DEPENDENCE OF INTENSITY OF LINES ON CONCENTRATION OF TIN DURING EXCITATION IN AN A.C.ARC

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Studies were carried out to show the real effect of tin on the precision of analysis especially for Cu, Pb and Sb together with Mo which is used as I.S. The effect of tin on the absolute intensity was remarkable if its concentration was less than about 40%. The maximum intensity change was attained at 10% tin. The detection limits were measured for the 3 elements viz Cu, Pb and Sb.

INTRODUCTION

The effect of gas composition on the intensity of spectral lines in the thermal excitation has been studied by many workers[1-4]. It has been pointed out [4,5] that the presence of an easily ionizable element as macrocomponent increases the intensity of micro nutrients, where as with less easily ionizable metal as macrocomponents the gain is lower. Kabeil *et al.*[5] have estimated the random errors introduced by tin in metallic alloys in the quantitative analysis and have emphasised that the amount of tin present in the alloy sample plays an important role vis-a-vis the reproducibility of the estimation especially when lead is also present in high concentration.

Considerable attention at this laboratory has been directed towards developing a spectrographic procedure for estimating over wide range, the concentration of metals in tin base alloys purified by zone melting[6,7].

The present communication aims to present a detailed evaluation of the effect of tin concentration on the precision of spectrographic analysis of tin base alloys.

EXPERIMENTAL

Six synthetic specimens were prepared, each containing 0.001 g of the analysed elements and 0.002 g on Mo as internal standard. 0.01, 0.1, 0.2, 0.4, 0.7 and 0.9 g of tin were added as tin oxide. A specpure carbon was then added in such quantity that the total weight of each specimen was one gram.

Finally, the specimens were sintered to smooth the excitation during exposure. The temperature and time of sintering adopted in these specimens were indicated in the previous work[7].

Samples were then tapped into the lower electrode cavity (5 mm depth) which was cut from 6 mm diameter spectrographic rods.

Excitation with a high voltage a.c. arc at 6 A was carried out and the arc image was focussed at the collimating lens of a medium quartz prism (NC II-30) spectrograph with a relative aperture (1:30) at 2500 A. The slit width used was 16μ. Pre-exposure was done for 2 seconds, then exposure was continued for 80 seconds until sample was completely burnt. Itford (special lantern) photographic plates were used and developed in 500 cc of Eastman D-19 developer for 5 minutes under standard temperature-controlled conditions. The emulsion was calibrated for intensity measurements by means of a 9 step filter.

The transmissions were measured directly on the recording (Mϕ-4) microphotometer. Absolute intensities were calculated using the emulsion calibration curve and a standard calculating board. The line contours were recorded on photographic plates and the widths were measured by means of a small scale-magnifier.

RESULTS AND DISCUSSIONS

a) Effect of Tin Concentration. The effect of tin on the absolute intensity for the trace elements Cu, Pb and Sb together with Mo which was used as I.s was determined graphically by plotting the logarithm of the absolute intensity versus the logarithm of tin concentration as shown in Fig (1). The result of the figure is believed to give some evidence that the change in the absolute intensity is remarkable only when the amount of tin is less than about 40%. and a maximum intensity change is attained when the concentration of tin is about 10%. Systematic errors occurred in our measurements when the calibration and specimen concentration markedly differed.

Accordingly it is useful to have standard specimens correspond in their composition to the specimens under investigations especially if tin concentration is less than about 40%. This prerequisite causes particular difficulties due to
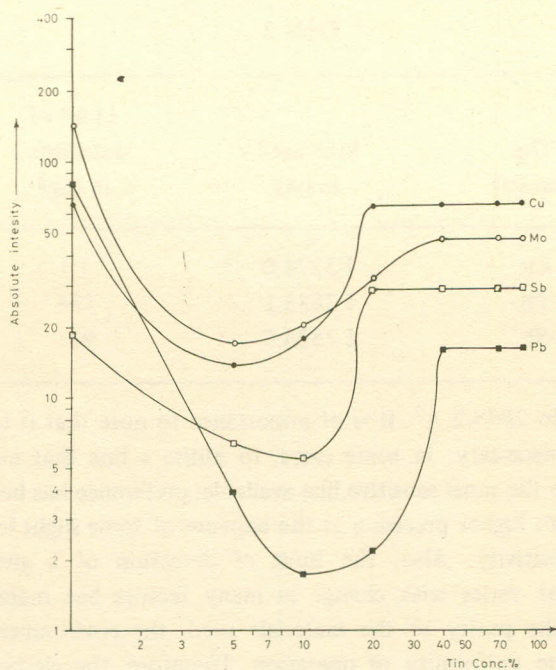
Fig. 1. Effect of Sn concentration on the precision of analysed elements.

the fact that the composition of the alloys to be investigated is not too accurately known.

In order to eliminate these errors we have used a spectroscopic buffer. For this purpose LiCl and KCl were checked by the method mentioned [6]. NaCl appeared to be the most suitable. Further studies emphasised that 10% NaCl was enough to ensure constant uniform vaporisation of the constituent elements.

Under the forecited conditions, repeated exposures of the same sample at 10% tin showed standard deviation from the mean for both intensity ratio and width respectively of 7 and 1.5% with the investigated elements. This result is in agreement with the finding of Kabeil *et al.* [7].

Additional tests have also been carried out in which tin alloys containing known amounts of the investigated elements were prepared. The measurements gave very satisfactory results for these increments even in the range beyond which the influence of tin is apparent (Cf Table-1).

These priliminary investigations prompted us to carry out the actual analysis of tin base alloys by means of the calibration and analysis specimens buffered with 10% NaCl whatever the concentration of tin may be.

b) Limit of Detection. The limit of detection characterizes one of the merits of an analytical procedure. The

Table 1.

No.	Det. Cu Con. in 5 replicate	Det. Pb Conc. in 5 replicate	Det. Sb Conc. in 5 replicate
1	0.0950	0.0305	0.100
2	0.0975	0.0320	0.095
3	0.0925	0.0285	0.105
4	0.0925	0.0325	0.095
5	0.0900	0.0295	0.100
MEAN	0.0935%	0.0306%	0.099%
Added amount	0.0927%	0.0305%	0.098%

limit of detection of a given element is the minimum concentration of the element that can be detected with a reasonable certainty. In spectrography, it is derived from the smallest intensity that is accepted with confidence as genuine and is not suspected to be only an artifact introduced by high value of the blank (noise) intensity. The blank is determined fundamentally by the statistical fluctuation of the back-ground in photographed spectrum. The relationship [8] that holds for the minimum line intensity (I_{Lu}) pertaining to the limit of detection can be written as:

$$I_{Lu} = I_u + K\ \sigma_u \qquad (1)$$

where I_u is the arithmetic mean of intensity of the background close to the measured in several spectra. σ_u is the standard deviation of the background intensity and K is a numerical factor chosen according to the specified confidence level, a value of K = 3 is strongly recommended [8].

Once (I_{Lu}) has been calculated, the limit of detection (C_L) can be calculated by using the lomaking-Scheibe equation(q)

$$\log C_L = \eta \log \frac{I_{Lu}}{I_R} + \log Co$$

or

$$\log C_L = \eta \log Y_{Lu} + \log Co \qquad (2)$$

Where I_R is the arithmetic mean of intensity of the internal standard line measured for all spectra of the reference

sample, Co is the concentration index, η is the slope, and I_{Π} is the ratio of the minimum-line intensity and I_R.

The value of η and log Co for a given element can be determined directly from its analytical curve plotted by the use of adequate reference samples or can be calculated statistically from both the intensity ratios and the concentrations of the adequate reference samples.

Using the given in Table 2, the limit of detection for Cu, as an example, was calculated as follows:

The statistical calculation of η, log Co and σ_u gave 2.756, 3.813, and 0.029 respectively.

Applying equation (1), we have;

$$I_{Lu} = 1.43 + 3 \times 0.029$$
$$= 1.517$$
$$\therefore \log Y_{Lu} = \log I_{Lu} - \log I_R$$

where I_R is the arithmetic mean of intensity of Mo 2848.2 A°.

$$\therefore \log Y_{Lu} = 0.180 - 1.557$$
$$= -1.377$$

Applying equation (2), we have;

$$\log C_L = 2.756(-1.377) + 3.813$$
$$= 0.018$$
$$C = 1.1 = \mu g$$

Table 2.

Concentraion of Cu (μg)	Intensity (Y_{Lu}) for $\dfrac{\text{Cu 3274.0 A}}{\text{Mo 2848.2 A}}$	Intensity of B.G. close to the Cu line (Iu)	Arithmetic mean of B.G. intensity (Iu)
5×10^4	2.10	1.47	
5×10^3	0.90	1.39	
5×10^2	0.40	1.43	1.43
5×10	0.17	1.44	

Table 3 summarizes the limit of detection for the three elements Cu, Pb and Sb together with the wavelength of the line used for each element. The internal standard line used

Table 3.

The element	Line used in (A)	Limit of detection in (μg)
Cu	I 3274.0	1.1
Pb	I 2833.1	184
Sb	I 2528.5	91

was Mo 2848.2 A°. It is of importance to note that it has been necessary, in some cases, to utilise a line that may not be the most sensitive line available; preference has been given to higher precision at the expense of some slight loss in sensitivity. Also, the limit of detection of a given element varies with change in many factors but mainly with the purity of the materials used, the environment; and the uniformity of operation. Therefore, the element is considered to have a constant value of detection limit only when strictly specified analytical procedures are used.

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