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ABSTRACT

The AC arc excitation has been employed for the determination of B, Cu, Fe, Mg, Mn, Si and Ti in aluminum oxide in the concentration range 0.025 - 1%. The aluminum metal is converted to oxide and glued to the flat tops of a pair of graphite electrodes without any further treatment. The standards are prepared synthetically on pure aluminum oxide by dry mixing. Spectra are recorded on Kodak SA 1 plate using the first order of a 15,000 lines per inch grating. Each spectrum is obtained in two steps of 10% and 1% transmission with the help of a neutral filter. One aluminum line is used as internal standard. The precision of the method varies from ± 4% for B to ± 17% for Cu.

1 - INTRODUCTION

Aluminum has many uses in reactor technology and industry. It readily combines with many other elements to form alloys and therefore many varieties of aluminum base alloys have been developed. At times, these alloying elements are in minor amounts. For example, the addition of 0.05 - 0.2% of Ti to aluminum results in an alloy with refined grain structure and this alloy gives better castings. The addition of B has a similar effect. The presence of Si has a deleterious effect on the tensile properties of aluminum but Si and Fe are present in it as an impurity during extraction from bauxite ore. A maximum of 1% is specified for these two elements in aluminum alloys. Manganese is normally added to aluminum to improve its tensile properties at elevated temperatures and the addition of Cu to aluminum affords greater response to heat treatment. The nominal composition of some of the aluminum alloys used in industry is given in Table I[3].

For its use in reactor technology, the most important factor to be considered is neutron economy. Table II lists the thermal neutron absorption cross section of aluminum and some of its alloying elements. It is seen that aluminum has a low thermal neutron absorption cross section which makes it useful as a cladding and structural material in reactors up to 100°C. At higher temperatures it corrodes and pits badly unless the water used is of very high purity. For its use at higher temperatures with ordinary water, it has to be alloyed with other elements to make it more corrosion resistant and strong. Since conservation of neutrons is the primary consideration in reactors, the alloying elements also should have a low thermal neutron absorption cross section. Table II also gives the relative cross section[8] of some alloying elements, on equal weight basis, taking the relative cross section for aluminum as 1.00. The elements having a relative cross section of less than 1 will reduce the overall neutron absorption when alloyed with aluminum and vice-versa. Thus, from this data it is possible to theoretically calculate the neutron absorption cross section of an aluminum alloy if the alloying components are precisely known.

$$\text{Relative Cross Section} = \frac{\text{At. Wt. Al}}{\text{Cross Sec. Al}} \times \frac{\text{Cross Sec. Elem.}}{\text{At. Wt. Elem.}}$$

Table I

Nominal Composition of Some Aluminum Alloys

Aluminum Association N°	1100	2024	6063	M-388
Commercial N°	2S	24S	63S	----
Nominal Composition, Weight %				
Al	99	Remainder	Remainder	Remainder
Cr	--	0.1 Max	0.1 Max	--
Cu	0.2 Max	4.5	0.1 Max	--
Fe	--	0.5	0.35 Max	0.5
Mg	--	1.5	0.7	--
Mn	0.05 Max	0.6	0.1 Max	--
Ni	--	--	--	1.0
Si	--	0.5	0.4	0.1
Ti	--	--	0.1 Max	--
Zn	0.1 Max	0.1 Max	0.1 Max	--
Others	0.15 Max	0.15 Max	0.15	--

Max = Maximum

Table II

Relative Absorption of Thermal Neutrons on Equal Weight Basis

Element	Atomic Weight, I	Absorption Cross-Section, Barns, II	Ratio I / II	Relative Cross-Section %
Al	26.96	0.23	117.3043	1
B	10.82	755	0.0143	8203
Cu	63.54	3.69	17.2195	6.8
Fe	55.85	2.53	22.0750	5.3
Mg	24.32	0.063	386.0317	0.3
Mn	54.94	13.12	4.1621	28.2
Si	28.09	0.13	216.0769	0.54
Ti	47.90	5.6	8.5535	13.17

1.1 Scope

This method is intended to serve for a quick analysis of aluminum alloys containing the elements B, Cu, Fe, Mg, Mn, Si and Zn in concentration range 0.02% to 1%. The method is not intended for attaining the lowest limits of detection for the elements but has been developed for the analysis in a limited predetermined range.

Samples having cold shapes, turnings, drillings, cuts, discs and powders can be analysed by this method after their conversion to aluminum oxide.

Samples containing more than 1% of these elements can be suitably diluted with aluminum oxide and analysed.

1.2 Previous Spectrographic Methods

Many [illegible] methods have been developed for the analysis of aluminum and its alloys. The [illegible] methods provide a quick and reliable [illegible] analysis at a low cost. Because of these advantages the spectrographic laboratory is a necessary and indispensable unit in all major aluminum industries. Efforts are continuously made to improve the analysis. For example recently SLICKERS and SCHMITT[3] have used a low temperature discharge in argon atmosphere and found that the results are independent of structural defects and metal working history of samples. They also found that a small number of lines is sufficient for the determination of many elements.

Earlier WALDEN [illegible] and PETIT[5] have used nitrogen gas sparking and spark excitation to obtain increased [illegible] environmental effects and reduction in the number of analytical curves.

NIELEN and STAUDINGER[7] studied the surface forms and depths of craters formed in aluminum alloys containing Mg, Cu and Zn after a high voltage spark was passed through them. They studied these characteristics in the atmosphere of air, He, N and Ar.[4] The effects of these gases on analytical curves were also [illegible].

MUNTZ[10] developed [illegible] aluminum by using solution samples and exciting them in a DC arc in an argon atmosphere. ASAI and TAKAHASHI[11] used a quantometer with argon gas flow to determine Cu, Fe, Mg, Mn and Si in aluminum alloys. CAMIELY and BLACK[15] also utilised the direct reading system for the analysis of alloys and found that new alloys could also be incorporated in the system. [illegible] EBERHARDT, EXLEBEN and [illegible][2] analysed alloys of aluminum with Si, Cu and Mg using a photoelectric spectrometer. WILCO and [illegible][17] have used a direct reading attachment for the spectrometric analysis of [illegible] alloys.

HAALAND[18] used the metal powders from commercially available standards (Johnson Matthey & Co.) whereas HANDOCA and KARNIK[51] used these standards as self electrodes, against a pointed graphite counter electrode. Drops of [illegible] stock and analysed the alloying elements in the rod samples.

ZAKHARIYA[19] has used the DC arc technique after converting the metal to oxide by dissolution in nitric acid, evaporation and calcination. In their method of conversion to oxide there is a possibility of the loss of some elements, therefore CHANDOLA and MACHADO[16] developed another method of obtaining the oxide which is through its hydroxide. They proved that there is no loss of many elements (including B) during this conversion. TOROK and PETHO[25] have determined only Cu in the range 0.1 - 1%.

American Society for Testing Materials (ASTM) have also suggested methods for the analysis of aluminum alloys. These methods include pin to pin spark technique of CALLON and RUSSEL[4], pin

to plane spark technique of CRAMPTON[7] and solution rotating disc spark technique of MURPHY and MORTENSEN[19]. JAYCOX[13] has suggested a method in which the sample is converted to sulphate, mixed with graphite and excited in a DC arc. A drop of phosphoric acid is added to the electrodes and they are heated prior to their excitation.

Though the AC spark and DC arc technique of excitation have been extensively used, the AC arc technique has not been utilised so often. LADER[14] has used the AC arc for the analysis of 65-35 and 50-50 magnesium-aluminum alloys by drying the sample solution on the top of flat electrodes. OLDFIELD and FERM[23] did some work on the analysis of aluminum alloys using an intermittent AC arc, but details of their work are not available. GUSARSKII and TARASEVICH[10] determined only Na in these alloys using AC arc. OBUKHOVA[22] and others have used a contact spark for simpling and then used AC arc for excitation of alloy samples.

1.3 – AC Arc Source of Excitation

Since the AC arc source of excitation has not been extensively used, it is appropriate to discuss some important features of this source.

The AC arc was first used by DUFFENDACK and WOLFE[9]. The AC arc source operates at high voltages of 2200 to 4400 volts if it is to be of self igniting type. Figure 1 gives the circuit diagram of a self ignited AC arc source[20]. A variable inductance L in the primary circuit and a variable resistance R in the secondary circuit control the current which is usually upto 5 amperes.

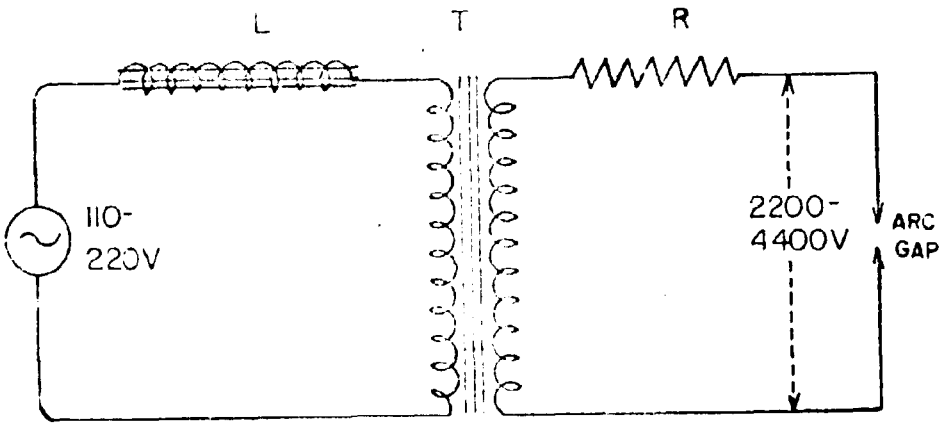

Figure 1 – Circuit Diagram For a Self Ignited AC Arc Source

Figure 2 shows the circuit diagram of an ignited AC arc source[12] which can operate at voltages of 1100 volts or less. Here a tesla transformer T_2 induces high frequency current in the main circuit containing analytical gap B. The voltage across capacitor C_2 rises rapidly and the arc starts through the gap B. The arc is extinguished automatically when the voltage is not enough to sustain it. Pfleisticker had used an outside means in the form of a rotating disc containing metallic (conducting)

and insulated segments to start and stop the arc. Transformer T_1 and condenser C_1 are used to give powder to tesla transformer T_2. By adjusting the auxiliary gap A, the power in the analytical gap B can be regulated. L_1, L_2 and C_3 are used to filter out the high frequency from the mains.

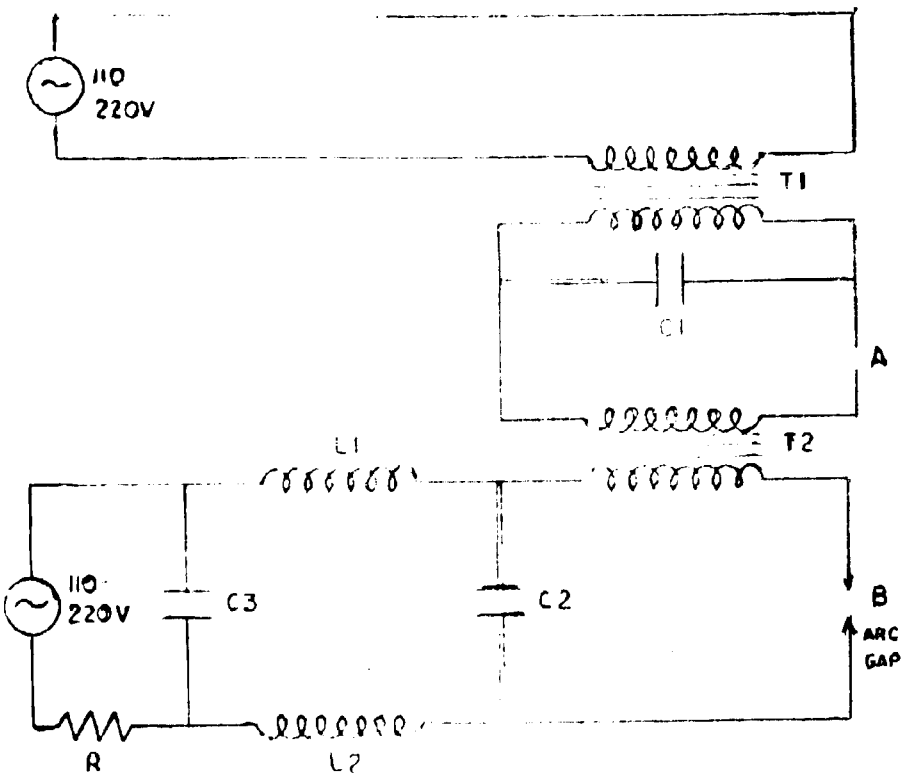

Figure 2 – Circuit Diagram of a Tesla Igniter AC Arc Source

The current and voltage characteristics of an AC arc are given in Figure 3[20]. As the current changes from zero at A to a maximum on positive side and back to zero at B and maximum on negative side and back again to zero at C, the voltage has a maximum twice; once in each cycle. In each half cycle, the arc breacks at maximum voltage, is sustained at lower voltage and then extinguished. Thus there are 100 or 120 different arcs per second between the electrodes depending upon whether the input has a 50 or 60 cycles frequency respectively.

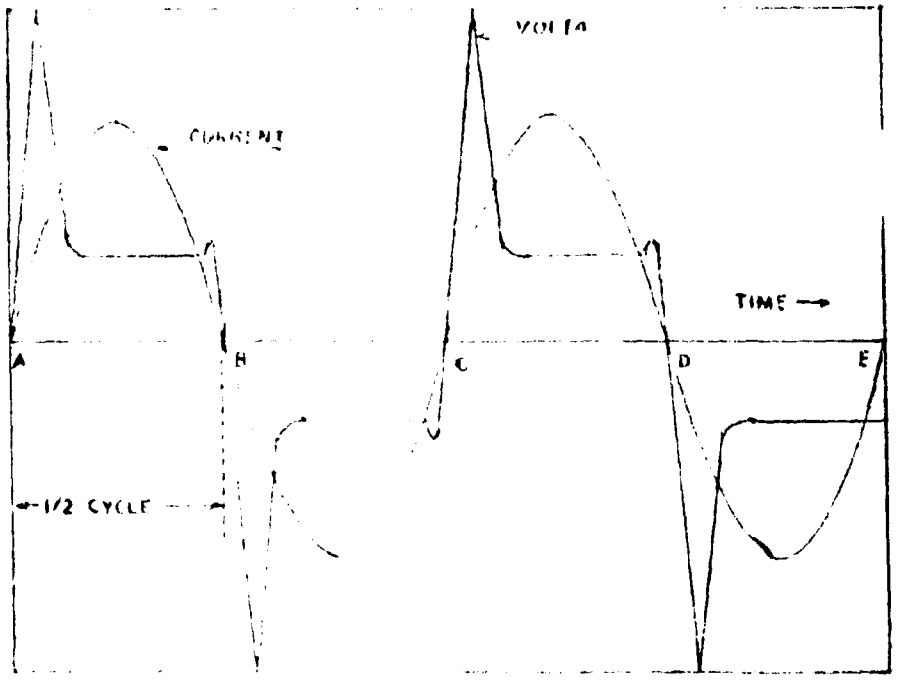

Figure 3 — Courrent and Voltage Characteristics of an AC Arc

It is observed that though the DC arc excitation gives the best sensitivity, the precision it gives is not satisfactory because two factors. First, it gives selective volatilisation of elements present in the arc according to their boiling points. Second, the DC arc has a tendency to strike at some selected points known as "hot spots" and it continues to burn at these points. In an AC arc the arc strikes 100 – 120 times per second (depending on the supply being 50 or 60 cycles per second) and each time the arc area is only a fraction of a square millimeter. Every time the arc strikes a fresh surface and entire electrode surface is sampled by the arc during the period of exposure. Thus the difficulty in a DC arc burning at few preferred spots is eliminated. Though the local temperature in the small arc area is high, the overall temperature attained is much less than in DC arc and thus the selective volatilisation is reduced.

2 – EXPERIMENTAL

2.1 – Outline of the Method

The aluminum alloy sample is converted to aluminum oxide. The oxide so obtained is glued to the flat ends of a pair of graphite electrodes without any further treatment. The standards are prepared synthetically on pure aluminum oxide. The samples and standards are excited by an ignited AC arc source and recorded on photographic plate with the help of a grating spectrograph. The densities of selected lines are obtained and their densities calculated by a calibration of the photographic plate. The intensity is also calculated for a line of aluminum which serves as an internal standard. Intensity ratios analysis line and internal standard line are calculated. These intensity ratios are related to the concentration by the help of the working curves obtained from synthetic standards.

2.2 – Preparation of the Sample

The sample is converted to aluminum oxide by the following procedure. The metal is dissolved in a minimum quantity of high purity hydrochloric acid and amonium hydroxide is added to it. Aluminum hydroxide is precipitated. The precipitate along with the supernatant solution is first evaporated in a water bath and then calcined over a bunsen burner in a platinum crucible till a constant weight is obtained. The aluminum oxide so obtained is directly used for analysis.

2.3 – Preparation of the Standards

Standards in the form of metal rods for the determination of elements mentioned except B could be obtained commercially from Johnson Matthey and Co. Since the determination of B was also required and no commercial standards were available for this, it was decided to do the analysis on oxide powder and prepare the standards on high purity aluminum oxide obtained from the same company. This method of standard preparation has the advantage that similar or other standards containing different elements can be easily in the laboratory. In the case of metal standards, the analysis is limited to nine elements only but even these nine elements are covered in five different sets. Many sets of the standards have to be maintained if the analysis is done on the metal itself.

The compounds taken for the preparation of the standards and their weights used to obtain 1% standard are given in Table III.

Further standards are prepared by diluting 1% standard with pure aluminum oxide. Six standards were prepared in all and these contained 1, 0.5, 0.25, 0.1, 0.05 and 0.025% of each of the seven elements mentioned, in aluminum oxide matrix.

2.4 – Selection of Electrodes and Fixing Glue

In an AC arc the polarity of the electrodes changes in each half cycle. Therefore, the most efficient excitation is obtained if both electrodes contain sample. For this, it is necessary to hold the sample to electrodes with a glue. Out of many glues tried, a glue named Ratio TV Service Cement (G. C. Electronics, Illinois, U.S.A.) when diluted with ethyl acetate and toluol was found to be most suitable. It was found that the sample sticks to the electrodes better for the purpose of excitation when the sample is uniformly spread over the flat ends of the electrodes. Other forms of electrodes were also tried but were found to be unsuitable. Both the electrodes used are 1/4 inch diameter, 2 inch long, have flat ends and 5 mg sample is glued to each. These electrodes were cut from 12 inch rods supplied by National Carbon Company. The loaded electrodes are dried under an infra-red lamp prior to excitation.

Table III

Preparation of 1% Standard on Aluminum Oxide

Element	Quantity Required mg	Compound Taken	Amount Taken mg
Boron	50	H_3BO_4	285.67
Copper	"	CuO	62.60
Iron	"	Fe_2O_3	71.50
Magnesium	"	MgO	82.90
Manganese	"	Mn_3O_4	69.40
Silicon	"	SiO_2	106.76
Titanium	"	TiO_2	83.40
Matrix	To Make 5 g	Al_2O_3	4,237.77
		Total	5,000.00

2.5 - Studies for Optimum Excitation Parameters

For the analysis, the ignited AC arc and AC spark sources of excitation were tried. Both sources were investigated with various combinations of capacitances (0.0025, 0.005, 0.0075 and 0.01 microfarads) and inductances (residual, 40 and 300 microhenries). From these studies the ignited AC arc excitation with residual inductance and 0.0025 microhenries capacitance was selected for the analysis. With these conditions, the spectrum obtained had suitable intensity for the analytical purposes.

2.6 – Spectrograph and its Conditions

The spectrograph selected for the analysis is a Jarrel-Ash 3.4 meter grating spectrograph having a 15,000 lines per inch grating. This grating gives a reciprocal linear dispersion of about 5 Å/mm in the first order and 2.5 Å/mm in the second order. Both first and second order spectrum were investigated. Since the spectrum of aluminum atom consists of very few lines, the first order spectrum obtained with a slit width of 25 microns gave enough dispersion for resolving the various analytical lines. When grating angle is fixed at 5.90°, the useful range of the spectrum i.e. 2200 to 3450 Å is contained in only one plate placed on the right side of the plate holder. It was found that the densities at the higher end of the concentration range for many elements was high. To make the densities of these lines suitable for densitometry a step filter was put in front of the slit. The step filter was placed in such a position that it produced a two step spectrum of 100 and 18% transmission.

2.7 – Volatilisation Studies

Having fixed the excitation and spectrographic conditions the volatilisation studies were undertaken. The volatilisation curves for various elements obtained by racking plate method are shown in Figures 4 & 5. From these studies the exposure time was fixed at 60 seconds.

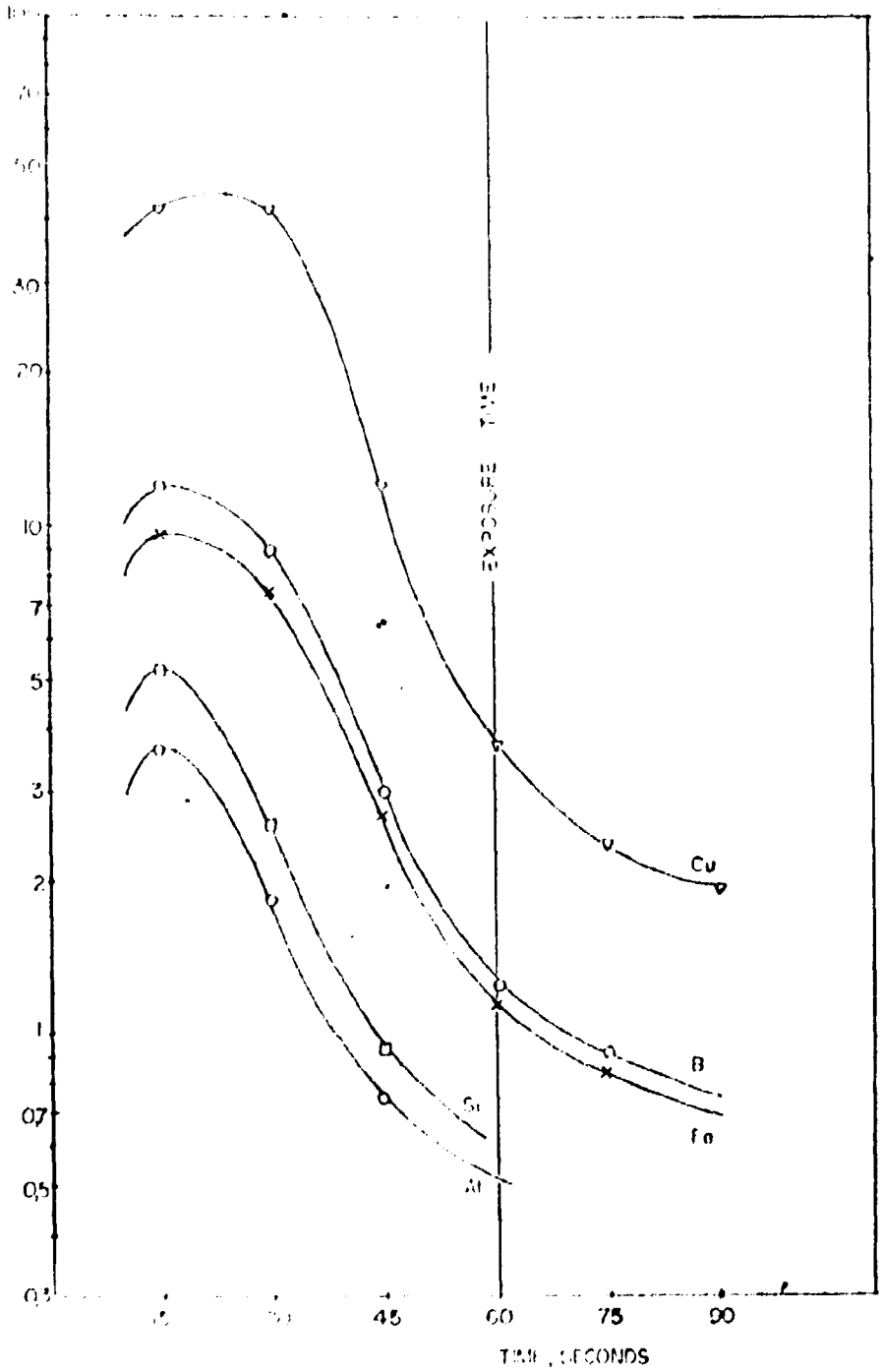

Figure 4 – Volatilisation Curves for Al, B, Cu, Fe and Si

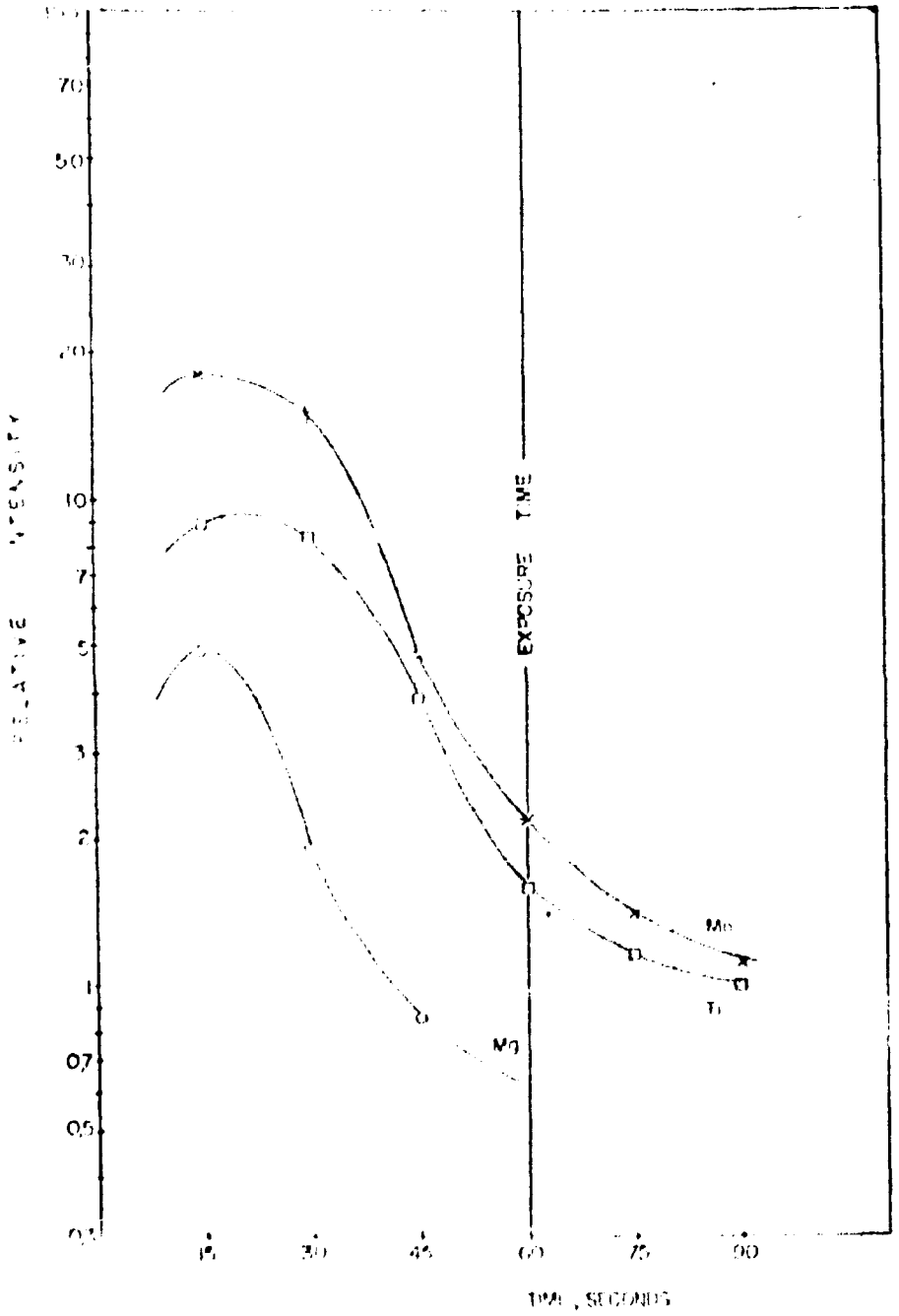

Figure 5 — Volatilisation Curves for Mg, Mn and Ti

2.8 – Emulsion and Processing

The emulsion selected is Kodak Spectrum Analysis (SA-1). The plate was developed in D 19 developer for 3 minutes at 18°C, washed in a stop bath for few seconds and fixed in F-5 fixer for 5 minutes. The plate was then washed in water and dried.

2.9 – Photometric Evaluation

The Jarrel-Ash microphotometer comparator is used for photometric evaluation. In the non-recording position of this instrument, either the transmitance or the density of the line and the background can be read sequentially.

The photographic emulsion was calibrated with the help of an iron spectrum photographed through a seven step rotating sector having individual step ratio of 2:1 and a maximum speed of 260 rotations per minute. The transmittance value (T) of each step of a line is obtained and converted to Seidel function Δ using the formula:

$$\Delta = \log \left(\frac{100}{\%\,T} - 1 \right)$$

The analytical lines are given in Table IV.

Table IV

Analytical Lines and Concentration Range

Element	Wavelength Å	Filter Step §	Concentration Range %
Boron	2497.73	a	0.025 – 0.1
Boron	2497.73	b	0.1 – 1
Copper	3247.54	b	0.025 – 0.25
Iron	2599.57	b	0.05 – 1
Magnesium	2779.83	a	0.025 – 0.1
Magnesium	2779.83	b	0.25 – 1
Manganese	2605.69	a	0.025 – 0.1
Manganese	2605.69	b	0.1 – 1
Silicon	2514.33	b	0.1 – 1
Titanium	3234.52	a	0.025 – 0.25
Titanium	3234.52	b	0.1 – 1
Aluminum	2652.49	a	Int. Std.

§ : a and b refer to 100% and 18% transmittance steps.

The transmittance values for the analytical lines and the internal standard line are measured in the appropriate step and their intensity ratios are calculated.

The intensity ratios for the standards are plotted against the concentration in a double log graph paper to obtain the working curves shown in Figures 6-11. In these figures "a" and "b" mean that *the density of the line of the element being determined is measured in 100% and 18% transmission step respectively.*

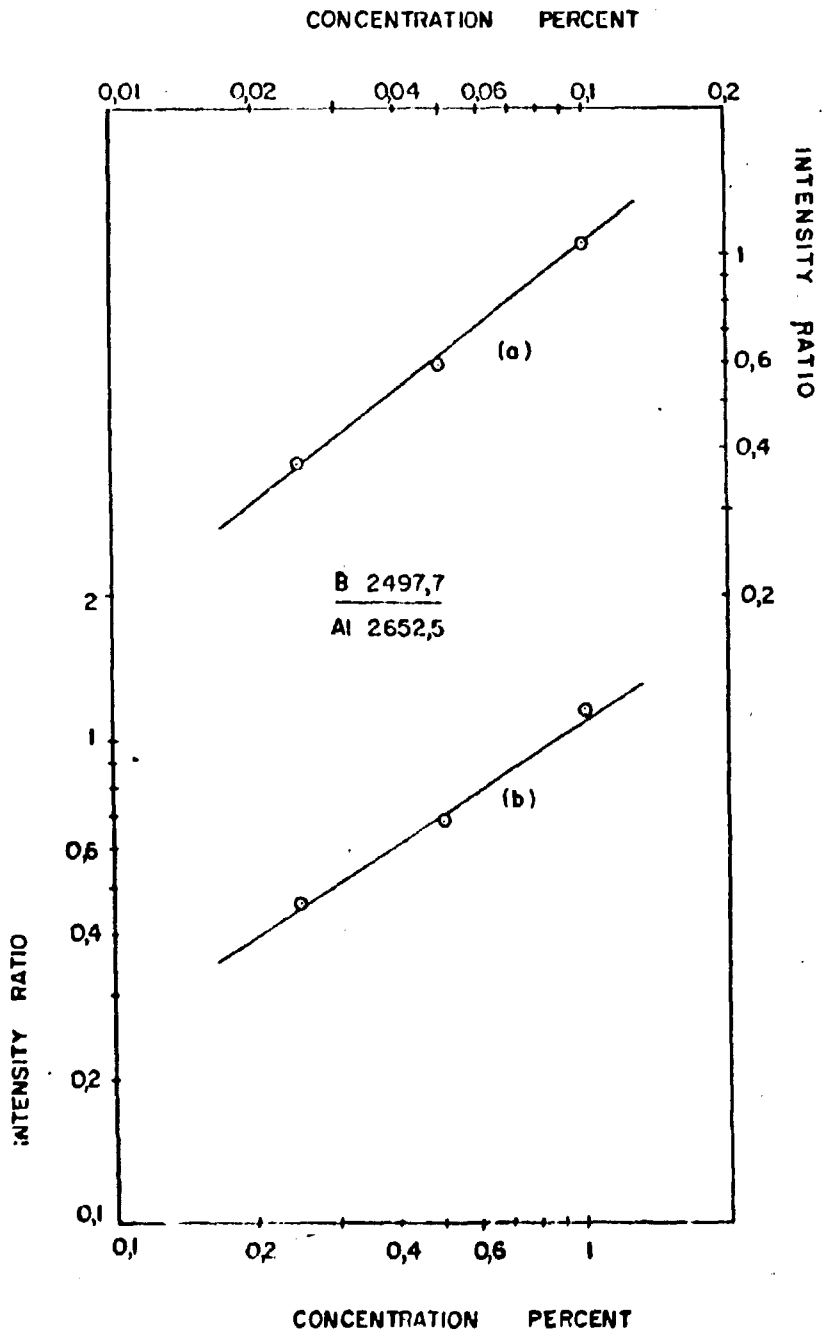

Figure 6 – Working Curves for B

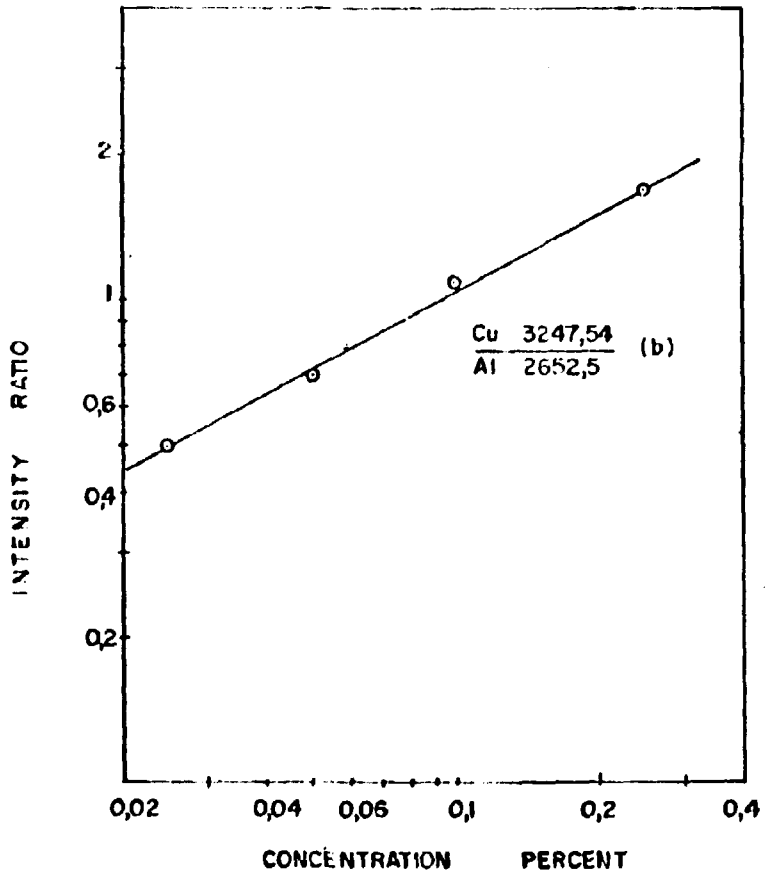

Figure 7 — Working Curve for Cu

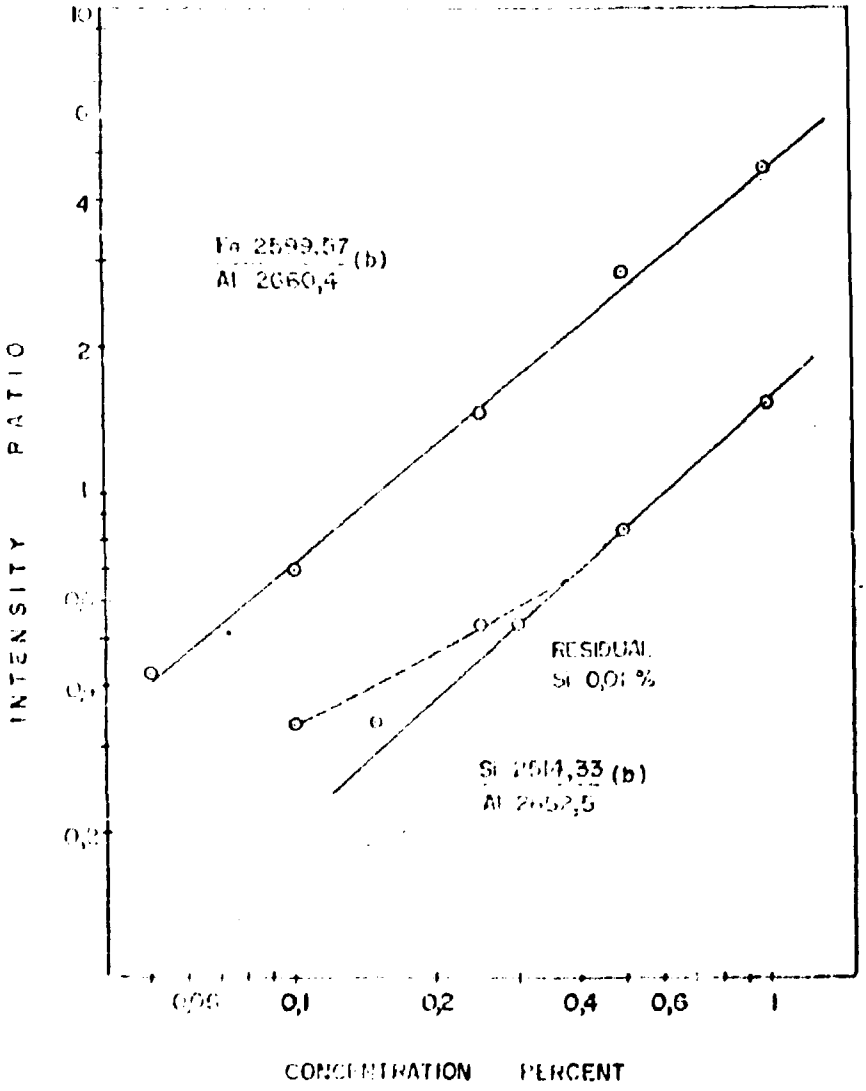

Figure 8 — Working Curves for Fe and Si

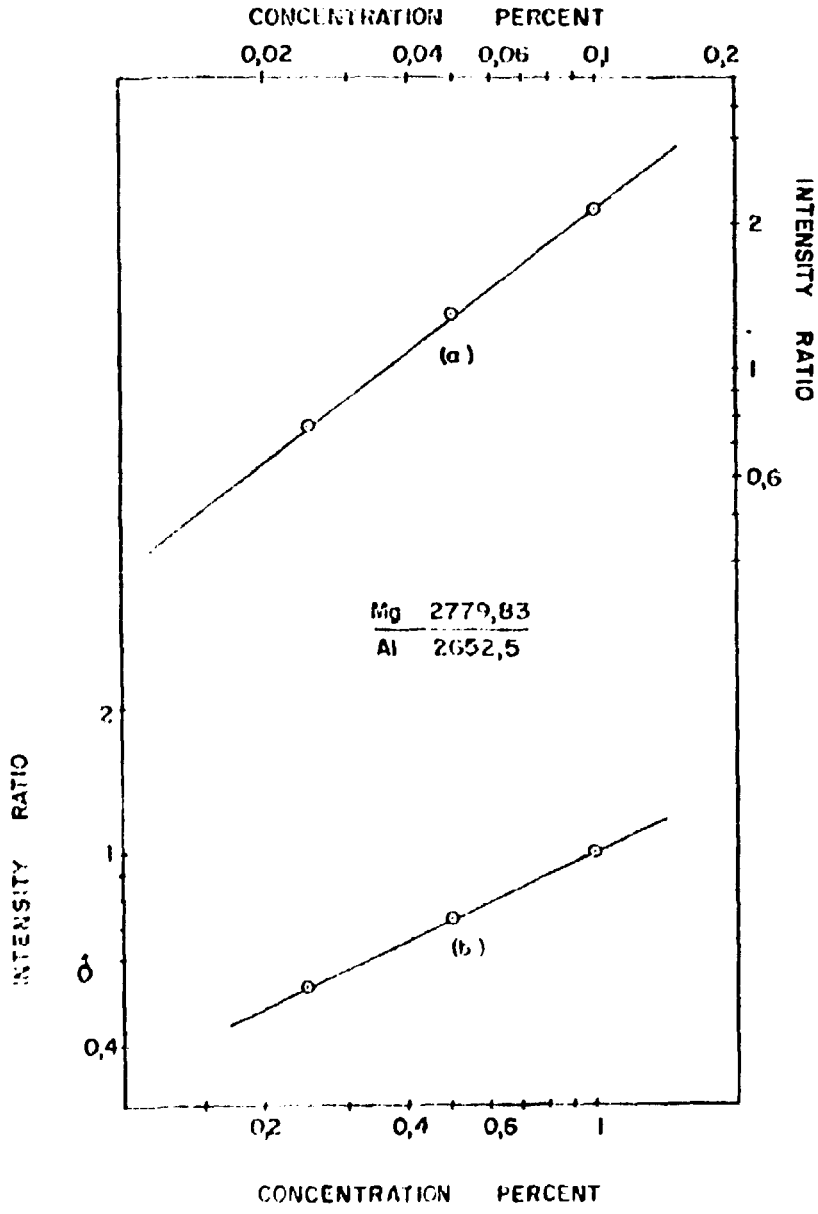

Figure 9 — Working Curves for Mg

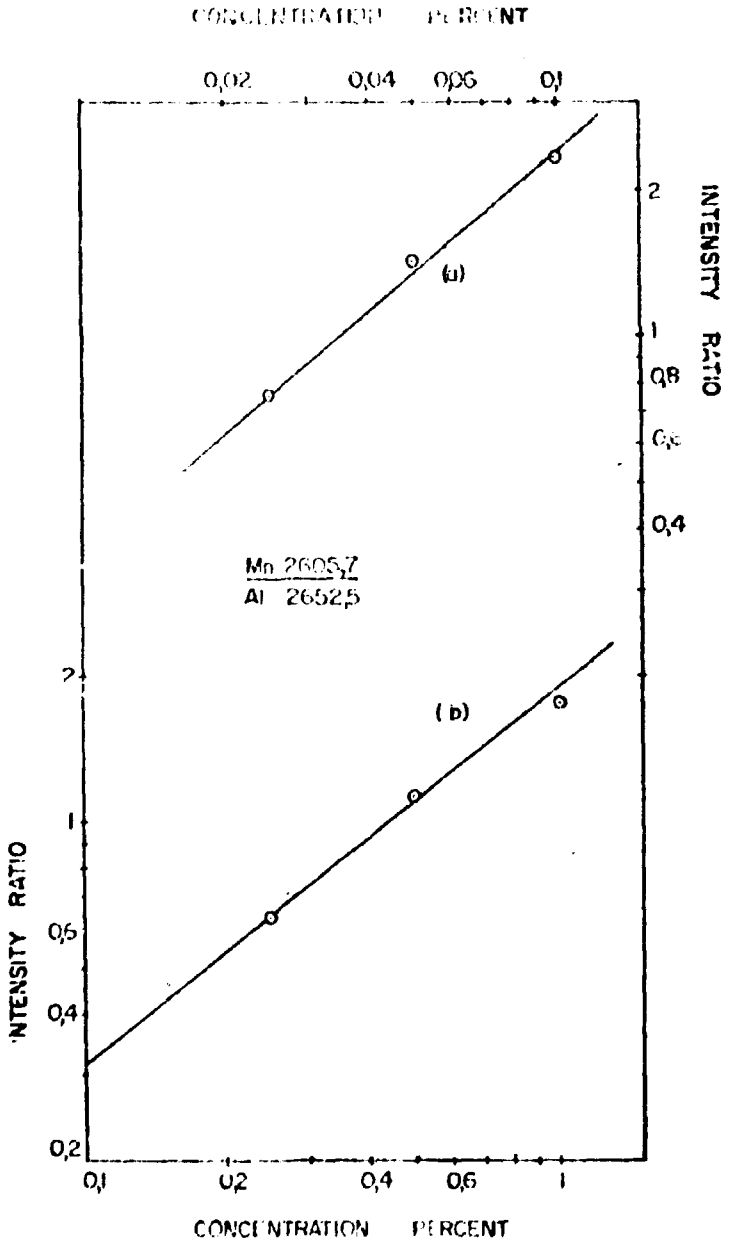

Figure 10 - Working Curves for Mn

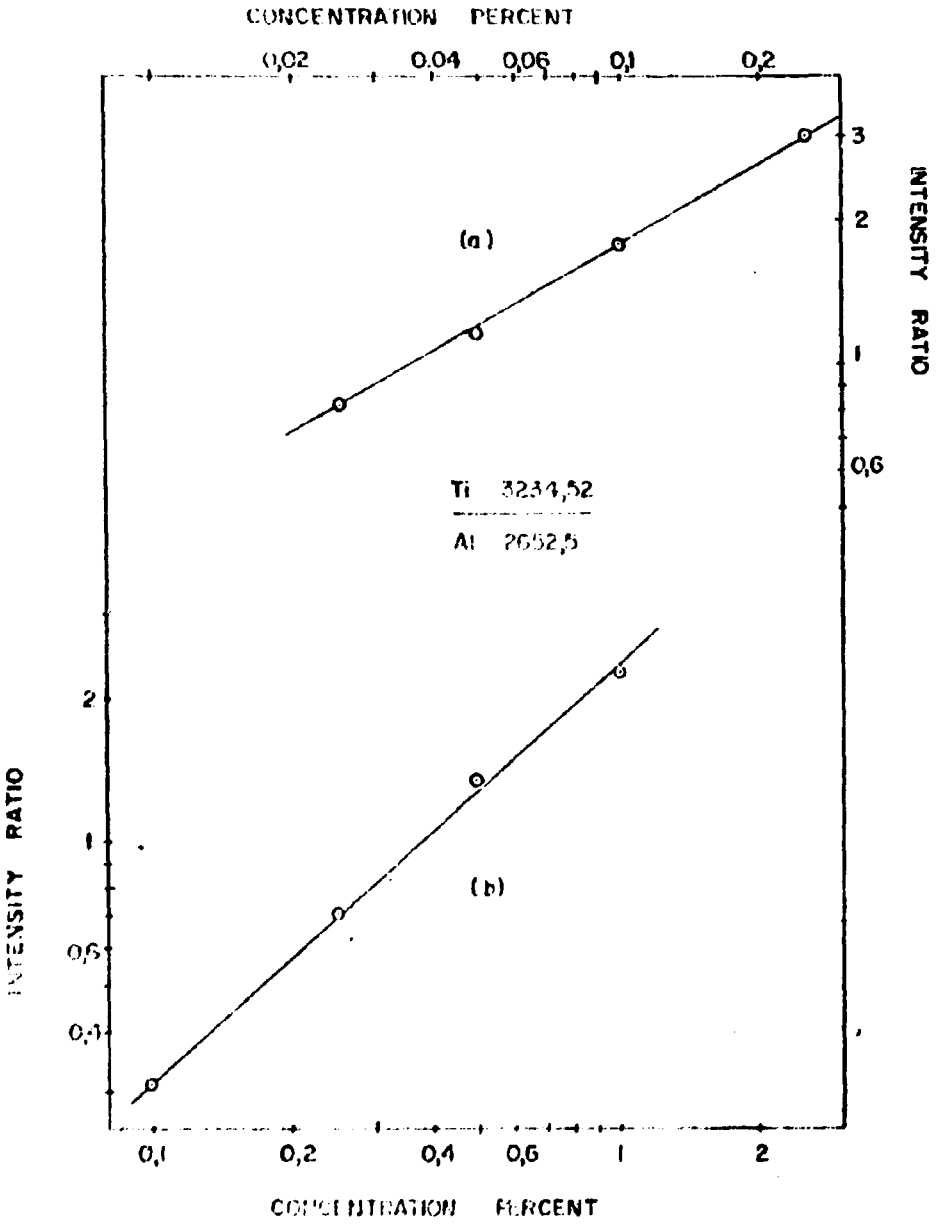

Figure 11 – Working Curves for Ti

3 – PRECISION

The precision has been calculated in terms of percent coefficient of variation from twenty values of concentrations obtained from intensity ratios. It is found that the highest coefficient of variation is for Cu. Earlier, JAYCOX had observed that Cu is not spectrographically compatible with aluminum. Even after this incompatibility a variation of ± 17% is obtained which is satisfactory. The precision data is given in Table V.

Table V

Coefficient of Variation for Elements

Element	Coefficient of Variation %
Boron	4
Copper	17
Iron	7
Magnesium	12
Manganese	6
Silicon	7
Titanium	8

4 – CONCLUSIONS

A simple method has been developed for the analysis of aluminum alloys. This method can replace the dry powder DC arc method of JAYCOX. This method has a better precision than that of JAYCOX while retaining all other advantages like ability to analyse the samples of all forms and sizes.

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RESUMO

Apresenta-se um método espectroquímico para a determinação de B, Cu, Fe, Mg, Mn, Si e Ti em óxido de alumínio. Transforma-se a amostra metálica em Al_2O_3 e, em seguida fixa-se o óxido na superfície plana de um elétrodo de grafita por meio de um adesivo.

Os padrões são preparados pela técnica de homogenização das impurezas em matriz de óxido de alumínio.

Registram-se os espectros em placas fotográficas Kodak, tipo SA-1, na primeira ordem de uma rede de difração de 15.000 linhas por polegada.

Como padrão interno utiliza-se o próprio elemento alumínio.

A precisão do método, em termos de desvio padrão relativo, varia de 4% para o elemento boro a 17% para o cobre.

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