

## Chemometrics Of Liquid –Liquid Extraction Of Metal Complexes. A Review I

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**Abstract:** Solvent extraction is an excellent technique for preconcentration and separation of metal complexes. The method is simple, rapid, and highly selective, can be manipulated, prevents co-precipitation, provides solutions to theoretical problems and is wide in scope. Parameters such as distribution ratio, percentage recovery, Sandel sensitivity, molar absorptivity, limit of detection, limit of quantification, separation factor, partition coefficient,  $p^H$ , concentration of chelating, organic, salting out and masking agents, temperature, equilibration time, colour stability and thermodynamic constants are optimized in solvent extraction of metal chelates. Accuracy, precision, reliability and relationship among and between extraction variables, equilibria of complexation and mechanism of complex formation of metal cations with chelating agents are always optimized and mathematically and statistically analyzed. Chemometrics has been found as a valuable tool for result comparison, building of models and as well a predictive tool in analytical research.

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### 1. Introduction

Liquid- liquid extraction also known as solvent extraction is the extraction of an analyte or analytes from one liquid phase into another. According to (Seader and Henley, 1998), solvent extraction is widely applied for bulk separations where appreciable quantity of analytes is considered. Consequently, liquid- liquid extraction involves the partitioning of the analyte between two immiscible liquid phases, achieved by shaking them in a simple separatory funnel.

As stated by (Nwabue and Okafor, 1992), the application of solvent extraction to inorganic problems started in the second half of 19<sup>th</sup> century when peligot discovered that ether could extract uranium(IV) from nitric acid, and cobalt could be separated from nickel, gold from platinum and iron from its many thiocyanates in ether. Nwabue(1982) noted that solvent extraction and partitioning deals with separating compounds based on their relative solubilities in two different immiscible liquids usually an organic solvent and water.

Mendham, Denney, Barnes and Thomas (2000) observed that there are two phases in solvent extraction, the aqueous phase (pure water, acidic, basic or buffered solution) and an organic solvent. Thus, the selectivity and efficiency of separation is controlled by the choice of the two phases. Solvent extraction of metal complexes is based on the interaction of cations with suitable organic chelating agents to give a neutral and less hydrophilic species.

The importance of liquid- liquid extraction of metal complexes and its application as an excellent separation technique is based on the fact that the method is simple, does not waste time (speedy), wide

in scope, does not involve co-precipitation, highly selective through judicious use of reagent and  $p^H$ , chelate is sometimes coloured therefore enhancing the isolation and determination of the metal. In addition, liquid- liquid extraction of metal chelates is crucial because it provides solutions to important theoretical problems related to composition and stability of metal complexes.

**Organic Phase:** The choice of solvent for solvent extraction must be based on the immiscibility of the solvent with water. So that two distinct layers are formed. Mendham et al (2000) noted that the solubility should not exceed 10% since no two solvents are completely insoluble in each other. Also the polarity of the solvent is crucial since the more polar the solute, the more polar the extracting solvent needs to be. Thus, like attracts like applies. **Aqueous Phase:** If the aqueous phase does not initially contain the analyte (when acting as the extracting solvent), there is need for purity to be maintained to prevent contamination of the sample.

In a situation where modifiers such as buffers, acids, bases, complexing agents and salting out agents are added, high purity need to be maintained. Rydberg, Musikas and Chopin (1992) noted that in a situation where the analyte is initially present in the aqueous phase, modification is needed to ensure efficient extraction of analyte into the organic phase. This accordingly is achieved by making the analyte more hydrophobic and less hydrophilic since the more non-polar the material the greater the tendency to transfer into the more non-polar (organic) layer and the more ionic the material the greater the tendency to transfer into the more polar layer.

Mushini, Veluri, Volety and Samba (2010) in their study of neutral network modeling used as a chemometric tool for kinetic investigation noted that chemometrics encompasses chemistry, advanced mathematics, statistics and information theory. Mendham et al (2000), Adam's (1995) and Massart, Vandeginste, Deming, Michotte and Kaufman (1998) viewed chemometrics as the application of mathematical and statistical methods to design, optimization and measurement of chemical information provided by the analysis of important data. Therefore, chemometrics applies classical statistical procedures in the design, optimization of measurement and analysis of result and information generated from data.

Chemometrics is an interdisciplinary area which emerged in late 1970's and includes subfields such as kinetometrics, environmetrics, pharmacometrics, synthometrics, qualimetrics and speciometrics (Kowalski, 2001 and Massart, Vandeginste, Buydens, Jong, Lewi and Smeyers-Verbeke, 1997).

### Objectives Of The Study

The general objectives of this study is to x-ray the parameters in solvent extraction of metal chelates and as well discuss exhaustively the common statistical approaches to data analysis, and optimization of measurement and information from data.

The specific objectives are

1. To discuss the various parameters involved in solvent extraction of metal chelates.
2. To discuss equilibria and thermodynamics of metal chelates extraction.
3. To list and explain the various inorganic extraction systems and factors that influence extraction of metal chelates.
4. To provide basic statistical analysis of data generated during measurement and optimize information from the data.

1. Dissociation constant of complex

$$K_c = \frac{[M^{n+}]_w [L^-]_w}{[ML_n]_w} \quad 3$$

2. Dissociation constant of ligand,

$$K_r = \frac{[H^+]_w [L^-]_w}{[HL]_w} \quad 4$$

3. Partition coefficient of complex,

$$P_c = \frac{[ML_n]_w}{[ML_n]_o} \quad 5$$

4. Partition coefficient of reagent,

$$P_r = \frac{[HL]_w}{[HL]_o} \quad 6$$

Note: c=complex, r=reagent,  $\omega$  = aqueous phase and o = organic phase

### 1.3 Measures Of Effectiveness In Liquid- Liquid Extraction

In solvent extraction, the aqueous solution comprises aqueous feed (solution before extraction) and extraction raffinate (solution after extraction) phases, whereas the organic solvent consists of solvent feed and loaded solvent phases.

### 1.2 Factors That Favour Solvent Extraction Of Inorganic Species

In the extraction of inorganic species, the analyte exists as an inorganic ion. To ensure efficient extraction of the analyte into the organic phase, certain measures are taken to modify the species. These measures according to Mendham et al (2000) are (1) Formation of chelated complexes using suitable chelating organic ligands (2) formation of ion associated complexes.

The rationale behind this is to change the small hydrated metal or anion into a species more hydrophobic and as such more soluble in the organic phase. Thus, the complex formed between the metal ions and the organic ligand being hydrophobic dissolves in organic solvents.

Rydberg et al (1992) noted that quantitatively if

$$Mn + nL \rightarrow ML_n \quad 1$$

Where L= ligand, M = Metal cation and n = number of moles of the ligand. Then, the assumption is that

(a) The metal complex and the organic reagent exist in their various phases as simple unassociated molecules.

(b) The extraction process is not governed by solvation

(c) The concentration of the solute is generally low and also exists as uncharged molecules. Thus, the behaviour of the solution in the presence of the solute departs to a little degree from ideality.

The dissociation of the chelating organic reagent (ligand) HL in the aqueous layer is



The complexation of the metal cation and the ligand, and the dissociation of the ligand in the aqueous phase are equilibrium reactions and can be expressed in terms of thermodynamic constant. These are illustrated below.

The metal ions are present in the aqueous phase as aquo-metal complexes. The organic diluent makes up organic phase. The ionic metal complexes distribute itself between the two liquid phases as neutral metal species. However, sometimes, the neutral metal chelate is highly soluble in the organic phase and insoluble in the aqueous phase.

**(a) Distribution ratio (D)**

Distribution ratio is the ratio of the concentration of a solute in the aqueous phase to that in the aqueous phase. In other words, it is the ratio of the amount of metal extracted as complex into the organic phases to that remaining in all forms in the aqueous phase. Distribution ratio for a particular set of experimental conditions is constant.

$$D = \frac{[M]_o}{[M]_w} \quad 7$$

$$\text{or } D = \frac{[MLn]_o}{[MLn]_w + [Mn^{+}]_w} \quad 8$$

Where o = organic phase, w = aqueous phase,

[M] = concentration of metal, [MLn] = concentration of complex and [M<sup>n+</sup>] = concentration of metal cation.

**(b) Percentage recovery (ε)**

The percentage recovery in solvent extraction depends on the amount of the metal species transferred to the organic phase. Studies (Nwabue, 1981) have shown that high value of D indicates high value of the percentage recovery consequently, % recovery where the volume of the organic phase (o) and aqueous phase (w) is not the same.

$$\epsilon = \frac{100D\%}{D + \frac{V_o}{V_w}} \quad 9$$

where the volume of the aqueous and organic phases is the same, then

$$\epsilon = \frac{100D}{D+1} \quad 10$$

If log of equation 10 is taken and rearranged then

$$\log D = \log \epsilon - \log(100 - \epsilon) \quad 11$$

As a measure of accuracy and sensitivity

$$\epsilon = \frac{\text{Amount extracted}}{\text{Total amount}} \times \frac{100}{1} \quad 12$$

**(c) Separation factor (Sf)**

This describes the measure of the ability of the system to separate two solutes. It is the ratio of one distribution ratio to another. Therefore for two metal species, the effectiveness or degree of separation is established as

$$Sf = \frac{D_A}{D_B} \quad 13$$

Where D<sub>A</sub> = Distribution ratio of A and

D<sub>B</sub> = Distribution ratio of B

**(d) Partition Coefficient:** Partition coefficient is the ratio of the activities of the organic phase to that of the aqueous phase.

This is in accordance with the Nernst distribution law which states that if a substance is soluble in both liquid phases (i.e. molecular state of the solute is the same in both phases) and at a particular temperature, the ratio of the activities of the material in each phase is a constant. Thus,

partition coefficient,

$$K = \frac{a_{s1}}{a_{s2}} \quad 14$$

Where a<sub>s</sub> = Activities of the material.

However, partition coefficient considers a material in only one form notwithstanding there may be more than one species of the metal in both phases. Consequently the classical phase rule of Gibb's can be applied.

$$P + F = C + 2 \quad 15$$

This is to give room for as many numbers of phases as possible. P is number of phases and F is the degrees of freedom.

**(e) Sandel Sensitivity:** This is the weight of a substance that can be determined in a column of solution having unit cross section.

$$\text{Sandel sensitivity} = \frac{\text{molecular weight} \times \text{no of atoms of element}}{\text{Molar absorptivity of species}} \quad 16$$

but sensitivity describes the detector response per unit concentration of analyte. It shows the number of micrograms of elements converted to the coloured product in a column of solution having unit cross section. Sensitivity is proportional to molar absorptivity (intrinsic) and reproducibility: Hence,

$$\text{sandel sensitivity} = \frac{\text{molecular weight}}{\text{Molar absorptivity}} \quad 17$$

expressed as μg/mL/Cm<sup>2</sup>

**(f) Molar absorptivity:** This describes the ratio of absorbance to that of concentration of the metal ion. It is a measure of the sensitivity of a given analytical method and an analytical tool for comparing two or more methods.

$$\text{(g) molar absorptivity} = \frac{\text{absorbance}}{\text{concentration}} \quad [1 \text{ mol}^{-1} \text{ cm}^{-1}] \quad 18$$

**(h) Limit of Detection (L.O.D)**

This shows the concentration or amount of analyte which produces a signal equal to twice the baseline noise. It is inversely proportional to sensitivity. L.O.D describes the lowest detectable signal for a given analytical process.

$$\text{L.O.D} = \text{blank measurement} + 3 \times \text{standard deviation} \quad 19$$

$$\text{or LOD} = 3.3 \times \frac{\sigma}{S} \quad 20$$

where

$\sigma$  = Standard deviation of intercept of regression equation and S, the slope of the corresponding calibration curve. The limit of detection and limit of quantification has been applied by (Lutf Ullah, Nafisur, Syed, Hanan and Masha'El Mansoor, 2009) in the comparison of two analytical methods.

**(H) Limit of quantification (L.O.Q)**

This describes the minimum level at which the solution of the analyte can be readily quantified with accuracy.

$$\text{L.O.D} = \text{blank measurement} + 3 \times \text{standard deviation} \quad 21$$

$$\text{or L.O.Q} = 10 \times \frac{\sigma}{S} \quad (\delta \text{ and } S \text{ retain their meaning}) \quad 22$$

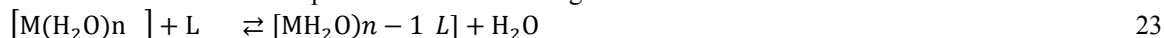
Both LOD and LOQ are in  $\mu\text{g/ml}$

**(1) Stability constant of complexes**

Stability constant also known as binding or formation constant is an equilibrium constant for complex formation in solution. Information needed for the calculation of concentration of the complexes in solution is provided.

Mendham et al (2000) maintained that the stability constant measures the propensity of the interaction between the constituent of aqueous feed (reagents that come together to form the complex, metal ion solution and chelating agent).

For a reaction between an aquo-metal cation and a ligand.



$$B' \text{ (stability constant)} = \frac{[\text{M}(\text{H}_2\text{O})_{n-1}\text{L}][\text{H}_2\text{O}]}{[\text{M}(\text{H}_2\text{O})_n][\text{L}]} \quad 24$$

The concentration of water in dilute solutions is constant i.e.  $[\text{H}_2\text{O}] = \text{constant}$  hence,

$$B = B' \frac{[\text{ML}]}{[\text{M}][\text{L}]} = \frac{[\text{M}^m \text{L}^g]}{[\text{M}]^m [\text{L}]^g} \quad 25$$

where m and g are stoichiometric coefficients of metal and ligand respectively.

The commonest method for determining stability constant of complexes is the job's method. In this method, absorbances are plotted against the reagent molar fractions (Juan, Eva, Ana and Lims, 2003). If CM is concentration of metal and CL concentration of ligand prepared according to literature (Nworie et al, 2013) and x reagent molar fractions,  $x = \frac{\text{CL}}{\text{C}}$  where C = CM + CL 26

is a constant. X max represents the curve with maximum signal for a particular value of molar fraction. Hence,

$$x_{\text{max}} = \text{Stoichiometric molar fraction} = \frac{g}{g+m} \quad 27$$

The ratio g : m represents the stoichiometry of the complex.

For proper calculation of stability constant, the degree of dissociation of the complex  $\alpha$ , has to be evaluated, Thus,

$$\alpha = \frac{S_0 - S_{\text{max}}}{S_0} = 1 - \frac{S_{\text{max}}}{S_0} \quad 28$$

Where  $S_{\text{max}}$  = Analytical signal of the maximum of the experimental curve.

$S_0$  = Theoretical value of the analytical signal under condition of maximum complexation.

Alternatively, the stability constant can be estimated

where  $\alpha$  is known according to

$$\alpha = \frac{S_{\text{ip}} - S_{\text{max}}}{S_{\text{ip}}} = 1 - \frac{S_{\text{max}}}{S_{\text{ip}}} \quad 29$$

Where  $S_{\text{max}}$  = analytical signal of the maximum at experimental curve that represents the maximum quantity of the complex that is formed with a degree of dissociation.

$S_{\text{ip}}$  = analytical signal corresponding to the intersection point of the straight lines (where maximum quantity of complex is formed i.e.  $\alpha = 0$ )

Stability constant of complexes were determined by ( Samir, Saber and Abdulrahman, 2010; Zumdal, 1997 and El-Bindary, El-Sonbati and Abd El-Kader, 2003) using the same and related methods.

**(J) Robustness:** This is the ability for an analytical procedure to remain unaffected by minute or small and deliberate method parameter variation. It indicates whether a method is reliable for a routine laboratory analysis. Robustness can be evaluated by analyzing same sample and varying accompanying parameters or variables. This is done by changing one experimental parameter while others are kept constant.

### 1.4 Equilibria In Solvent Extraction

The formation of a metal chelate in liquid-liquid extraction is as given by (Nwabue, 1982)



$M^{n+}$  the metal ion,  $HA_{org}$  the organic chelating reagent,  $MA_{norg}$ , the metal chelate,  $n$ = no of moles of HA.

The equilibrium or extraction constant,  $K_{ex}$  is given as

$$K_{ex} = \frac{[MA]_{org}[H^+]^n}{[M^{n+}][HA]_{org}^n} \quad 31$$

$$K_{ex} = \frac{D[H^+]^n}{[HA]_{org}^n} \quad 32$$

$$D = \frac{[MA]_{org}}{[M^{n+}]} \quad 33$$

The ionic strength and the temperature of the aqueous phase affect the  $k_{ex}$ . Thus, if the concentration of the reagent is kept constant then,

$$K_{ex} = \frac{D[H^+]^n}{C} \quad 34$$

$$D = \frac{K_{ex}C}{[H^+]^n} \quad 35$$

Taking the logarithm of equation 32

$$\ln K_{ex} = \ln D + n \ln[H^+] - n \ln[HA]_{org} \quad 36$$

$$\log D = \log k_{ex} + n \log[HA] + np^H \quad 37$$

$$\therefore \ln D = \ln K_{ex} + 2.303 npH + n \ln[HA]_{org} \quad 38$$

$n$ =slope

The value of  $K_{ex}$  for a particular complex can be evaluated from this relation.

### 1.5 Thermodynamics Of Complexation

Complexation involves the reaction between an aquo-metal cation and a ligand in which there is replacement of one or more of the co-ordinated solvent molecules by the nucleophilic groups.

$$\Delta G = \Delta G_n^0 - RT \ln [ML_n]/[M][L]^n \quad 39$$

$$\text{but } \Delta G_n^0 = -RT \ln \beta_n \quad 40$$

$$\text{also } \Delta G_n^0 = -2.303RT \ln \beta_n \quad 41$$

$$\frac{d \ln \beta}{dT} = -\frac{\Delta H_n^0}{RT} \quad 42$$

$$\Delta G_n^0 = \Delta H_n^0 - T\Delta S_n^0 \quad 43$$

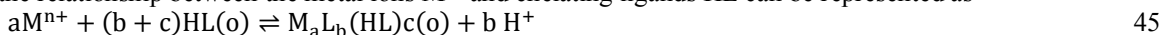
$$\Delta G_n^0 = -2.303RT PK_a \quad 44$$

From the above relations, the stability constant,  $\beta_n$ , the free energy change  $\Delta G$ , the enthalpy  $\Delta H$  and entropy  $\Delta S$  of a complex can be evaluated.

Houria, Tayeb, Hasnia and Mohamed(2013) has used the relation  $\Delta G_n^0 = -2.303RT PK_a$  to calculate the free energy change of bis(salicylidene)ethylenediamine.

### 1.6 Mechanism Of Extraction Of Metal Species

Studies (Kalagbor, Uzoukwu and Chukwu, 2011) and other works (Uzoukwu and Okafor, 1998) has shown that the relationship between the metal ions  $M^{n+}$  and chelating ligands HL can be represented as



$$K_{ex1} = \frac{[M_aL_b(HL)_c(o)][H^+]^n}{[M^{n+}][HL(o)]^{b+c}[M^{n+}]^n} \quad 46$$

The distribution ratio

$$\log D_1 = \log K_{ex1} + (a - 1) \log[M^{n+}] + (b + c) \log[HL](o) - (b) \log[H^+] \quad 47$$

However, in the presence of a solvating agent acting as a synergist(syng) such as butanol, then distribution ratio becomes

$$\log D_2 = \log K_{ex2} + (a - 1) \log[M^{n+}] + (b + c) \log[HL](o) + d \log[syg](o) - (b) \log[H^+] \quad 48$$

The method of slope analysis can be used to evaluate the values of a, b, c and d for the interaction between one mole of the metal and the ligand. Thus,

$$\frac{d[\log D]}{d[\log[H^+]]} = b \quad 49$$

$$\frac{d[\log D]}{d[\log[HL](o)]} = b + c \quad 50$$

$$\frac{d[\log D]}{d[\log[synergist](o)]} = d \quad 51$$

$$\frac{d[\log D]}{d[\log[M^{n+}]]} = a - 1 \quad 52$$

Also, if an acid is used as solvating agent in the extraction of the metal ion, (Okafor and Uzoukwu, 1990) proposed a mechanism as shown below.

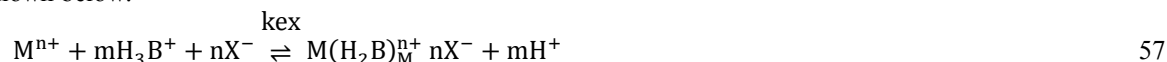


$$K_{ex_3} = \frac{[H^+]^e M_a L_b (HL)c(0).XA^-(0)[H^+]^n}{[M^{n+}]^a [H_2L]^b [HA]^c} \quad 54$$

$$\log D_3 = \log K_{ex_3} + (a - 1) \log[M^{n+}] + (b + c) \log[H_2L](0) + e \log[HA] + (b) \log[H^+] \quad 55$$

$$e = d \log \frac{[\log D_3]}{d[\log[HA]]} \quad 56$$

In acid extraction, ion pair complex is expected thus, when the chelating agent is a Schiff base, the extraction mechanism as described by (Nwabue and Okafor, 1992 and Nworie et al,2013) involves a protonation of the ligand as shown below.



$$k_{ex} = \frac{[M(H_2B)_M^{n+} \cdot nX^-][H^+]^m}{[M^{n+}][H_3B^+]^m[X^-]^n} \quad 58$$

$$\log D = M \log[H_2B] + n \log[X^-] + M \log K_1 + \log k_{ex} \quad 59$$

Where  $X = Cl^-, ClO_4^-, NO_3^-,$  or  $HSO_4^-$ ,

### 1.7 Classification Of Inorganic Extraction Systems

Inorganic extraction system may be ion pair or ion association metal complex and metal chelates or additive complexes. Ion association complex results when the metal exists in anionic complex form and the chelating agent can form cationic specie in acidic aqueous phase. Mendham et al (2000) noted that analytical species in ion associated complex may be associated with oppositely charged ions to form a neutral extractable species more soluble in organic phase.

A neutral metal chelate is formed when a complexone (organic chelating agent) having two or more uncharged donor atoms reacts with a cationic aquo metal complex. Metal chelates are hydrophobic or hydrocarbon like, large and dissolve preferably in organic phase.

Additive complexes are metal chelates or ion pair association complexes with co-ordinated solvent molecules which facilitates the solvent extraction of salts (chlorides, nitrates and sulphates) as they add to the size of the cation and resemblance of the complex to the solvent. Additive complexes can be formed with an organic solvent where the geometry of the ligand and the co-ordination number of the metal is at maximum and favourable and reagent concentration is very high. They are formed with hydroxyl groups at high  $p^H$  values and upon hydrolysis of the metal, are not neutral, and have low partition coefficient compared to neutral metal chelate (Nwabue, 1982).

### 1.8 Factors That Influence Solvent Extraction Of Metal Chelates

The extraction of metal chelates according to many authors (Sandel, 1959, Nwabue and Okafor, 1992, Kalagbor, Uzoukwu, and Chukwu, 2011 and

Houria, Tayeb, Hasnia and Mohammed, 2013) are influenced by factors such as acidity, concentration of organic reagent, masking agent, salting out agent, organic solvent, dissociation constant and partition coefficient, stability constant of metal chelates, solubility of metal chelates and kinetic factors.

Studies (Nwabue and Okafor,1992 and Nworie et al, 2013) has shown that the distribution ratio increases exponentially with  $p^H$  if the metal chelate has large partition coefficient and hydroxycomplex formation is neglected at  $p^H$  of investigation. Also increase in organic reagent concentration leads to increase in the value of D and excess of chelating agent leads to quantitative extraction.

Masking agents such as oxalate, cyanide, tartrate and thiocyanate can mask a particular metal making the distribution very low or diminished and helps in selective extraction of a particular metal in the presence of others. Studies (Nworie, 2011) shows that Fe(II) can be masked by KCN and EDTA but not Fe(III) in the presence of bis(2,2'-methylidene)phenol diaminoethane). This can be used as a method of separating the two species in solution.

Salting out agents enhances the distribution ratio of the metal, increases the dielectric constant of the aqueous phase, decreases the solubility of the metal chelate in aqueous phase and increases the solubility of the metal chelate in organic phases. Organic solvent solubility enhances partition coefficient and ensures solubility of metal chelates, inflammability, low toxicity, insolubility in aqueous phase and recoverability of solute.

The stability constant of a metal chelate according to Irving and Rossotti as stated in (Nwabue, 1982),shows that increase in the stability constant of

the metal chelates leads to increase in the extraction constant. Also the quantitative description of solvent extractions of metal complex lies on the fact that the organic and aqueous phases are in equilibrium. The rate of attainment of equilibrium depends on the rate of formation of extractable species and rate of transfer of the various species from one phase to the other. Nwabue and Okafor (1992) noted that there exists a correlation between the extraction constant (K<sub>ex</sub>) and rate of equilibration. The higher the value of K<sub>ex</sub>, the more rapid is the rate of extraction and the equilibrium time increases with the partition coefficient of the organic reagent.

### 2.1 Statistical Considerations

**Accuracy:** The accuracy of a determination is the correctness of a measurement or concordance between it and the true or most probable value. This can be evaluated by performing recovery studies.

**Precision:** This always accompanies accuracy and is defined as the concordance of a series of measurements of the same quantity. It shows the reproducibility of a measurement. A between-run precision shows reproducibility (when analysis are done separate days when laboratory conditions vary)

**Mean:** The arithmetic mean ( $\sigma$ ) for a given distribution  $x_1, x_2, x_3$ , is given by

$$\sigma = \frac{x_1 + x_2 + x_3}{n} \quad 61$$

It is otherwise regarded as the average which is the summation of the total number divided by the number of occurrence (n)

$$\text{Standard deviation (s)} = \sqrt{\frac{\sum(x-\sigma)^2}{(n-1)}} \quad 62$$

Variance is square of the standard deviation

$$\text{variance} = \frac{\sum(x-\sigma)^2}{(n-1)} \quad 63$$

n-1 is used rather than n if the number of values/ distribution is small

$$\text{Relative standard deviation } RSD = \frac{\text{standard deviation}}{\text{mean}} \quad 64$$

$$\text{Standard error of the mean (S}\sigma) = \frac{\text{mean standard deviation}}{\sqrt{\text{number of observation}}} \quad 65$$

Coefficient of variation: This is percentage of relative standard derivation.

$$C.V = \frac{\text{standard deviation} \times 100}{\text{mean}} \quad 66$$

It gives the percentage error of a determination.

### 2.3 Reliability Of Results

Results obtained from experiment can be considered on how reliable it is and how it compares with the true value or other sets of data (Miller and miller , 1993)

**Q- test:** Q –test is used to decide whether a value in a set of experiment would be accepted or rejected.

$$Q = \frac{\text{questionable value} - \text{nearest value}}{\text{largest value} - \text{smallest value}} \quad 67$$

If the value of Q calculated exceeds the critical value in the Q –table then, the questionable value may be rejected for the given sample size (Liteanu and Rica, 1990 and Funk, Dammann and Donnevert, 1995).

#### Confidence interval and confidence limit.

The confidence interval of a distribution describes the range within which the true mean may be located. This is so because standard deviation does not show how close the mean of a distribution is to the true value. Confidence limits  $\mu$  for a set of distribution, say  $\pi$  is

$$\mu = \sigma \pm \frac{ts}{\sqrt{n}} \quad 68$$

while a within-run precision shows repeatability (when analysis are done same day in rapid succession) (Shobhana, Bloomika, Kuldeep, Pinkesha and Ravindra, 2012).

**Absolute Error:** This describes the difference between the observed or measured value and the true value of the quantity measured. In any measurement, absolute error shows the accuracy of the determinations.

$$\text{Absolute error, } \Delta = \frac{ts}{\sqrt{n}} \quad 60$$

(t at 95% confidence limit for n-1 degree of freedom)

**Relative error:** The relative error is absolute error divided by the true value expressed in percentage or parts per thousand.

### 2.2. Measurement And Assessment Of Variability. Measurement Of Precision

The precision of any analytical measurement involves the calculation of the following measures of central tendencies and dispersion. Mean, coefficient of variation, variance, standard deviation, standard error of the mean, relative standard deviation.

where  $s$  = standard deviation,  $\sigma$  = mean,  $t$  is a parameter which depends on the number of degrees of freedom,  $V$  (table of the values of  $t$  and  $V$  are available).

## 2.4 Significance Test

### Comparison Of Results

The accuracy and precision of analytical procedure can be evaluated by comparing the values obtained in a test with the true value or with other sets of data. The student t-test and f-test or variance ratio test is used and in each case the number of degree of freedom is important.

**Number of degrees of freedom:** Deming and Morgan (1993) maintained that the number of degree of freedom in a statistic is the number of independent values relevant to the determination of the quantity or simply put number of independent measurements.

**Student's t-test:** - This comparative tool is used to test the difference between the mean of two sets of experimental data. The t-statistics is also applied in the comparison between the mean of a data and some standard value with some level of confidence in the significance as determined in the comparison. It is a one-tailed test.

$$t = \frac{(\sigma - \mu)\sqrt{n}}{s} \quad 69$$

where  $\mu$  is the true value

When comparing the mean and precision of two analytical methods say a new method and a reference or established method, the t-statistic is used.

$$t = \frac{\sigma_1 - \sigma_2}{sp \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \quad 70$$

Where  $Sp$  is the pooled standard deviation,

$$sp = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}} \quad 71$$

$S_1$  and  $S_2$  are standard deviations of the two samples.

### Comparism of variance

**F- test:** This compares the results of two different analytical procedures to ascertain the precision. The F-test compares the variance of two sets of data.

$$F = \frac{s^2_A}{s^2_B} \quad 72$$

Where, the larger value always serves as the numerator and the smaller value the denominator. The significance of the f-value is checked from the f-table.

### Paired t-test:

Apart from the use of student t-test to validate a new analytical method, the paired t-test can be used to compare results obtained from samples of varying proportions with different acceptable method. For instance, two or more methods may be used for the analysis of different compounds of copper where the content of copper in each sample expressed in percentage will be evaluated and method applied validated.

$$sd = \sqrt{\frac{\sum(x - \sigma)^2}{(n - 1)}} \quad 73$$

$x$  is the difference between each pair of results  $\sigma$  the mean difference  $Sd$  the standard deviation

$$t = \frac{\sigma\sqrt{n}}{sd} \quad 74$$

**Note:** If the tabulated value of  $t$  at 5% level of probability and at the given degrees of freedom is less than the calculated value, there is significance between the two methods and vice versa.

### Comparison Of Several Means

#### Analysis Of Variance (Anova)

ANOVA can be used to compare mean results obtained from more than two different analytical chelating agent using the same spectrophotometer or mean results obtained from different spectrophotometers all using the same sample or mean results of three analysts each using the same solutions for four replicate analysis.

**One way analysis** of variance involves analysis of variance for one way classification, that is One source of variation e.g. investigation into the effect of storage on the absorbance of solution of iron(II) bis (2,2<sup>1</sup>-methylidene phenol)diaminoethane. Complex.

**Two way analysis** of variance: More than one source of variation is involved. Thus, two variables or more as the case may be. Example, comparison of the % efficiency of different acid solutions in the extraction of metal chelates from aqueous solutions of bis(2,2<sup>1</sup>-methylidene phenol)diaminoethane.

A table showing an example of two-way analysis of variance.



**Table 1.** Analysis of variance for % efficiency

Source of variation	SS	Df	MS	F
Acid solutions (A)	SSA	a-1	$S_1^2 = SSA/(a-1)$	$F_1 = S_1^2/S_2^2$
Metal chelates (B)	SSB	b-1	$S_2^2 = SSB/(b-1)$	$F_2 = S_2^2/S^2$
Interaction (AB)	SS(AB)	(a-1)(b-1)	$SS_3^2 = SS(AB)/(a-1)(b-1)$	$F_3 = S_3^2/S^2$
Error	SSE	Ab(n-1)		
Total	SST	Abn-1		

Where Df= Degrees of freedom, SS= Sum of squares, Ms= mean square and F= computed F.

Giokas, paleologos, Tzouwara-Karayanni and Karayannis (2001) used ANOVA and regression as a chemometric tool in the determination of iron, cobalt and nickel in environmental samples.

### Correlation

Pearson's correlation coefficient is used to establish whether a linear relationship exists between two variables.

Pearson's correlation coefficient.

$$r = \frac{n\sum x_1 y_1 - \sum x_1 \sum y_1}{\sqrt{[n\sum x_1^2 - (\sum x_1)^2][n\sum y_1^2 - (\sum y_1)^2]}} \quad 75$$

n= number of data points and r lies between +1 and -1. Values close to +1 indicates positive relationship whereas values close to -1 indicate negative relationship. The significance of r calculated is determined from the table at say 5% significance.

### linear regression

The equation of straight line is

$$y = bX + a \quad 76$$

y is the dependent variable, x the independent variable, b the slope of the line and a the intercept. If  $\sigma_1$  is mean of x and  $\sigma_2$  mean of y, then  $a = \sigma_2 - \sigma_1$ .

The least square method is used for such calculation. E.g to calculate the equation for the effect of concentration of manganese complex of bis(2,2'-methylidenephenol) diaminoethane on the absorbance. The dependent variable is absorbance while the independent variable is the concentration.

$$b = \frac{n\sum x_1 y_1 - \sum x_1 \sum y_1}{n\sum x^2 - (\sum x_1)^2} \quad 77$$

### Conclusion

The application of solvent extraction in the preconcentration, separation and analysis of metal complexes is not a new sample preparation technique. However, the application of mathematical and statistical technique in the analysis, measurement and optimization of information generated from data is relatively a new area in chemistry. This study seeks to x-ray the parameters effective in complex formation, discusses the mechanisms of complex formation, and justifies the application of mathematics and statistics, in the determination of accuracy, precision, reliability and robustness of the practice, solvent extraction.

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