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# H Point Standard Addition Method for Simultaneovs Spectrophotometric Determination of Toxic Metals and Pesticides in Micellar Media

### Raghvendra Rao Sanapala

Research Scholar, CMJ University, Shillong, Meghalaya

Abstract – India, being a developing nation, has undergone rapid industrialization in the last few decades. With the enormous growth and expansion of technology, a serious problem of environmental pollution has cropped up, which has now become a major threat for vegetation and animal life. In various forms, cruel hands of pollution are throttling the living humanism. Water, is being contaminated more and more by the toxic metals and pesticides and is responsible for water pollution. Thus pollution is an unavoidable consequence of industrialization and the ultimate cause of the poorer global environmental quality. Although some of the metals are essential nutrients for plants and animal metabolism (glucose metabolism, amino acid metabolism), yet accumulated at high levels, these can cause serious disorders and diseases (nausea, skin ulceration, lung cancer etc.) and they ultimately become lethal. Thus metals like nickel, iron, manganese and mercury pose potential danger so, it is necessary to develop a rapid and accurate analytical method for their determination. Quantitative analysis often involves the spectrophotometric resolution of mixtures of two components with partly or completely overlapping spectra - the greater the extent of overlapping the more difficult the resolution is rendered. The multicomponent linear additive model is frequently used in resolving mixtures. Its application requires assuming the measured response to be made up of the sole contributions of the known components of the sample. This in turn requires knowledge not only of the analytes of interest, but also of all interferon's potentially present. A modification of the 'Standard Additions Method' called 'H-Point Standard Addition Method (HPSAM)' was developed in order to determine unbiased analytes concentration in the presence of direct interferent.

Keywords: H-Point, Method, Simultaneovs, Spectrophotometric, Determination, Toxic, Metals, Pesticides, Micellar Media

#### INTRODUCTION

The 20th century, with its promise of 'better living through chemistry' has also brought a host of chemical toxin-related illness. Acquiring more and more of physical comforts for the people has been the accepted goal for prosperity and development of the society. India, being a developing nation, has undergone rapid urbanization and industrialization in the last few decades. With the enormous growth and expansion of technology, a serious problem of environmental pollution has cropped up, which has now become a big threat for vegetation and animal life. Cruel hands of pollution are throttling the living humanism in various forms. Water, the elixir of life is being contaminated more and more by the toxic metals and pesticides and is responsible for water pollution. Environmental contamination due to exposure to heavy metals such as mercury, cadmium and lead is a serious growing problem throughout the world. Human exposure to heavy metals has risen dramatically in the last 50 years because of an exponential increase in the use of heavy metals in industrial processes and products. Many occupations involve daily heavy metal exposure; over 50 professions entail exposure to mercury alone. In today's industrial society, there is no escaping exposure to toxic chemicals and metal pollutants. The 25 environmental toxins which cause the most problems are toxic metal pollutants, pesticides and organic solvents. Metals are inorganic substances that occur naturally in geological formations. Metals are natural part of our environment. Life has evolved in this natural milieu and requires that metals to be present in appropriate levels and combinations. Some metal are essential for our life and are naturally available in our food and water. Concentrations of metals that are too low can lead to health problems as a result of nutrient deficiencies, whereas metal concentrations that are too high can be toxic to plants, animals, and humans.

#### **REVIEW OF LITERATURE**

The building blocks of our bodies are minerals. They are required for body structure, fluid balance, protein structures and to produce hormones. They are a key for the health of every body system and function. They act as co-factors, catalysts or inhibitors of all enzymes in the body. Copper and iron, for example, along with other minerals are required for the electron transport system, and thus needed for all cellular energy production. Minerals are classified into four groups:

- 1. Macro minerals are those which are needed in large quantity and include calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), phosphorus (P), sulfur (S), iron (Fe), copper (Cu) and zinc (Zn). 26
- 2. Required trace minerals include manganese (Mn), chromium (Cr), selenium (Se), boron (B), vanadium **(V)**, (Li), silicon (Si), lithium molybdenum (Mo), cobalt (Co), germanium (Ge) and others.
- Possibly required trace minerals include 3. arsenic (As), rubidium (Ru), tin (Sn), strontium (Sr), gold (Au), silver (Ag) and nickel (Ni).
- Toxic metals include beryllium (Be), mercury 4. (Hg), lead (Pb), cadmium (Cd), aluminum (Al), antimony (Sb), bismuth (Bi), barium (Ba), uranium (U) and others.

These categories overlap slightly because assessing minerals that are required by humans is problematic. Some may be needed in minute amounts. Also, essential minerals are usually toxic in greater amounts. Examples are Cu, Fe, Mn, Se and V. Even Ca and Na are quite toxic in excess.

#### H-POINT STANDARD ADDITION METHOD

Analytical methods rely on methods in which the analytical signal (Ax) is proportional to the analyte concentration  $(C_x)$ . Thus,

$$A_x = kC_x$$

If all the constituents in the sample are not known, then a standard solution with the same chemical composition cannot be prepared, and a calibration curve cannot be constructed. The method of standard addition provides a useful approach for measuring the analyte concentration in a complex matrix. The matrix effect problem occurs when the unknown sample 54 contains many impurities. If impurities present in the unknown interact with the analyte to change the instrumental response or themselves produce an instrumental response, then a calibration curve based on pure analyte samples will give an incorrect determination.

- Measure the analytical response produced by test i. solution diluted to volume VT. The total volume must remain constant for all parts of the experiment.
- Spike the test solution with known amounts of ii. analyte (standard), and the combined solution diluted to VT
- Measurement is followed by extrapolation of the iii. calibration line to zero response (y = 0). The method assumes that a zero response is obtained when the total concentration of analyte is zero. Standard addition plot is as shown in Fig. 1. Limitation of standard additions is that the method is effective only in overcoming 'rotational' matrix effects (Fig 2 and 3).



Fig. 1 Standard addition plot

Standard additions cannot correct for 'translational' matrix effects. A rotational matrix effect arises when the size of the analytical signal (response) derived from a fixed concentration of the analyte is affected by other constituents of the test solution. A rotational matrix effect changes the size of the analytical signal from the same concentration of analyte in different matrices. The effect is usually proportional to the signal and therefore it is also referred to as a 'proportional effect'. The baseline of the signal (which could for example, represent time or wavelength) is unchanged. It gives rise to changes in the slope of the calibration line, but not its intercept.

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Fig. 2 A rotational matrix effect- the baseline of the signal is unchanged



Concentration

## Fig. 3 A rotational matrix effect- slope of the calibration line is changed.

This effect is independent of the concentration of the analyte and occurs even when the analyte is absent. This effect is produced not by analyte but by concomitant substances present in the test solution. A translational effect changes the intercept of a calibration line but not the slope. Translational effects have to be eliminated or corrected before the method of standard additions is effective.

#### INTRODUCTION TO REAGENTS

#### 1-(2-pyridylazo)-2-naphthol (PAN)

PAN, a heterocyclic azo dye forms coloured complexes with most metals. These are red with the alkaline earths, rare earths, Al(III), Sc(III), Y(III), Ti(IV), Zn(II), Cd(II), Hg(II), Ga(III), In(III), TI(III), Pb(II), Bi(III), Ni(II), Mn(II) and U(IV) etc. With Cu(II), V(IV) and V(V), Fe(II) and Fe(III) and Ru(III), they are of varying shades from red to violet, whereas with Co(II), Pd(II) and Pt(II) they are green. The alkali metals, Ge(IV),

As. Se and Te do not react. The pH of the solution is of great importance, and the minimum pH for chelation varies from metal to metal. Correct pH control is of absolute importance in all analytical work with PAN [1-5]. Many of these chelates are insoluble in water but can be extracted into various organic solvents as investigated in detail [7]. PAN shows both hypsochromic and bathochromic shifts on protonation and ionisation respectively [6]. It is insoluble in water, dilute acids and alkalis, but is soluble in strong acid (pH < 12) to give a yellow-green cation, and in strong alkali (pH > 12) to give a red anion as shown below:



PAN act as tridentate ligands complexing with most metals through the ortho-hydroxyl group, the azo nitrogen nearest to the phenolic ring and the heterocyclic nitrogen atom, giving two stable, 5membered chelate rings [8]. The most common metal-to-ligand ratios encountered are 1:1 and 1:2 and the structures for these two types of complexes are as shown below



Most PAN complexes have absorption maxima lying between 530 and 570 nm, but some complexes absorb at longer wavelengths, for instance, vanadium(V) (615 nm), palladium(II) (620 and 675 nm) and rhodium(III) (598 nm). The

Spectrophotometric applications with a wide range of metals make PAN a useful sensitive and selective reviewed use reagent. [9] has its for spectrophotometric determination of a number of metals in various samples.

#### 4-(2-pyridylazo) resorcinol (PAR)

PAR is soluble in water but to a lesser extent in alcohol. It is insoluble in ether. [10] made a complete investigation of the visible spectrum of the dye as a function of pH in aqueous and 50% aqueous dioxin solutions. They were able to identify the following four chromophoric species:



Water solubility of PAR and its complexes was studied [10]. PAR reacts with large number of metals to give red or red-violet complexes at wavelengths between 495 and 550 nm except palladium for which  $\lambda$  max is 440 or 630 nm. The complex with palladium is green in acid and red in neutral solutions. PAR does not react with the alkali metals, Cr (VI), Sb(III), Mo(VI), W(VI), As(III) or (V).

The formation of metal-PAR complexes is very dependent on pH. PAR acts as tridentate ligand chelating through the pyridine nitrogen atom, the azonitrogen atom farthest from the heterocyclic ring and the o-hydroxyl group [11] thus forming two stable 5membered chelate rings. Commonest chelates are of the type M (PAR) and M (PAR).



An interesting and important point to note about the chelation of PAR concerns the ionization of the two hydroxyl groups. Normally the p-hydroxyl group ionizes first because of the internal hydrogen bonding in the molecule.

#### INTRODUCTION DITHIOCARBAMATE TO PESTICIDES

The dithiocarbamates form a very important group among fungicides. Most of these are foliage fungicides, while some are used for soil and seed treatments. Tisdale [10] first demonstrated the fungicidal possibilities of the carbamates in 1931 in the laboratories of E.I. DuPont Company, USA, but the commercial production started about a decade later. The dithiocarbamates were discovered as a class of chemical compounds early in the history of organosulphur chemistry e.g., [11] gave the synthesis of dithiocarbamic acids in 1850. [12] Was one of the pioneers in the field to recognize the metal binding properties of dithiocarbamates? This property is due to the insolubility of the metal salts, with the exception of Na and other alkali and the alkaline earth metals and to the capacity of the molecules to form chelate complexes. It is due to this characteristic that various dithiocarbamates e.g. sodium dimethyldithiocarbamate, have found practical outlet in the field of inorganic analysis and antioxidants.

Carbamates are the half amides of carbonic acid. Their sulfur analogs, the dithiocarbamates are the half amides of dithiocarbonic acid. The synthesis and the general formula of dithiocarbamates are given below:



The ammonium salt of carbamic acid



#### The ammonium salt of dithiocarbamic acid

#### **SURFACTANTS**

A surfactant (surface active agent) is an amphiphilic molecule or ion that possesses both hydrophobic and hydrophilic moieties. A simple typical surfactant has the structure R-X illustrated in Fig. 4, where R is a long chain hydrocarbon of 8-18 atoms and X is the polar (or ionic) head group [11]. Depending on X, surfactants can be classified as non-ionic, cationic, anionic or zwitterionic. Surfactants tend to congregate at the interface between the aqueous medium, and the other phase of the system such as air, oily liquids and particles thus imparting properties such as foaming emulsification and particle suspension.

#### Journal of Advances in Science and Technology Vol. III, Issue No. VI, August-2012, ISSN 2230-9659



#### Fig 4 Structure of a surfactant

Because of the presence of the hydrophilic group a surfactant is more or less readily soluble in water; however, the hydrophobic group is repelled by water so that there is a tendency for that portion of the molecule to leave the aqueous phase. This leads to higher concentration at the boundaries or surfaces than in the main body of the solution. At the air waterinterface i.e. at the surface of the solution, the surfactant molecule orient themselves with the hydrophilic groups in the water phase, the hydrophobic groups extending as far as possible in the other direction. The result of this oriented surface film is the lowering of surface tension and greater tendency towards bubble and foam formation. A similar layer tends to form in the presence of an immiscible liquid, at the liquid-liquid interface, hydrophilic groups oriented towards water, hydrophobic group toward the liquid. This promotes dispersion other and emulsification as droplets.



#### Fig 5 Four different types of surfactants depending on charge on hydrophilic head

#### CONCLUSION

A modification of the 'Standard Additions Method' called 'H-Point Standard Addition Method (HPSAM)' was developed in order to determine unbiased analyte concentration in the presence of direct interferent. Application of the HPSAM to analytical spectroscopy is the quantitative analysis of binary mixtures with partly or completely overlapping absorption spectra. The method uses multi-point signal data (analytical signal data obtained at two accurately selected wavelengths) to transform otherwise uncorrectable to correctable errors and evaluate the analyte and interferent

concentrations. The proposed HPSAM is rapid, simple precise and accurate. The developed procedure is advantageous over other studies, since no previous sample treatment is needed, thus minimizing errors due to solvent extraction or hot acid decomposition procedures. Determination of dithiocarbamates by gas chromatography involves formation of CS<sub>2</sub>, extraction and then determination of CS<sub>2</sub>. HPSAM possesses some distinct advantages over determination of dithiocarbamates by gas chromatography.

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