboratory Manual" was submitted for review by Dominion Magnesium Limited, Haley, Ontario, in their letter of March 2nd, 1960 (Appendix I). Five samples of alloy with beryllium contents ranging from 0.0001 to 0.05 per cent accompanied the request. The review of the method was carried out to assist Dominion Magnesium Limited, in their assessment of methods proposed for acceptance as Referee Methods for the Canadian Standards Association, Magnesium Alloy Sub-Committee.

As stated in the firm's letter, however preferable it were to use the direct point-to-plane spark method on alloy samples, for the present, this method is inapplicable for lack of adequate standards of known beryllium content.

The method devised by the firm, concentrated the trace impurity, beryllium, before spectrographic analysis. Since the beryllium was present in such small quantity that it could not be precipitated quantitatively by itself, it was co-precipitated with another element, aluminum, of similar properties. In the subsequent spectrographic analysis, the aluminum present in the carrier precipitate was used as the spectrographic internal standard, in a semi-quantitative D.C. Arc technique. The method is reproduced



in its entirety in Appendix II.

For comparison the samples of alloy were examined by two other methods, neither requiring separation of the trace beryllium from the magnesium matrix. The first method was the Mines Branch Semi-Quantitative D.C. Arc technique (Appendix III) devised by B.J. Stallwood and employing an air-jet for arc stabilization, with "external" beryllium standards recorded on the same spectrographic plate as the samples. The second method employed by the Dow Chemical Company (Appendix V) used spark analysis of a solution of the alloy samples in hydrochloric acid, with the magnesium of the matrix serving as the spectrographic internal standard.

## EXPERIMENTAL

The full details of the three experimental procedures used are presented in Appendices II, IV and V.

The resulting spectrographic plates were examined by two techniques:-

### 2.1. Internal Standard Technique

2.1.1. The Domag Method plates using the Be Arc line and Al as internal standard.

2.1.2. The Domag Method plates using the Be Spark line and Al as internal standard.

2.1.3. The Dow Chemical Co. Solution-Spark Method plates using the Be Spark line and Mg as internal standard.

2.2. External Standard Technique

- 2.2.1. The Domag Method plates using the Be Arc line and comparing its intensity with that of the same line on standards on the same plate.
- 2.2.2. The Domag Method plates using the Be Spark line in the same manner.
- 2.2.3. The plates from the Stallwood Method on the Domag  $Al_2O_3$  precipitate, using the Be Spark line in the same manner.
- 2.2.4. The plates from the Stallwood Method direct on metal filings from the samples using the Be Spark line in the same manner.
- 2.2.5. The plates from the Dow Chemical Co. Solution-Spark Method, using the Be Spark line in the same manner.

The analytical results are summarized in Tables 1 and 2.

TABLE 1

Percentage Be: Internal Standard Technique

Method	Magnesium Sample No.				
	D32	D35	D37	D44	D49
Domag (Arc Line)		0.0002	0.002	0.07	0.09
(Spark Line)	0.0001	0.0005	0.002	0.01	0.02
Average	0.0001	0.0004	0.002	0.04	0.06
Dow Solution-Spark	0.0001	0.0002	0.001	0.02	0.02
Average both methods	0.0001	0.0003	0.002	0.03	0.04
Nominal	0.0001	0.0005	0.002	0.05	0.05

TABLE 2

Percentage Be: External Standard Technique

Method	Magnesium Sample No.				
	D32	D35	D37	D44	D49
Domag (Arc Line)		0.0004	0.001	0.02	0.02
(Spark Line)	0.0003	0.0005	0.001	0.01	0.02
Average	0.0003	0.0005	0.001	0.02	0.02
Stallwood on Ppt	0.0001	0.0003	0.003	0.03	0.02
on Metal	0.0001	0.0002	0.002	0.05	0.05
Average	0.0001	0.0003	0.003	0.04	0.04
Dow Solution-Spark	0.0001	0.0004	0.002	0.02	0.03
Average all methods	0.0002	0.0004	0.002	0.03	0.03
Nominal	0.0001	0.0005	0.002	0.05	0.05

## DISCUSSION

The Domag and Stallwood Methods are semi-quantitative D.C. Arc Methods and high precision is not to be expected of them.

Of the semi-quantitative techniques, the Stallwood directly on the metal sample would appear slightly better than the techniques involving separation of the Be on  $Al_2O_3$  carrier.

When using the Domag Method there was some confirmatory evidence that the excitation of the Al was affected by the temperatures of ignition of the  $Al_2O_3$  ppte.

Even with the D.C. Arc Methods, measurement of the Be Spark line at 3130 Å was preferred to measurement of the Be Arc line at 2348 Å. The latter lies outside the wavelength range in which the Kodak SA-2 plates possess uniform gamma, and it is also far removed in wavelength from Al or Mg lines suitable as internal standards.

In both arc and spark methods, the internal standard procedure does not appear to show a marked advantage over that using external standards.

In both arc and spark methods, for greatest accuracy, it would appear preferable by appropriate choice of the size of sample taken, to work in the range giving intensities comparable with that of the 0.001 per cent Be standard.

The Stallwood Method direct on the metal sample showed the least overall differences from the nominal percentages, while the Dow Solution-Spark Method presented the least overall differences from the mean of all the results.

### CONCLUSIONS

Where the equipment is available, the Stallwood Method direct on the metal would appear preferable because of its simplicity. It has the additional advantage that a large number of other elements, eg Zn, Al, Si, Fe, Cu inter alia, can be simultaneously determined.

The next simplest method is the Dow Solution-Spark technique, but, as in all solution methods, there is always the possibility of retention of elements in an insoluble residue and Si estimation in particular is never reliable.



APPENDIX I

DOMINION MAGNESIUM LIMITED

plant office

HALEY, ONTARIO

Canada

Mar. 2/60

Mr. W.R. Inman,  
Dept. of Mines and Technical Surveys,  
555 Booth St.,  
OTTAWA 1, Ontario.

Dear Mr. Inman:

When your staff are reviewing the spectrographic methods for beryllium and aluminum in magnesium, in addition to checking the analysis by other methods will they please comment on the suggested methods as well as contributing any ideas of their own. Direct point-to-plane on the original metal sample with an arc source is very good, but has to be ruled out for now because of the dependence on standards.

Whilst on the subject of spectroscopy, would your staff please tell me what lines they prefer to use for calcium in magnesium oxide over the range from 1% to 0.0001%. We have agreed that spectroscopy on a sample converted to oxide is the best way of determining calcium in magnesium. Now, I am surveying the lines various people prefer.

With thanks,

Yours sincerely,

L.R. Pittwell,  
Chief Chemist.

APPENDIX II

DOMINION MAGNESIUM COMPANY (DOMAG) METHOD  
"MAGNESIUM BERYLLIUM LOW"

Range:

0.00005 to 1%. At the upper end of the range take aliquots (and add extra aluminum if necessary to AZ alloys.) By using a 100 g sample 0.000005% Be can be reached. (Note: When using Al as carrier it is advisable to run standards with the samples as the intensity of the Al line increases greatly with the degree of ignition. Care should be taken that all samples etc., are uniformly ignited. Some muffles have cold spots inside).

Reagents:

Hydrochloric Acid

Aluminum Metal

Ammonium Chloride

Ammonium Hydroxide

Bromocresol Green

Procedure:

If an AZ alloy, determine Al by "Magnesium Aluminum Medium".

Weigh out a 10.00 g sample, and dissolve in 200 ml of 1:1 hydrochloric acid in a 1 litre beaker.

If the alloy does not contain Al, dissolve 50 mg of

Al in hydrochloric acid, and add to the sample.

Add about 5 gm  $\text{NH}_4\text{Cl}$ , warm to dissolve, and precipitate with  $\text{NH}_4\text{OH}$  using bromocresol green until the indicator turns blue. Filter on a Whatman No. 41H paper, wash well with a 1%  $\text{NH}_4\text{Cl}$  solution made just alkaline with  $\text{NH}_4\text{OH}$ .

For alloys high in Al, e.g. AZ80 and AZ91, redissolve the washed ppte in HCl, add  $\text{NH}_4\text{Cl}$  and repeat the  $\text{NH}_4\text{OH}$  precipitation twice more.

Ignite this ppte at  $1000^\circ\text{C}$  for 1 hour. Then weigh up and proceed as in "General Spectrographic Harvey".

Read Be 3130.4A and 2348.6 A and Al 3050.1 A.

"GENERAL SPECTROGRAPHIC HARVEY" QUOTATION  
"MAGNESIUM SPECTROGRAPH IMPURITY" QUOTATION

Range:

See Harvey Tables.

This is only a Semi-Quantitative Method.

Reagents:

High Purity Graphite (Powder) .

Harvey Electrodes (United 101L or National L3903).

Eastman S.A. No. 1 35 mm film.

Kodak D 19 Developer.

Eastman Liquid X-Ray Fixer.

2% Acetic Acid.



Equipment:

ARL 1.5 m Spectrograph No. 2060.  
ARL D.C. Arc Source Unit No. 2000.  
ARL Densitometer.  
Calculating Board with calibrated scales.  
Developing Machine (set at 20°C + 0.25°C)  
Infra-Red Film Drier.

Exposure:

Source	D.C. Arc
Current	13 Amp (adjusted with electrode clamps short circuited)
Preburn	None
Exposure	Complete Burning
Upper Electrode	Negative. 1/4 in. high-purity graphite rod, conical end with spherical tip.
Lower Electrode	Positive. Harvey type.
Cooling Water	On
Gap	5 mm
Screen	On
Aperture	No. 4
Gates	3
Slit	40 $\mu$

Note: If rare earths or other dense spectra are to be examined, it is advisable to reduce the slit width, though this may upset the densitometer reading (but not the Sturrock Densitometer at the Mines Branch,

Ottawa). The slits must be reset to  $40\ \mu$  immediately afterwards to avoid error.

Developing:

Machine rocking, heater control on, water precooled.

Bath temperature  $20^{\circ}\text{C} + 0.25^{\circ}\text{C}$ .

Developer	D19 for 3 min (use timer).
Short Stop	2% acetic acid for 15 sec.
Fixer	"Liquid X-Ray" for 30 sec.
Wash	$1\frac{1}{2}$ min in running water.
Rinse	Distilled water and sponge off drops.
Drying	75 sec in drier.
Safe Light	On. Main lights off until film is fixed.

After developing number the film and make out a sheet at once.

Note: Film is loaded into the camera in total darkness.

Developer and Short Stop are changed daily (400 ml).

Fixer is changed twice weekly or when milky, if

sooner. (400 ml).

## CALCULATION AND CALIBRATION

Run a set of standards along with the samples, using the carrier and impurity right through the process above. Read as for "Titanium Spectrographic Impurities". From these results draw up a working curve.

There are three ways of calculating these standards:

(a) Use a standard amount of carrier (50 mg of metal, in the form of a salt) for each.

Add to this solution sufficient of the impurity as a soluble salt to give the amounts present at the expected percentages for a 10 g sample weight.

This allows the working curve to be plotted directly in per cent for 10 g samples.

Then read the samples and calculate intensity ratios, and read off the impurity from the working curve.

For higher or lower sample weights, the percentage is corrected by dividing by the sample weight and multiplying by 10.

### Example:

For 0.001% of impurity in a 10 g sample and 50 mg carrier  
0.001% of 10 g is  $10 \times 0.001/100 = 0.0001$  g.

This amount is then added to 50 mg of carrier and dissolved in any convenient amount of water (preferably the same as the sample volume).



Note: Very small weights as above are best measured by dissolving a larger amount in a standard volume and taking aliquots. Curve would be plotted in percentages and samples read directly for 10 g samples.

(b) As (a) above but use actual weights of the impurity as salt comparable to the weights expected in the actual samples.

Plot the working curve in micrograms per 50 mg of carrier. This then gives the weight of impurity in the sample and the percentage impurity is this weight expressed as a percentage of the sample weight.

If an alloy element is used as a carrier, it is possible to calculate the weight of carrier in the sample taken, then by proportion, knowing the weight of impurity for the actual weight of carrier, express this as a percentage of the sample weight.

Example:

Same problem as (a).

The curve would be prepared as in (a) but is plotted in micrograms per 50 mg. The above standard would give the 100 microgram point.

If a sample was equivalent to Z micrograms using Y g sample.

$$\text{Then } \% = \frac{Z \times 0.000001 \times 100}{Y}$$

If W mg of carrier had been used instead of 50 mg for the sample, but 50 mg had been used for the standards.

$$\text{Then } \% = \frac{Z \times 0.000001 \times W \times 100}{50 \times Y}$$

(c) For alloys it is also possible to take a convenient value of the carrier element percentage, calculate the ratio of impurity to carrier present in alloys at such a median percentage and prepare standards from the two metals (as salts) in these ratios.

Then prepare the working curve in per cent. To correct for the true carrier percentage, divide by the assumed value and multiply by the true value of the carrier metal per cent.

Example:

For 0.0001% of impurity in an alloy containing about 10% of carrier as an ingredient. Assume carrier to be 10%.

$$\text{Ratio } \frac{\text{Impurity}}{\text{carrier}} = \frac{0.0001}{10} = 0.00001$$

Standards must therefore contain these two metals in this ratio. Thus, if 50 mg (0.050 g) of carrier is used to make the standard, 0.0000050 g of impurity will be required. To reduce the amount of aliquotting of impurity necessary, larger carrier weights are usually used in the standards.

Then, if Y g sample gives a reading equivalent to Z %, when the true carrier per cent is W and the assumed value 10%.

$$\text{True Impurity \%} = \frac{Z \times W}{100}$$

Note: Sample size Y does not come into the calculation and hence is unimportant.

Standardization:

Take a salt of known analysis (check this if salt is wet or caked) and a master solution of known strength  $\text{AlCl}_3$  prepared from metal.

Then by aliquotting, prepare mixed solutions with suitable Al/Be ratios. Carry out a hydroxide precipitation and shoot the precipitate on the spectrograph as above.

Theory:

The method is based on the fact that trace impurities which are at concentrations so low that they are not precipitated, can be carried out of solution by other similar precipitates and the impurity determined using the carrier as matrix.

Procedure:

Using a microbalance, weigh out equal quantities of sample and graphite (powder) - at least 30 mg of each is preferred. Mix well in an agate mortar. Weight out 20 mg portions of the mixture, pack into electrodes and tamp down well. Shoot in triplicate as below.



APPENDIX III  
CHECK ON DOMAG METHOD

Because of the nature of equipment and materials available, the following differences from the Domag Method are noted.

Reagents:

(a) Harvey electrodes were not available, so use was made of National L3918 Anode Caps in their place.

Anode Cap L3918		Harvey L3903
0.281 in.	Depth of cup	0.156 in.
0.187 in.	I.D. of cup	0.136 in.
0.242 in.	O.D. of cup	0.180 in.
0.00772 cu/in.	Vol of cup	0.00227 cu/in.

(b) Eastman S.A. No. 2 plates

(c) Fixer - Eastman F-10

(d) Eastman S.A. No. 2 Plate. 10 in. x 4 in.

Equipment:

Baird 3-metre Grating Spectrograph

(2300 - 3600 A; First Order)

ARL. D.C. Arc Source Unit No. 02825A.

Sturrock Cathode-Ray Tube Densitometer.

Exposure:

Current 12 amp. (maximum of unit)

Screen	)	
	)	
Aperture	)	None
	)	
Gates	)	
Slit		25 $\mu$
Sector		1-10-100% Rotary.

Developing:

Machine rocking, but no precooled water available.

Temperature of bath initially 20°C.

Developer	D-19 for 6 min
Short Stop	Water for 15 sec
Fixer	F-10 for 10 min
Rinse	Running water for 30 min
	Sponge off with tap water.
Drier	8 min approx.

Procedure:

The Domag loading of 20 mg (10 mg sample or standard + 10 mg graphite powder) was used for standards and samples of low Be content. 2 mg loading were used for all standards in addition and for samples D44 and D49 (0.05% nom).

STANDARDS

Standard solutions were made up from  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  (M.W. 117.114 g). A Master Solution I containing 0.1 g Be (equivalent to 1.967 g  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ ) in 100 ml was used to make the following dilutions and standards. Solution II was a 10-fold dilution of I.

<u>Standard Solution</u>	<u>ml</u>	<u>Solution</u>	<u>g Be</u>	<u>% Be in 10 g sample</u>
1	1	II	0.0001	0.001
2	5	II	0.0005	0.005
3	10	II	0.001	0.01
4	50	II	0.005	0.05
5	1	I	0.001	0.01
6	5	I	0.005	0.05
7	10	I	0.01	0.1
8	50	I	0.05	0.5

---

The volumes quoted were added to an HCl solution containing 50 mg Al (weighed as metal). These solutions were run through the precipitation, filtering washing, drying and igniting along with the samples.

## APPENDIX IV

### STALLWOOD SEMI-QUANTITATIVE D.C. ARC METHOD

#### Procedure:

(a) Coarse powders or crystals are ground to a fine powder in an agate mortar for ten minutes. With metals, approximately 20 mg of filings are removed from the cleaned surface of the metal by means of a file, milling machine or high speed grinding tool.

(b) Weigh 1 mg of prepared sample and 40 mg of (100 mesh) Specpure graphite powder into the rhodium plated mixing dish and stir with a graphite rod for one minute.

(c) Transfer to a prepared 1/8 in. graphite electrode by means of the rhodium plated funnel.

(d) Place electrode in electrode holder box and seal electrode top with a drop of celluloid solution.

(e) Weigh 10 mg of prepared sample and 40 mg of graphite powder and load into electrode similarly.

#### Reagents:

As for Check on Domag Method with the following exception:

Lower electrode: National Carbon Co. L-3803, 1/8 in. rod drilled to a depth of 1 in. with a 0.086 in. diameter hole (Drill No. 44), and of overall length 1 5/8 in.

#### Equipment:

As for Check on Domag Method.

Exposure:

As for Domag Method with the following exception:

Current 6 amp.

Plate Development:

As for Check on Domag Method.

(f) Turn on water for electrode cooling system.

(g) Place air jet in position and adjust manometer to read 5 in. of water.

(h) Place sample electrode in lower positive electrode holder, and 1/8 in. pointed electrode in upper negative electrode holder.

(i) By means of the lamp and screen, adjust the gap between the electrodes to 2 mm.

(j) Ignite the arc by pressing the H.F. Igniter button and maintain the gap at 2 mm by continually adjusting the position of the electrodes as seen on the screen.

When the sample is completely burned, switch off the arc. Completion of sample burning is indicated by:

(i) the change in the colour of the arc and the shape of the electrodes as seen on the screen;

(ii) an increase in the rate of burning of the electrodes and the accompanying change in the noise of the arc.

Complete burning of the sample normally takes from 2 to 2½ minutes. For the analysis of the Domag Magnesium Alloy samples,



10 mg of metal or of  $\text{Al}_2\text{O}_3$  precipitate were used for all samples and standards, except for samples D44 and D49, for which, owing to their high nominal content of 0.05% Be, only 1 mg was taken.

APPENDIX V

SPARK-SOLUTION METHOD (Dow Chemical Co.)

Range:

0.0001% to 1%

Reagents:

Hydrochloric Acid

Nitric Acid

Magnesium Oxide (Specpure)

1/4 in. dia flat-topped Graphite Electrodes

Equipment:

Bausch and Lomb Dual Grating Spectrograph

ARL Multi-Source Unit

Sturrock Densitometer

Exposure:

2400-3400 A 1st Order

Mask 2 mm

Turret # 3

Slit 20 $\mu$

Multi-Source Unit: Capacitance 60  $\mu$ fd

(Arc-like Spark) Inductance 400 millihenry

Resistance 155 ohms

Charge - Discharge

Electrode Gap 2mm

Exposure 30 sec

Preburn - None

Bi-prism 0-0

Light 100% Upper Grating only.

Procedure:

Dissolve 0.4 g Mg alloy in 3.9 ml conc. HCl plus 0.5 ml conc. HNO<sub>3</sub> and make up to 10 ml.

Pipette 0.2 ml using micropipette on to previously water-proofed surface of a pair of electrodes, dry under infra-red lamp, and shoot.

Standards:

Add 3.3148 g specpure MgO to 30 ml 1:1 HCl and make up to 50 ml with 1:1 HCl in a volumetric flask.

Solution I. Make up 100 ml of Be solution in 1:1 HCl, by dissolving 0.27738 g BeO (specpure) - "1% Be" solution.

Solution II. Dilute Solution II, ten-fold to give Solution III and dilute this solution and one hundred-fold with 1:1 HCl to give Solution IV.

Pipette 5 aliquots each of 5 ml of Solution I into 10 ml volumetric flasks, add 0.5 ml concd HNO<sub>3</sub> to each, and then add the following amounts of Be solution.

<u>Standard</u>	<u>Be Solution</u>	<u>Vol</u>	<u>% Be in 0.4 g Mg</u>
I	II	4	1.0
II	II	0.4	0.1
III	III	4	0.01
IV	III	0.4	0.001
V	IV	4	0.0001

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AHCPG:DV