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APPENDIX

APPENDIX A

Determination of Percentage Extraction

For a metal that distributes between immiscible phases, the Nernst distribution law which provides the distribution coefficient or distribution ratio is defined as;

$$D = \frac{\text{total metals in organic phase}}{\text{total metals in aqueous phase}} \quad [1]$$

In this present work, atomic absorption spectrometric method was used to quantitatively determine the concentration of the metal in aqueous phase.

Calculations

Distribution ratio, is given by ;

$$D = \frac{[M]_t - [M]_a}{[M]_a} \quad [2]$$

where

$[M]_t$ is the total initial concentration of metal in the aqueous phase before extraction.

$[M]_a$ is the concentration of metal in aqueous phase at equilibrium after extraction.

The percentage extraction (%E)

The extraction efficiency is considered as the percent extracted (%E) as given by,

$$\% E = \frac{[S]_o V_o}{[S]_o V_o + [S]_a V_a} \times 100\% \quad [3]$$

where

$[S]_o$ is the concentration of metal in organic phase

$[S]_a$ is the concentration of metal in aqueous phase

V_o and V_a are the volumes of the organic and aqueous phases, respectively

It can be shown from equations [1] and [3] that the percent extracted is related to the distribution ratio, D , by

$$\% E = \frac{100D}{D + (V_a/V_o)}$$

if $V_a = V_o$, thus

$$\% E = \frac{100D}{D + 1}$$

APPENDIX B

Spectrophotometric Studies of Complex
Ions in Solution

Spectrophotometry is a valuable tool for elucidating the composition of complex ion in solution and for determining their formation constants

The method of continuous variations or Job's method is one of the three most common techniques employed for complex-ion studies ; they are

- 1 the method of continuous variations (Job's method)
- 2 the mole-ratio method
- 3 the slop-ratio method

In the method of continuous variations, cation (M) and ligand solutions with identical analytical concentrations are mixed in such a way that the total volume and the total mole of reactants in each mixture is constant but the mole ratio of reactants varies systematically (for example, 1:9 , 5:5 , 3:7). The absorbance of each solution is then measured at a suitable wavelength. The corrected absorbance is then plotted against the volume fraction of one reactant ; that is ,

$$V_M / (V_M + V_L)$$

where

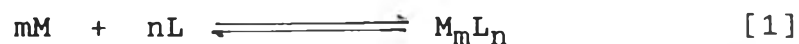
V_M is the volume of the cation solution

V_L is the volume of the ligand

A typical plot is shown in Figure B.1. A maximum (or minimum if the complex absorbs less than the reactants) occurs at a volume ratio V_M/V_L corresponding to the combining ratio of cation and ligand in the complex. In figure B.1 $V_M/(V_M + V_L)$ is 0.33 and $V_L/(V_M + V_L)$ is 0.66 ; thus V_M/V_L is 0.33/0.66, which suggests that the complex has ML_2 formula.

If the result of the complex formation reaction is incomplete(weakly complex formation), a formation constant for the complex can be evaluated from measurements of the deviations from the theoretical straight lines (dotted line in Figure B.1)

If only a single complex M_mL_n , is formed by the reaction of m moles of cation M with n moles of ligand L, thus, the complexation reaction may be written as the equation [1].



mass balance expressions for this system can be written as:

$$C_M = [M] + m[M_mL_n] \quad [2]$$

$$C_L = [L] + n[M_mL_n] \quad [3]$$

where

C_M and C_L are the molar analytical concentration of metal and ligand, respectively, prior to reaction and reaction can be determined from the Job's plot.

$[M_mL_n]$ can be evaluated from theoretical straight line at complete complex formation, so

$$\begin{aligned} A_y &= b[M_mL_n]_y \\ \text{or} &= b C_M/m \quad \text{or} \quad b C_L/n \end{aligned} \quad [4]$$

At the apex of the experimental curve, one can write

$$A = b[M_mL_n] \quad [5]$$

And from equations [4] and [5]

$$\frac{A}{A_y} = \frac{b[M_mL_n]}{b[M_mL_n]_y}$$

$$= \frac{b[M_m L_n]}{b C_M/m}$$

if $m=1$,

$$= \frac{b[M_m L_n]}{b C_M}$$

so

$$[M_m L_n] = \frac{A \times C_M}{A_y} \quad [6]$$

$$\text{from [1]} \quad K = \frac{[M_m L_n]}{[M]^m [L]^n} \quad [7]$$

substituting equations [2] and [3] in [7]

$$K = \frac{[M_m L_n]^m}{[C_M - m[M_m L_n]]^m [C_L - n[M_m L_n]]^n} \quad [8]$$

by substituting equation [6] in equation [8]

the formation constant can be determined from the data in the curve of Job's method.

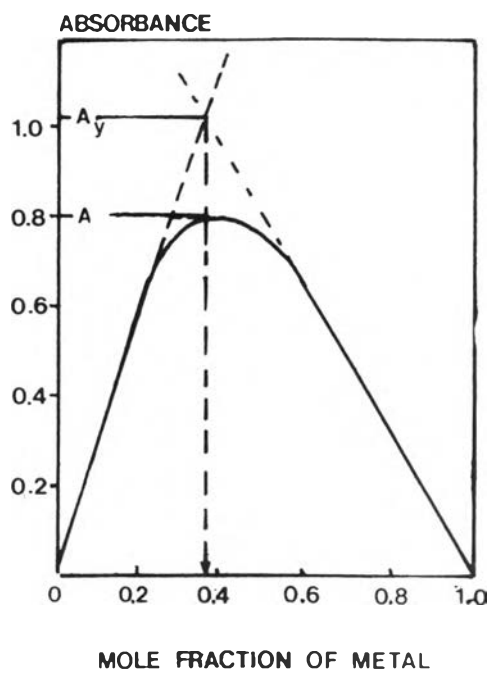


Fig B.1 Plot of Job's method for the 1:2 complex ML_2

APPENDIX C

Accuracy and Precision

Accuracy

The term "accuracy" denoted the closeness of a measurement or set of measurements to the accepted value and is expressed in term of "error" , normally refers to the difference between the mean value of set of results and the value which is accepted as the true or corrected value for the quantity measured. It is also used as the difference between an individual value and the mean value of the set of results. There are various ways and units in which the accuracy of a measurement can be expressed, an accepted true value for comparison being assumed.

Absolute Error (E) of the mean value is given as

$$E = \bar{X} - \hat{X}$$

and

Absolute Error of the individual value is expressed as $X_i - \hat{X}$,

where

\hat{X} is the true, or accepted value of the quantity

\bar{X} is the mean of the set of results

X_i is the individual value of each measurement

The Relative Error (E_r)

Often, the relative error is a more useful quantity than the absolute error. The percent relative error is given as this expression

$$E_r = \frac{X_i - \hat{X}}{\hat{X}} \times 100$$

or

$$E_r = \frac{\bar{X} - \hat{X}}{\hat{X}} \times 100$$

Relative error is also expressed in parts per thousand, ppt.

\bar{X} is defined as the sum of X_i of values of individual result divided by the number, n , of results in the set, as follow:

$$\bar{X} = (X_1 + X_2 + X_3 + \dots + X_i + \dots + X_n) / n$$

Thus,

$$\text{RSD} = \frac{S}{\bar{X}} \times 100 \%$$

or

$$\text{RSD} = \frac{S}{\bar{X}} \times 1000 \text{ ppt}$$

APPENDIX D

Sensitivity on UV Spectrometric Method

The functional relationship between the quantity measured absorbance, A and the quantity sought (the analyte concentration, C) is known as Beer's Law and can be written as ;

$$A = abc$$

where

a is a proportionality constant called specific absorptivity

b is absorption path length, expressed in centimetres

C is the concentration, in grams per litre

when

C is expressed in moles per litre and

b is in centimetres

the proportionality constant is called "the molar absorptivity", and

$$A = \epsilon bC$$

where

ϵ has the unit of $L \text{ cm}^{-1} \text{ mol}^{-1}$.

Sensitivity on UV spectrometric method can be expressed in term of molar absorptivity, ϵ ;

$$\epsilon \text{ (L cm}^{-1} \text{ mol}^{-1} \text{)} = \frac{A}{bC}$$

or specific absorptivity, a ;

$$a \text{ (mL g}^{-1} \text{ cm}^{-1} \text{)} = \frac{\epsilon}{\text{atomic weight} \times 1000}$$

or Sandell sensitivity, S ;

$$S \text{ (} \mu\text{g cm}^{-2} \text{)} = 10^{-3} / a$$

APPENDIX E

Calculations of % Copper in Solder Ingot

$$\% \text{ Cu} = \frac{g_{\text{Cu}}}{g_{\text{S}}} \times 100\%$$

where

g_{Cu} represents the grams of the analyte species, Cu

g_{S} represents the grams of sample taken for analysis

g_{Cu} could be determined from calibration curve of standards (see section 2.3.5 and Figure E.1).

The obtained data from this experiment was indicated as detailed in Tables E.1 and E.2 .

Table E.1 Percentage of Copper in solder ingot

Number of measurements	weight (g)	Absorbance	% copper
1	0.4595	0.176	0.201(0.202) ^a
2	0.4574	0.194	0.194(0.195)
mean	-	-	0.198(0.199)
% RSD	-	-	2.525(2.525)

^a Percentage of copper was determined by atomic absorption spectrophotometric method

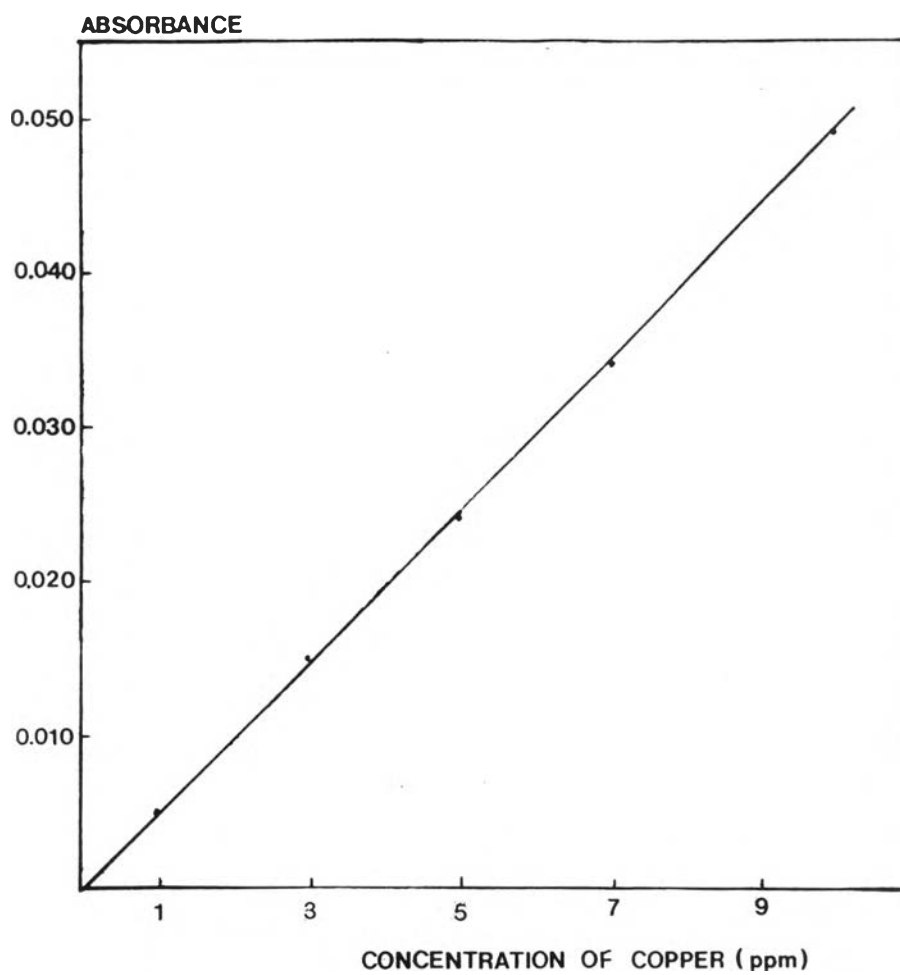


Fig E.1 Plot of Calibration on Cu-Salen complex at 562 nm, pH 4.5.

Table E.2 Calibration Data of Cu-Salen Complex at 562 nm

Copper concentration (ppm)	Absorbance
1.00	0.005
3.00	0.015
5.00	0.024
7.00	0.034
10.00	0.049



VITA

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