# STANDARDISATION OF SPECTROGRAPHIC METHODS OF ANALYSIS AND ITS ROLE IN THE ZINC DIECASTING ALLOY INDUSTRY IN INDIA

by

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## ABSTRACT

Some spectrographic methods of analysis in general and their application to die-casting alloys in particular have been discussed.

## Introduction

With the rapid industrial development of the country, the need for Zinc die-casting alloy industry is an urgent necessity. Die-casting process provides a rapid method of production of Engineering components of simple as well as of intricate designs. Die-cast components of importance and of various types are used in many industries like the motor car, electrical, domestic appliances and Defence Industries.

In India Defence Industries are the users of large quantities of zinc-alloy for die-casting ammunition components. The satisfactory performance and stability in services of zinc die-cast components depends on limiting the presence of elements like lead, tin, cadmium, indium etc. to small percentage ranges. If these elements are present above certain limits, failure of the components due to inter-crystalline corrosion occurs. Hence the presence of these elements in the alloy has to be restricted and controlled rigidly during the manufacture of the alloy as well as during the die-casting process. Therefore a careful and quick determination of these harmful elements as well as the alloying elements is imperative. At present, Polarographic and Spectrographic methods are considered to be suitable for this purpose from many respects.

## Spectrographic Methods of Analysis used in Defence

Spectrographic methods of analysing zinc die-casting alloys have been accepted. Although the published literature [1—4] reflects a general improvement in the techniques, the amount of published literature is small compared to the great extent to which the Spectrograph is used for this alloy analysis in many of the countries in the past fifteen years or so.

Spectrographic methods of analysis have also been in use in the Defence Metallurgical Research Laboratory, Ishapore, for the past several years and it is proposed to give here a short account of some of the methods adopted in the Laboratory.

The methods described here are for determining the alloying elements and also deleterious elements in Mazak type of die-casting alloys, using the electrodes technique for the range of concentration shown below:—

| | | |
|---|---|---|
| Aluminium | .. .. | 3·0 to 5·0% |
| Magnesium | .. .. | 0·02 to 0·07% |
| Lead | .. .. .. | 0·003 to 0·010% |
| Tin | .. .. .. | 0·001 to 0·0006% |
| Cadmium | .. .. .. | 0·0005 to 0·001% |
| Indium | .. .. .. | 0·0005 to 0·001% |
| Thallium | .. .. .. | 0·001 to 0·002% |

The methods described are:—

(1) Determination of impurity elements by Trigger ignited D. C. Arc;

(2) Determination of alloying elements by simple condensed spark;

(3) Determination of impurities by the A. C. Intermittent Arc.

The first two methods provide a means of determining the composition of zinc alloys to clause 4.1.1 of the specification I.S. 713-1955 and clause 5.2 of specification I.S. 742-1955.

These methods are suitable for Inspection testing of zinc die-casting alloy samples and also for the production control of zinc die-casting alloy manufacture and also die-casting process where rod samples could be drawn.

**Outline of the Methods**

The simple condensed spark method of excitation of self electrodes of the sample was employed for the determination of alloying elements, aluminium and magnesium; for the impurity elements, lead, tin and cadmium, the trigger ignited D.C. Arc struck between the sample electrode and a pure graphite rod (made the positive) were used. The A.C. Intermittent arc method of excitation was used in the determination of Indium where the sample rod formed one of the electrodes against a silver counter electrode. The intensity values of the selected spectral lines were obtained from photometric readings. The photographic plates were calibrated by the Iron group method whose relative intensities had been previously determined by the step-sector method. The concentration percentages of the elements were obtained from the appropriate analytical curves relating intensity ratios (of each of the element line and the zinc internal standard line) to the respective log percentages of the elements.

**Equipment**

The equipment manufactured by Hilger and an A.C. Intermittent Arc source built in the Laboratory were employed in establishing these methods.

The trigger ignited D.C. Arc is a Walsh-type source unit. This unit was used for the determination of impurity elements lead, tin and cadmium.

A.C. Intermittent Arc source is basically a Pfeilsticker type of source unit.

The Hilger Medium Quartz Spectrograph E 498 was used in all the methods.

Hilger's Non-recording Microphotometer had been used for reading the spectral lines.

**Preparation of Samples**

Samples for spectrographic analysis could be easily obtained during the alloy manufacture and also during die-casting process. Samples in the form of rods of 8 mm dia. and about 15 cm long were drawn by casting the molten alloy into a simple steel mould so as to obtain four electrode rods at a time of uniform size and under same metallurgical conditions.

The rods were parted in the middle and these ends were faced on a lathe. For analysis these ends were used. The machined ends of the rods were cleaned with spirit to remove loosely adhering contaminations.

TABLE 1

*Standard Mazak alloy used and their composition*

| | Al% | Mg% | Pb% | Sn% | Cd% | Tl% | In% | Cu% | Fe% |
|---|---|---|---|---|---|---|---|---|---|
| 1D | 3·5 | ·02 | ·003 | ·001 | ·003 | ·001 | ·0005 | ·03 | ·01 |
| 2D | 4·1 | ·04 | ·005 | ·002 | ·005 | ·002 | ·001 | ·03 | ·01 |
| 3D | 4·47 | ·06 | ·010 | ·005 | ·010 | .. | .. | ·03 | ·01 |
| A9 | .. | .. | ·007 | ·0045 | ·007 | .. | .. | .. | .. |

**Determination of Alloying elements—Aluminium and Magnesium**

For the determination of aluminium and magnesium content in zinc alloys, the simple condensed spark method of excitation of self electrodes of the samples, separated by 4 mm gap was used. The gap adjustment was made by means of a precision dial-gauge suitably attached to the upper movable electrode holder arm of the spark stand. The optical alignment of electrodes was adjusted by the "image projection" method.

(*i*) *Excitation*—The constants of the excitation source unit are stated below—

| | |
|---|---|
| Power of Transformer | ¼ KVA |
| Induction (added) | 0·13 mH |
| Primary Voltage | 230 V. |
| Capacitance | 0·005 μF |

(*ii*) *Exposure*—The exposure conditions in this method using Hilger's Medium Quartz Spectrographs (E 498) were:

| | |
|---|---|
| Slit width | 0·015 mm |
| Slit length | 2 mm |
| Spark preburn period | 10 Sec. |
| Spark exposure period | 15 Sec. |

The analytical curves are shown in figures 1 and 2.

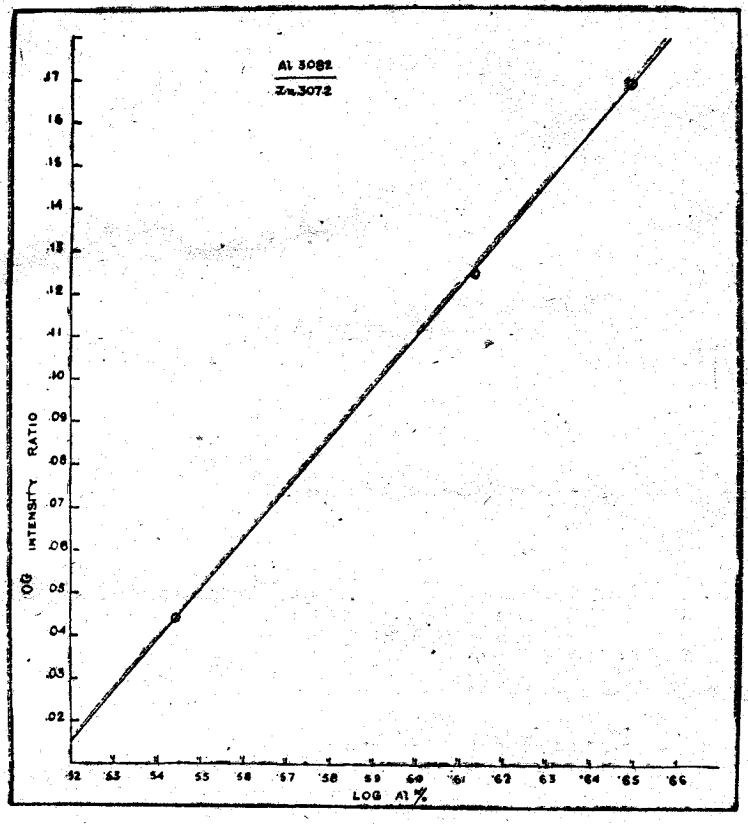


**Fig. 1. Analytical curve for Aluminium.**

Triplicate spectra of samples were often recorded specially for non-routine samples and for the routine ones, duplicates were found to be sufficient.

For triplicate spectra, three pairs of sample electrodes of the alloy or the same pair newly machined each time was used.

The spectra of standards were also similarly recorded on the plate. The photographic processing and microphotometer procedure and the evaluation of the elements are described later in subsequent paragraphs.

**Determination of impurity elements—Lead, Tin and Cadmium**

For assessing lead, tin and cadmium impurities which are present in trace amounts in zinc alloys, the trigger ignited D.C. arc method of excitation of samples had been used. In this arrangement of the source, a high frequency discharge passes across the electrodes enabling a D.C. arc to strike. As soon as the arc is struck, it results in the switching off of the H. F. Ionising discharge.

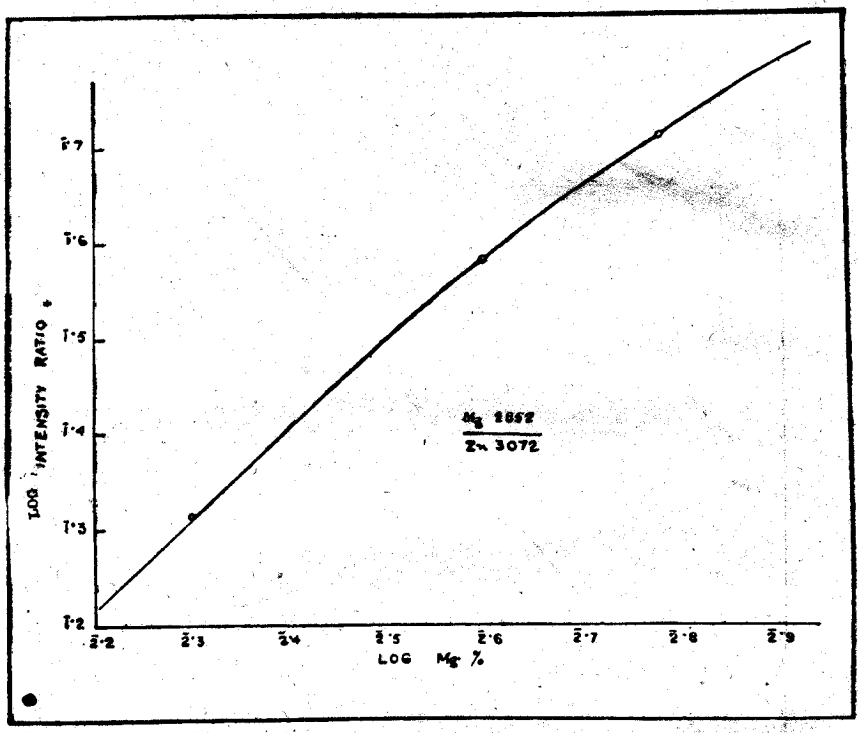


**Fig. 2. Analytical curve for Magnesium.**

Should the D.C. Arc fail or become erratic the high frequency Ionizing discharge begins to function automatically to keep the D.C. Arc burning. Thus, this type of trigger ignited D.C. Arc combines the sensitivity and stability of excitation required for low amounts of elements to be determined.

(*i*) *The Electrode System*—The sample was made the lower electrode (Cathode) and the counter electrode of pure graphite rod of 6 mm dia. (Mathey J. M. 4 B) tipped with a 80° cone was made the upper electrode (anode); the gap between the electrodes was set to 3 mm. The resistance in the source circuit was adjusted to give a current of 4 amps.

(*ii*) *Exposure conditions*—

| | |
|---|---|
| Spectrograph— | Hilger Medium Spectrograph |
| Slit width | 0·015 mm |
| Preburn period | 5 Seconds |
| Exposure period | 15 Seconds |

Photographic Plate—Ilford Ordinary.

NOTE—Spectra in triplicates were recorded along with those of standards to give analytical curves. These are shown in figures 3, 4 and 5.

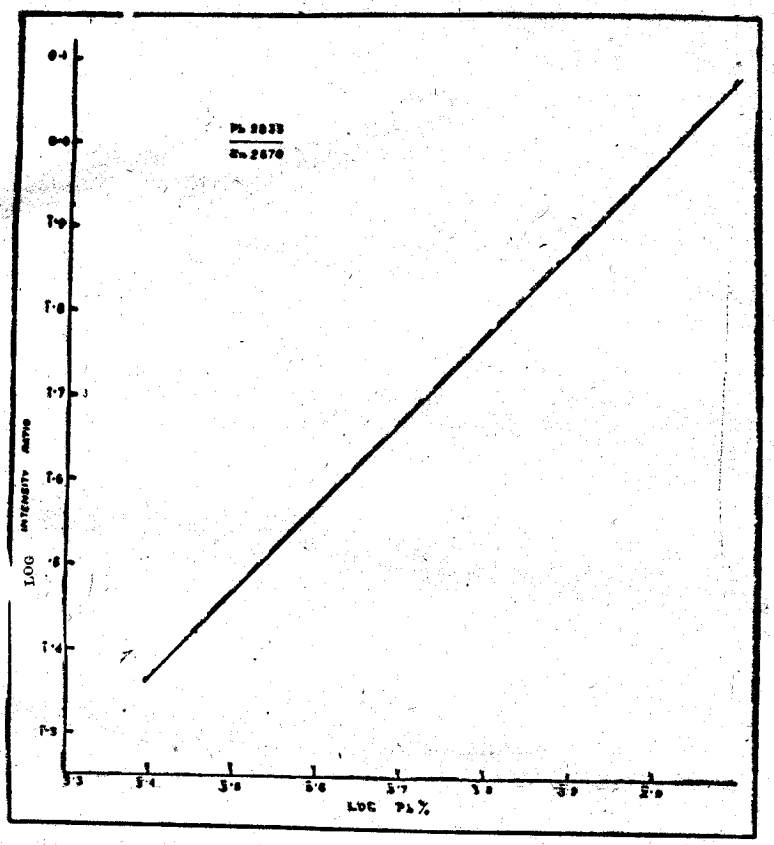


**Fig. 3. Analytical curve for Lead.**

## Determination of Indium

A limit for this element in zinc die-casting alloy is now stipulated in the British Specifications. Although the incidence of Indium had been rare and had never been detected in zinc alloy samples so far in our laboratory, nevertheless a method had been evolved by which it could be determined spectrographically.

The sample forms the electrode (lower) and a counter electrode of pure silver of 7 mm dia. tipped with 110° cone, forms the upper, thus constituting the electrodes system.

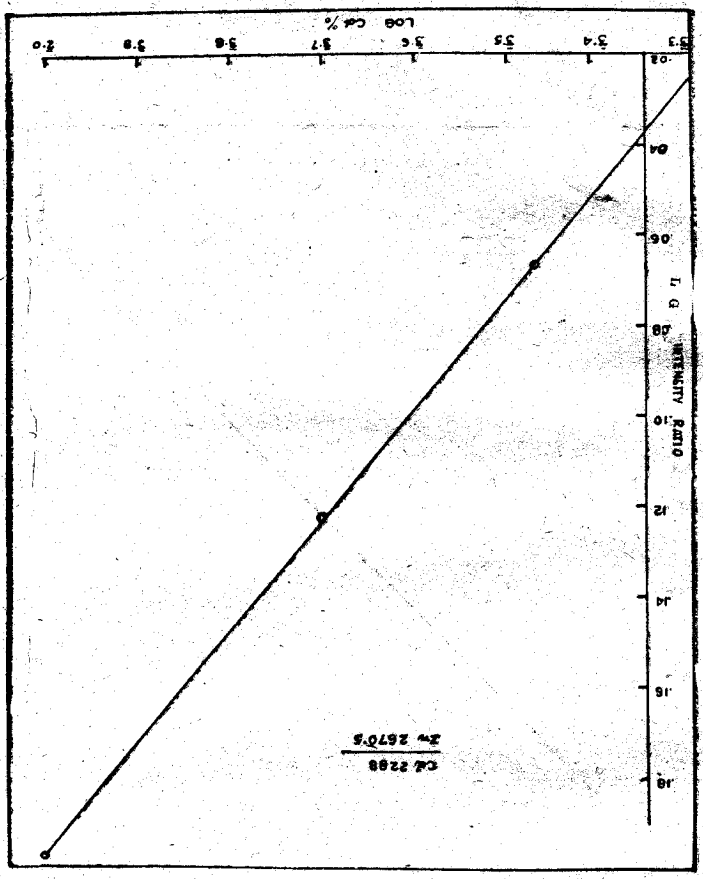

**Fig. 4. Analytical curve for Cadmium.**

For the excitation of the sample, an A.C. intermittent arc source, based on Pfeilsticker type of source, was used. The circuit was arranged to give an Arc current of 6·0 amp in the low voltage discharge circuit. Exposure conditions and the constants used are given below—

| | |
|---|---|
| Spectrograph | Hilger Medium Quartz E 498 |
| Slit width | ·015 mm |
| Slit to Electrode distance | 38 cm |
| Prearc period | 10 Seconds |
| Exposure period | 30 Seconds |
| Arc gap | 4 mm |

The spectra of samples along with the standards were recorded on Ilford ordinary plate, and the spectral line In 4101 was photometered and compared with those in the spectra of standards.

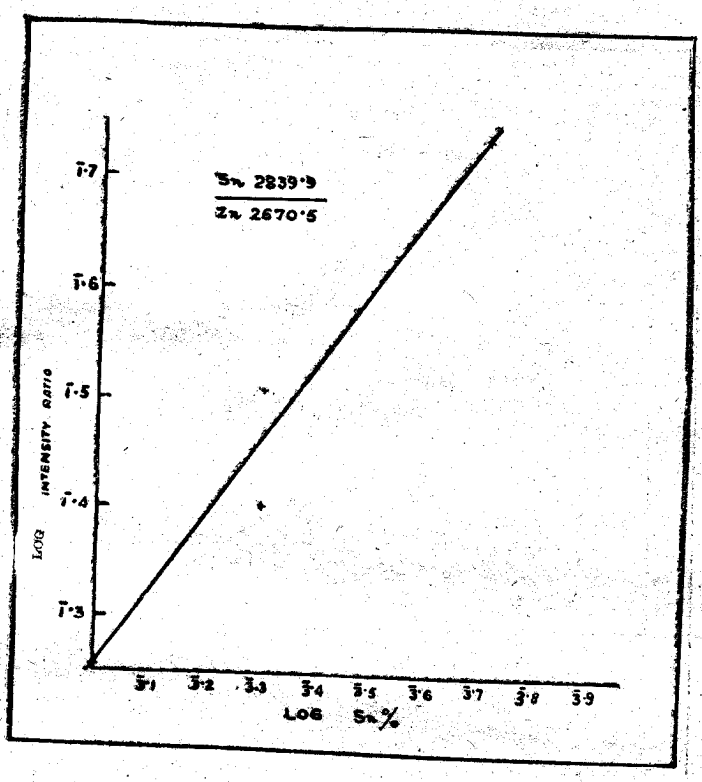


**Fig. 5. Analytical curve for Tin.**

This metod had been found to be sufficient to meet the requirements of testing samples to specification. However if the determination of Indium is necessary, the spectral line intensity of In 4101 with background intensity near the line may be obtained from a calibration curve (see fig. 6) from which concentration of Indium could be obtained from analytical curve drawn from standards.

**Photographic plates and Processing**

*Photographic plates:* Ilford ordinary plates of 10 in. × 4 in. size were used for the determination of impurity elements Pb, Sn, and Cd, by D.C. Arc method and also for In and Tl by the A.C. intermittent Arc method. Ilford thin film half tone plates were used in spark technique for the determination of Al and Mg.

The speed and contrast of these two types of plates are well suited for the different requirements of determination viz. sensitivity and contrast required for small trace amounts of impurity elements and the contrast required for lloying elements respectively.

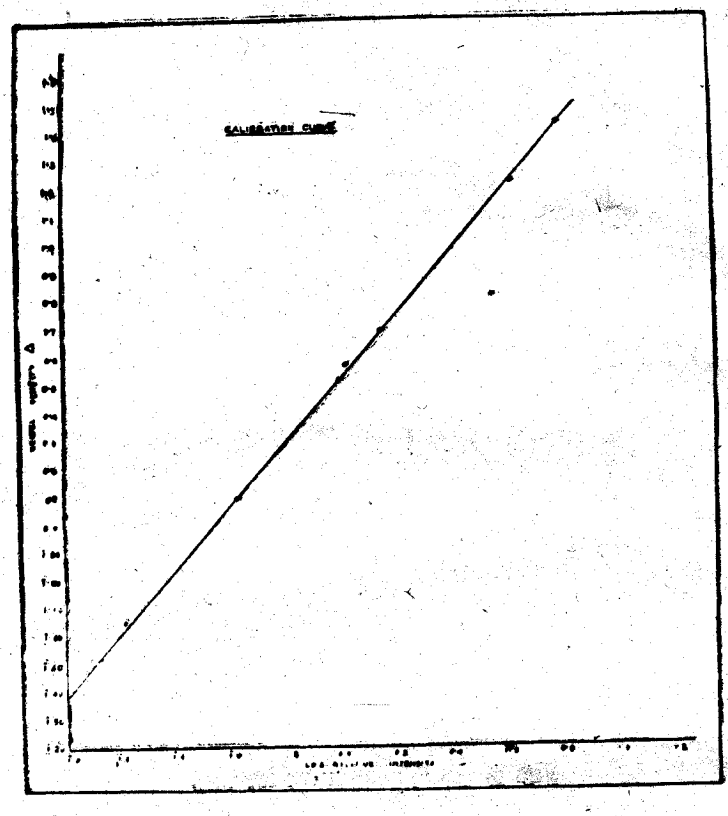

**Fig. 6. Calibration curve.**

*Emulsion calibration :* Calibration of the plates was made by means of the Iron spark spectrum between a pure iron rod and a graphite rod tipped with 80° cone. The spark gap was adjusted to 2 mm. Emulsion calibration curve of each plate was drawn by plotting transformed $\Delta$ values obtained from microphotometer deflexions of the group of Iron lines. The relative intensity values of these Iron lines were determined previously.

*Photographic processing :* The plates were processed in a dish of 11 in. × 5 in. size containing 150 m*l* of developer solution made to following formula—

| | | |
|---|---|---|
| Metol | .. .. | 1·0 gms |
| Sodium Sulphite (anhydrous) | .. | 13·0 „ |
| Hydroquinone | .. .. | 2·2 „ |
| Sodium Carbonate (anhydrous) | | 9·0 „ |
| Potassium Bromide | .. .. | 0·3 „ |
| Water to make | .. .. | 1000 m*l*. |

Ilford ordinary plates and thin film half tone plates were developed at 20°C for 100 seconds and 2 minutes respectively.

After development, the plates were immersed for 20 seconds in a stop-bath containing 2 per cent acetic acid and then fixed for 6 minutes in 300 ml of acid hypo solution of the following composition—

| | | |
|---|---|---|
| Hypo | .. .. | 300 gms |
| Potassium metabisulphite | .. | 25 ,, |
| Chrome Alum | .. .. | 12·5 ,, |
| Distilled water | .. .. | 1 litre |

The plates were washed for 20 minutes in water, with 5 changes of water. Finally the plates were immersed in a wetting agent for 2 minutes.

The plates were allowed to dry in still air.

*Photometry* : Microphotometer readings *i.e.* deflexion values of the different analytical lines and the appropriate internal standard Zinc line shown in table were read on a Hilger's Non-recording microphotometer and the calibration Iron group of lines were also similarly photometered, and from these readings of Iron lines the calibration curve for each plate was drawn. The △ values obtained from the deflexions of the analytical line pairs were converted into log intensity ratios from the plate calibration curve. This process was applied to the spectra of standard samples and from these intensity values of line pairs, the analytical curve relating log relative intensity values with log percentages of each of the elements were drawn.

The log relative intensity ratios when applied to the appropriate analytical curve gave the concentration of the corresponding elements. The average of triplicate determinations, corrected by two controlled standards or duplicates of one standard, is usually reported for each of the impurity elements as well as for each of the alloying element for all non-routine samples.

TABLE 1

*Wave lengths of Iron Lines used for Plates Calibration*

| Wavelength | Relative Intensity |
|---|---|
| 2783·696 | 6·92 |
| 2831·562 | 4·22 |
| 2793·888 | 1·41 |
| 2728·636 | 1·05 |
| 2799·286 | 1·00 |
| 2827·454 | 0·42 |
| 2819·333 | 0 16 |
| 2827·493 | 0 14 |

TABLE 2

*Table showing Precision of the Method*

| *Sample* | *Element* | *Concentration* | *Coefficient of Variation* | *No. of determination* |
|---|---|---|---|---|
| P 2 .. | Aluminium | 4·10 | 2·93 | 10 |
| P 2 .. | Magnesium | 0·04 | 10·64 | 20 |
| A 1 .. | Lead | 0·003 | 7·02 | 10 |
| A 1 .. | Tin | 0·0002 | | |
| A 1 .. | Cadmium | 0·005 | | |
| A 1 .. | Thallium | 0·001 | | |
| A 1 .. | Indium | 0·0005 | | |

TABLE 3

*Spectral lines used for analysis*

| *Element* | *Source* | *Element line A°* | *Interval Sb. Line A°* | *Concentration Index* |
|---|---|---|---|---|
| Aluminium | Spark | Al 3092 | Zn 3072·1 | 3·22 |
| Magnesium | Spark | Mg 2852 | Zn 3072·1 | 0·15 |
| Lead .. | Arc | Pb 2833 | Zn 2670·5 | 0·11 |
| Tin .. | Arc | Sn 2899 | Zn 2670·5 | |
| Cadmium .. | Arc | Cd 2288 | Zn 2670·5 | ·0016 |
| Thallium .. | A.C. Int. Arc | Th 3775 | Background | |
| Indium .. | A.C. Int. Arc | In 4101·8 | Background | |

## Precision and Accuracy

To assess the reproducibility of the determinations with spark technique for Aluminium and Magnesium and with the trigger ignited D.C. Arc for Lead, Tin and Cadmium and A.C. Intermittent Arc for Thallium and Indium, the coefficient of variation of some of these elements at concentrations shown in table 2 were calculated using a number of results obtained on several plates and on same plates. The samples used for these determinations may be considered to be fairly homogenous, exhibiting very little segregations.

For accuracy assessment of these methods, a comparison with chemical results are essential which have not been available for impurity elements excepting Aluminium and Magnesium. The difference between the results have however been quite small

## Acknowledgements

The methods described had been based on the work carried out some years back. Some changes in the methods specially in the evaluation of the results had been introduced in recent years. Considerable part of experimental work had been done by Shri D. Das Gupta and others. Grateful acknowledgements are due to these workers.

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