SPECTROPHOTOMETRIC DETERMINATION OF TOXIC ELEMENTS IN AQUEOUS MEDIA.

SUBMITTED BY

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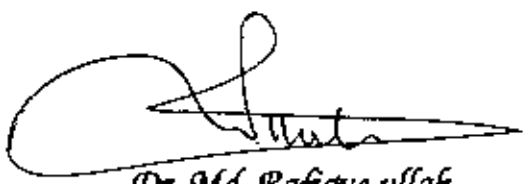

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DECLARATION

This thesis work has been done by the candidate himself and does not contain any material extracted from elsewhere or from a work published by any body else. The work for this thesis has not been presented elsewhere by the author for any degree or diploma.

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A thesis on

"SPECTROPHOTOMETRIC DETERMINATION OF TOXIC ELEMENTS IN AQUEOUS MEDIA"

BY

MOHAMMAD ENAMUL HAQUE

has been accepted as satisfactory in partial fulfillment of the requirements for the degree of Master of Philosophy (M. Phil) in Chemistry and certify that the student has demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on March 18,2007 .

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Author

MOHAMMAD ENAMUL HAQUE (Tareq)

Contents

SUMMARY

Analytical Chemistry deals with the detection of kinds (qualitative analysis) and the measurement of the amounts (quantitative) of the substance present in the sample material. Many metals listed as environmental hazards are essential dietary trace elements required for normal growth and development of animals and human beings. These elements are Ag, Al, As, Ba, Bi, Cd, Co, Cu, Ce, Cr, Fe, In, Mn, Mo, Pb, Se, Sn, Te, Tl, Ti, U, V, W and Zn.

Metals such as Be, Cr, Co, Ni, Cd and Zn are proven carcinogens. They induce acute toxicity at high concentration.

Therefore accurate determination of trace level for all those metals using simple and rapid method is very important. Spectrophotometry is very sensitive technique in inorganic trace analysis because picogram 10-12 per gm level can be determined.

This thesis comprises of two parts, part I and part II. To maintain the continuity and conformity with the title of the thesis, part I deals with the general introductions covering on–

(A) Spectrophotometry.

(B) Toxicology.

(C) Environmental pollution and

(D) Aim of the Project.

(A) Spectrophotometry : It includes a general introduction of molecular absorption spectrophotometry, basic essentials of molecular spectrophotmetry as trace and ultra-trace analytical technique and its advantage over other techniques, their merits and demerits.

(B) **Toxicology** : It deals with the different terms frequently met with while studying toxicology and irritology, classification of toxicology, essential elements with potential for toxicity in detail discussion of essentiality and irriticity of cadmium which embodied in the thesis. Some hygienic standards of exposure, treatment and therapy for cadmium intoxication.

(C) **Environmental Pollution :** It deals with the different terms frequently met with while studying pollution and its control; e. g. classification of environmental pollution, detail discussion about inorganic and organic pollutants, pollution due to toxic chemicals (trace elements) in the environment. It also deals the growing hazards and some preventive measures for pollution control in Bangladesh. Summary of elemental content in the human body and the standard values for water quality standard for Bangladesh have been discussed.

(D) **Aim of the Project :** The concluding section of part I is the "Aim of the project" where essential characteristics of absorbing reagents, merits and demerits of both direct and indirect spetrophotometry have been discussed.

Part II describes extensively with experimental work. It is divided into two subchapters :

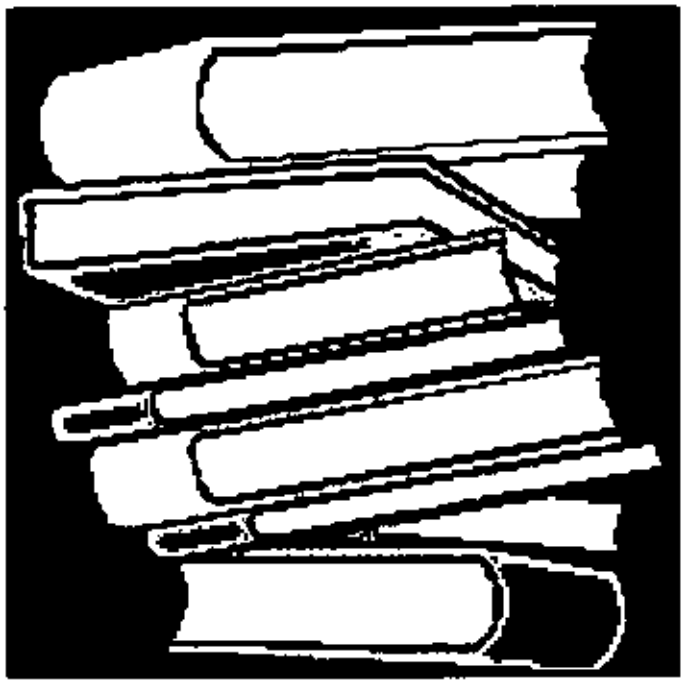
(A) Reviews of existing spectrophotometric methods for determination of the metal with some important physical properties, occurrences, uses, etc.

(B) Sub-chapter (B) is entirely devoted to experimental works and finally details ultra-trace determination procedures are outlined. This part has its own Bibliography tagged at the end.

Sub-Chapter (A) opens up with the review of available spectrophotometric methods for determination of cadmium.

Sub-Chapter (B) is devoted to experimental works. A very simple, ultra-sensitive and highly selective non-extractive spectrophotometric method for the determination of trace amount of toxic element cadmium using 1, 2-dihydroxyanthraquinone-3-sulphonic acid, sodium salt (Alizarin red S) as a new spectrophotometric reagent has been developed. Alizarin red S reacts in slightly acidic solution (0·05 – 1·0 M H_2SO_4) with cadmium to give a deep greenish yellow chelate which has an absorption maximum at 422 nm. The reaction is instantaneous and absorbance remains stable for over 24hrs. The average molar absorption co-efficient and Sandell's sensitivity were found to be $2{\cdot}24 \times 10^3$ L $mol^{-1}cm^{-1}$ and 20 ng cm^{-2} of Cd respectively. Linear calibration graphs were obtained for 0·1–40 μg mL^{-1} of Cd. The stoichiometric composition of the chelate is 1 : 2 (Cd : Alizarin red S). Large excess of over 50 cations, anions and some common complexing agents (e. g. EDTA, oxalate, citrate, phosphate, thio-urea, SCN^-) do not interfere in the determination. The method was successfully used in the determination of cadmium in Several Standard Reference Materials (alloys, steels and water) as well as in some environmental waters (In land and surface) and complex synthetic mixtures. The method has high precision and accuracy. (S = ± 0·01 for 0·5 μg mL^{-1})

PART—I



GENERAL INTRODUCTION

(A) SPECTROPHOTOMETRY

(B) TOXICOLOGY

(C) ENVIRONMENTAL POLLUTION

(D) AIM OF THE PROJECT

REFERENCES

(A) SPECTROPHOTOMETRY

"MOLECULAR ABSORPTION SPECTROPHOTOMETRY IS THE BACKBONE OF MODERN ANALYTICAL TECHNIOUES FOR TRACE ANALYSIS"

This prediction was made by an eminent Scientist (T.S.West) in the field of analytical chemistry about spectrophotometry at its infancy (1967) [1]. Spectrophotometry, particularly in the visible region of the electromagnetic spectrum, is one of the most widely used methods of analysis [2]. It is very widely used in clinical chemistry and environmental laboratories because many substances can be selectively converted to a colored derivative. Spectrophotometry is extremely sensitive so much so that sometimes picogram (10^{-12}g) per gram level can be determined. The instrumentation is readily available and generally fairly easy to operate.

Spectrophotometry as a Trace Analytical Technique :

Trace and Ultratrace: On the outset of this discussion few points are raised to expose the ambiguity associated with the term 'trace'. An analytical chemist is frequently encountered with this term regardless the technique employed spectrophotometry, spectrofluorimetry, conventional atomic absorption, atomic emission, polarography, activation analysis etc. For the academic and scientific interests some clear out distinction between the two extremes is felt urgently necessary. The term 'Trace' originally was used to mean very low concentration and defined as that amount upper limit of which was 100 ppm be weight [3] (i.e. 100μg/gm). Though the lower limit was not fixed at that time (neither as yet), perhaps it was originally intended somewhere in the order of microgram/gm levels then the lowest possible levels that could be

instrumentally detected/estimated. The triumph of electronics, the development of sophisticated instrumentation and methodology in recent times have led analytical chemists to measure unbelievably small concentration of elements with incredible success of amazing accuracy. Even femtogram (10^{-15}g) quantities of substances are being measured these days. Thus the term trace amount is pushed back from the range of 10^{-3} to 10^{-6}g to a range of 10^{-7}g to 10^{-15}g-certainly a very wide range which needs at least two subdivisions. Therefore, some authors are in favour of calling those ultramicrogram quantities as 'ultratrace' to differentiates it from 'trace'. While others are in opinion to preserve the classical 'trace' now be reserved for ultramicrogram quantities. Because there is and will be every demand and necessary of conventional technique, e.g. spectrophotometry, etc. in some sphere of scientific field dealing with micro-quantities, e.g. Geo-science, metallurgy, for example, the term 'trace' will be continued in its classical sense. To fit the smallness of ultramicro concentration 'ultratrace' seems to be more appropriate. It will not only do justice to conventional analytical chemists but also help to remove the ambiguity prevailing now. Some authors also use nano-trace, picotrace, microtrace to pinpoint the smallness of the material used.

The inorganic analytical chemists dealing with chemical spectrophotometry for trace measurement from solutions belong to twin schools of spectrophotometric analysis:

(1) Molecular absorption spectrophotomery

(2) Molecular fluorescence spectrophotometry

Molecular absorption spectrophotometry is more sensitive technique in inorganic trace analysis [4-15]. Molecular fluorescence spectrophotometry, on the other hand, experimentally similar and akin to molecular absorption spectrophotometry, fortunately is free from all limitations of absorptiometry [16-19].

Theory of UV-VIS Spectroscopy :

Radiant energy can be emitted by substances under high excitation conditions, such as high temperature or by an electric discharge. It can be absorbed, transmitted, reflected and refracted by various substances in different states (solid, liquid, solution and gas) if the incident radiant energy is of appropriate wavelength. These phenomena serve as the basis of the branch of measurement known as photometry. In spectrophotometry the measurements are concerned with radiant energy of a single wavelength (monochromatic radiation) or, for practical reasons, a narrow band of wavelengths. A few subdivisions of photometry used in analytical chemistry are as follows:

(i) **Emission spectrography** : In this type of photometry energy emitted by excited atoms, ions or molecules is recorded photographically and measured for wavelength and intensity.

(II) **Absorption spectrophotometry** : In this method radiant energy of a definite wavelength (or a narrow band of wavelength) is absorbed by a homogenious medium. Often, the spectral region concerned is designed, such as ultra-violet, visible or infrared. Actually, the measurement is usually made of the energy transmitted by the sample and various schemes can be used to translate this absorption measurement.

(iii) **Colorimetry** : The method, in its usual sense, applies to the visual observation of the fraction of "White light" from an incandescent source, which has passed through a liquid or solution medium. By interposing a light filter, such as a plate of colored glass, between the source and the sample, the radiant energy incident upon the sample consists of a more or less wide band or wavelengths and this sharpens the sensitivity of the measurement of observation.

Although all branches of photometry have analytical applications, the present discussion will be limited mainly to the absorption and transmission of radiant energy in the visible region of the spectrum by substances in solution.

Interaction of Electromagnetic Radiation with Matter :

In spectrometric methods, the sample solution absorbs electromagnetic radiation from an appropriate source and the amount absorbed is related to the concentration of the analyte in the solution. A solution of copper is blue because it absorbs the complementary color (yellow) from white light and transmits the remaining blue light. The more concentrated the copper solution, the more yellow light is absorbed and deeper the resulting blue color of the solution. In spectrometric method, the amount of this yellow light absorbed would be measured and related to the concentration. We can obtain a better understanding of absorption spectrometry from a consideration of the electromagnetic spectrum and how molecules absorb radiation.

The Electromagnetic Spectrum :

Electromagnetic radiation, for our purposes, can be considered a form of radiant energy that is propagated as a transverse wave. It vibrates perpendicular to the direction of propagation and produces a wave motion.

The wave is described either in terms of its wavelength, the distance of one complete cycle or in terms of the frequency, the number of cycles passing a fixed point per unit time. The reciprocal of the wavelength is called the wave number, which is the number of waves in unit length or distance per cycle.

The relationship between the wavelength and frequency is

$$\lambda = {}^{c}/_{\nu} \quad \text{.....(1)}$$

Where λ is the wavelength in centimeters (cm.), ν is the frequency in reciprocal seconds (s^{-1}) or hertz (Hz) and c is the velocity of light (3×10^{10}cm/s). The wave number is represented by $\bar{\nu}$ in $cm.^{-1}$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \quad \text{.....(2)}$$

The wave length unit preferred for the ultra-violet and visible regions of the spectrum is nanometer, while the micrometer (μm) is preferred for the infrared region. In the last case, wave numbers are often used in place of wavelength and the unit is $cm.^{-1}$

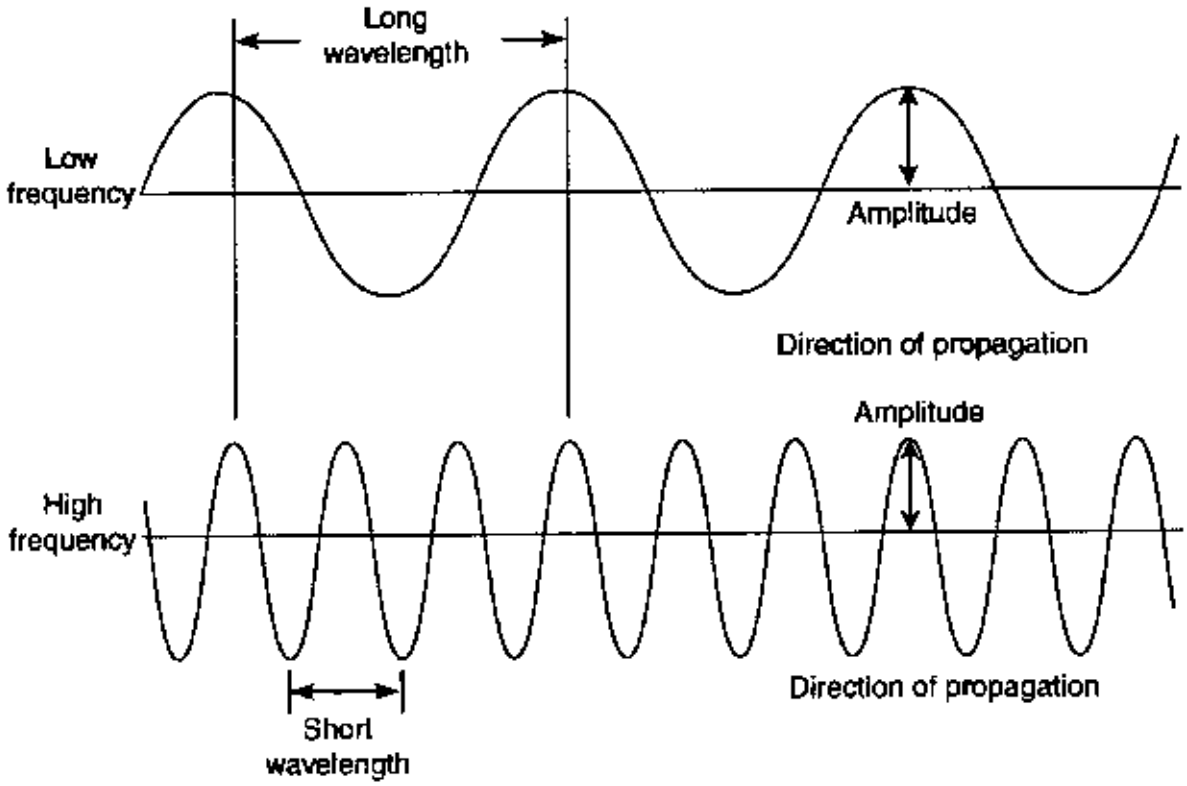


Fig.-1 : Wave motion of electromagnetic radiation.

Electromagnetic radiation possesses a certain amount of energy. The energy of a unit of radiation, called photon, is related to the frequency or wavelength by: -

$$E = h\nu = {}^{hc}/_{\lambda} \quad \ldots\ldots (3)$$

where E is the energy of the photon in erg and h is plank's constant, 6.62 x 10^{-27} erg-s. It is apparent, the shorter the wavelength or the greater the frequency, the greater is the energy.

As indicated above, the electromagnetic spectrum is arbitrarily broken down into different regions according to wavelength. The various regions of the spectrum are shown in figure -2.

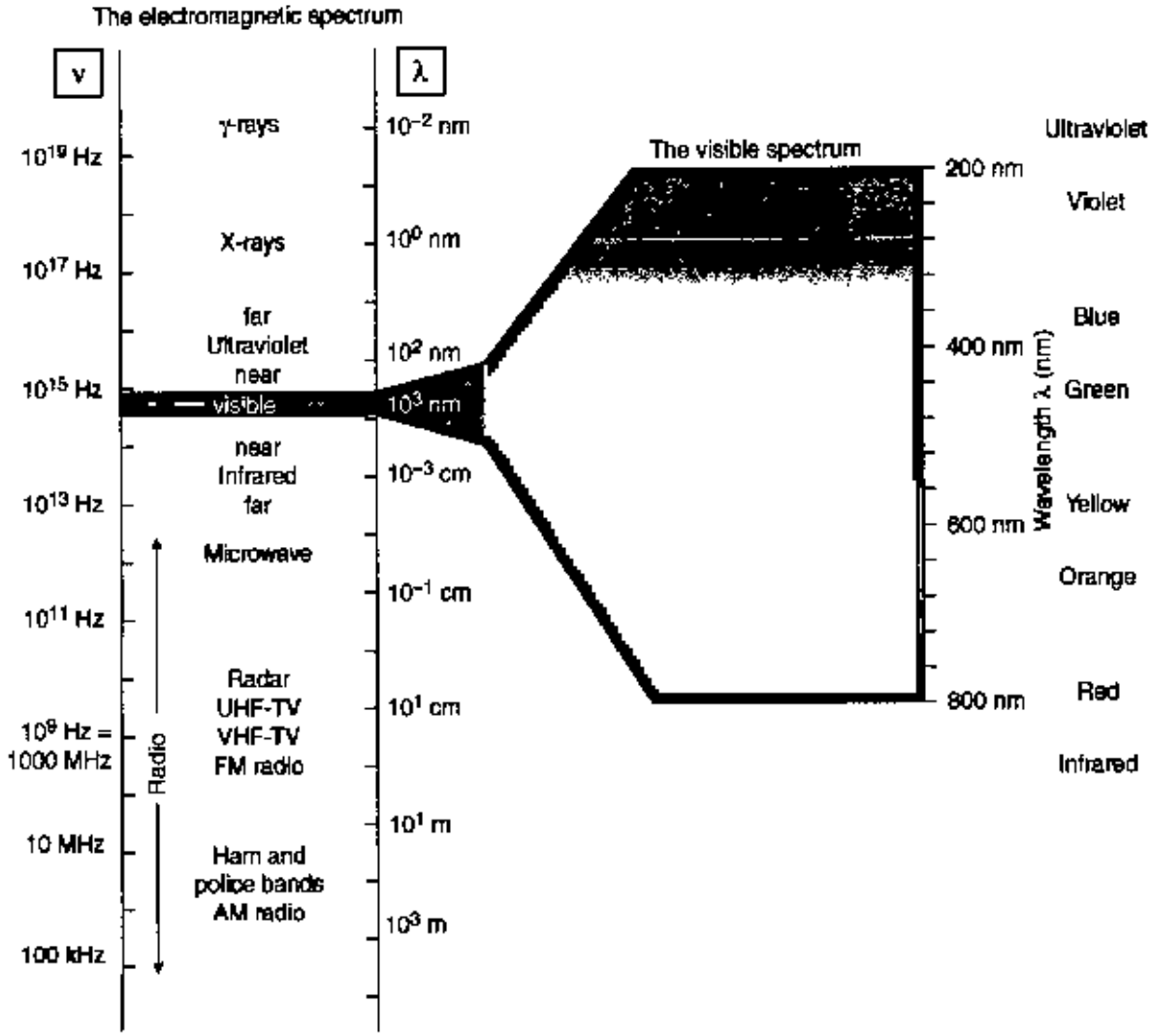


Fig.-2 : Parts of the electromagnetic spectrum which employed for spectrophotometry.

The ultra-violet region extends from about 10 to 380 nm, but the most analytically useful region is from 200 to 380 nm, called the near ultra-violet region. Below 200 nm, the air absorbs appreciably and so, the instruments are operated under a vacuum; hence, this wavelength region is called the vacuum ultra-violet region. The visible region is actually a very small part of the electromagnetic spectrum and it is the region of wavelengths that can be seen by the human eye, that is, the light appears as a color. The visible region extends from near ultra-violet region (380 nm) to about 780 nm. The infrared region extends from about 0.78 μm (780 nm) to 300 μm, but the range from 2.5 to 15 μm is the most frequently used for analysis. The 0.8 to 2.5 μm range is known as the near-infrared region, the 2.5 to 15 μm range as the NaCl-infrared region and longer wavelengths as far infrared region.

The Absorption of Radiation:

The qualitative picture of the absorption of radiation can be obtained by considering the absorption of light in the visible region. We 'see' objects because they transmit or reflect only a portion of the light in this region. When polychromatic light (white light), which contains the whole spectrum of wavelengths in the visible region, is passed through an object, the object will absorb certain of the wavelengths leaving the unabsorbed wavelength to be transmitted. These residual transmitted wavelengths will be seen as a color. This color is complementary to the absorbed colors. In a similar manner, opaque objects will absorb certain wavelength, leaving a residual color to be reflected and 'seen'.

Quantitative Application of UV-Visible Absorption :

(a) BEER LAW :

The amount of monochromatic radiation absorbed by sample is described by the Beer-Bouguer-Lambert Law, commonly called Beer's Law. Consider the absorption of monochromatic radiation of radiant power P_0 which passes through a solution of an absorbing species at concentration c and path length b, and the emergent (transmitted) radiation has radiant power P. This radiant power is the quantity measured by spectrometric detectors. Bouguer in 1729 and Lambert in 1960 recognized that when electromagnetic radiation is absorbed, the power of the transmitted energy decreases in exponential manner as,

$$P = P_0 10^{-kb}$$

$$\frac{P}{P_0} = 10^{-kb} = T \quad \text{.....(4)}$$

where K is a constant and T is called the transmittance, the fraction of radiant energy transmitted. Logarithmic form of the equation is

$$\log T = \log \frac{P}{P_0} = -kb \quad \text{.....(5)}$$

In 1852, Beer and Bernard, each stated that a similar law holds for the dependence of T on the concentration, c

$$T = \frac{P}{P_0} = 10^{-k'c} \quad \text{.....(6)}$$

or, $$\log T = \log \frac{P}{P_0} = -k'c \quad \text{.....(7)}$$

where k' is a new constant. Combining these two laws is obtained what is know as Beer's law. It described the dependence of T on the path length and the concentration of the absorbing species as,

$$T = \frac{P}{P_0} = 10^{-abc} \quad \text{.....(8)}$$

where 'a' is a combined constant of k and k′. The logarithmic form of (8) is

$$\log T = \log \frac{P}{P_0} = -abc \quad \text{.....(9)}$$

It is more convenient to omit the negative sign on the right hand side of the equation and to define a new term, absorbance:

$$A = -\log T = \log \frac{1}{T} = \log \frac{P_0}{P} = abc \quad \text{.....(10)}$$

Where A is the absorbance. This is the common form of Beer's law. It is the absorbance that is directly proportional to the concentration. The path length 'b' in Equation (10) is expressed in centimeters, the concentration c is in gram per liter. The constant 'a' is then called the absorptivity or extinction coefficient. When 'c' is expressed in moles/litre; b in cm, the constant 'a' is replaced by ε and the Beer's law is written as

$$A = \varepsilon bc \quad \text{.....(11)}$$

This new quantity, ε is known as Molar Absorptivity. Since A is unitless, ε has the unit of litre mol^{-1} cm^{-1}. Molar absorptivity and absorptivity are dependent on the nature of the absorbing material and the wavelength of measurement. Beer's law holds strictly for monochromatic radiation, since the absorptivity varies with wavelength.

APPLICABILITY OF BEER'S LAW :

Beer's law is the basis of all quantitative applications of uv-visible spectroscopy. Generally a method of calibration of stendardization is used for determining the concentration of the analyte.

Beer's law will generally hold over a wide range of concentration if the structure of the colored ion or of the colored non electrolyte in the dissolved state does not change with concentration. Small amounts of electrolytes, which is chemically unreactive with the colored components do not usually

affect the light absorption; large amounts of electrolytes may results in a shift of the maximum absorption, and may also change the value of the absorptivity. Discrepancies are usually found when the colored solute ionizes, dissociates or associates in solution, since the nature of the species in solution will very with the concentration. The law does not hold when the colored solute forms complexes, the composition of which depends upon the concentration. Beer's law holds strictly for the monochromatic radiation. But no instrument can attain such resolution of wavelength. In practice a narrow band is used. With the broadening of band width, the system tends to show increasing deviation from Beer's law. The behaviour of a substance can, however, always be tested by plotting Absorbance-versus-concentration; a straight line passing through the origin indicates conformity to the law.

The slope of the spectrum increases as the concentration is increased, with the result that the fractions of each wavelength absorbed may change, particularly if the instrument setting should drift over the period of the measurement. A negative deviation in the absorbance-versus-concentration plot will, in this case, be observed. The greater the slope of the spectrum, the greater is the deviation.

Other instrumental factors that may contribute to deviation from Beer's law include stray radiation entering the monochromator and being detected, internal reflections of the radiation within the monochromator and mismatched cells used for different analyte solutions in double-beam instruments. It has been calculated that the minimum error should occur at T = 0.136 or A = 0.87. All instruments have a working range of about 0.1 to 1.5A and some sophisticated instruments have a range of 0.001 to 2.5A.

Any chemical reaction that can alter the concentration of an absorbing species can result in a deviation from Beer's law. If the concentration is decreased because of the chemical reaction and the product does not absorb radiation at the wavelength at which the measurement is made, a negative deviation occurs. If a product of the chemical reaction absorb more strongly than the

assayed substance, a positive deviation occurs. Among the types of chemical reactions which can lead to a deviation from Beer's law are association-dissociation reactions, acid-base reactions, polymerization reactions, complexation reactions and reactions with the solvent.

Selection Rules:

Requirements for the absorption of light by matter are summarized in the selection rules. Transitions which are possible according to these rules are referred to as 'allowed' transition and those not possible as 'forbidden' transitions. The following selection rules are pertinent to electronic absorption spectroscopy.

(i) Transitions between states of different multiplicity are multiplicity forbidden, that is, electronic transitions in which the spin of an electron changes are forbidden.

(ii) In a molecule which has a center of symmetry, transitions between two grade or two ungrade states (that is, g < - > g or u < - > u) are Laporte forbidden. The allowed transitions are g < - > u and u < - > g. As a result of this rule, d < - > d transitions in octahedral complexes are Laporte forbidden.

(iii) Simultaneous excitation of more than one electron is forbidden.

However, the term "forbidden" refers to rules set up for a simple model and while the model is a good one "forbidden" transitions may occur by mechanisms not included in the simple model. Since intensity of absorption or emission accompanying a transition is related to probability of the transition, the more probable transition give rise to more intense absorption, forbidden transitions (low probability) give absorptions of very low intensity.

Absorption Instrument:

The quality and cost of uv-vis absorption instruments may differ tremandously from one another. But their basic components are remarkably similar. The required properties of these components are the same regardless of the spectral regions for which they are designed.

Spectroscopic instruments contain five components, such as;

(i) a stable source of radiant energy;

(ii) a wavelength selector that permits isolation of a restricted wavelength regions;

(iii) a transparent container for holding the sample ;

(iv) a radiant detector or transducer that converts radiant energy to a usuable signal (usually electrical); and

(v) a signal processor and readout.

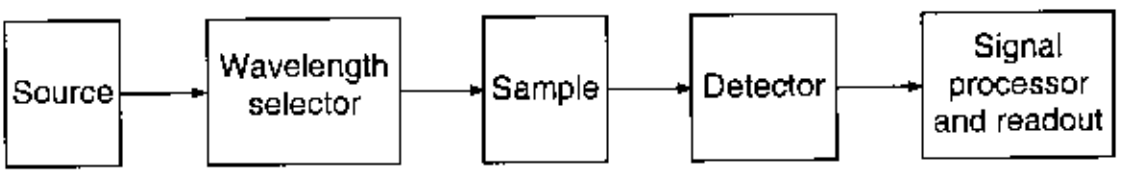


Fig. –3: Shows a block diagram of uv-vis absorption instrument.

A brief descrIption of the components follows:

(I) **Source:** In instruments for the visible range (about 400 to 750 nm) the source is usually a tungsten-filament lamp. For ultra-violet region the hydrogen discharge tube is commonly used. Close voltage control is required for a stable source.

(ii) **Wavelength selector:** In the simple instruments, filters may be used to eliminate or diminish the radiant energy of certain wavelength and pass other selected regions.

A suitable filter for a given substance should transmit well in the spectral region where the desired constituent absorbs strongly. In spectrophotometers, the radiant energy from the source is dispersed into a continuous spectrum by passage through a prism or by diffraction from a grating consisting of fine parallel rulings on a solid surface. Prisms or diffraction gratings, with their accessory lenses, mirrors and slits, are called monochromators. From the continuum of wavelengths emitted by the source, a single wavelength or usually a very narrow band of wavelengths, can be selected for use in the measurements. Different spectral regions require optional components of different materials. Glass is not transparent far outside of the visible region. For use in the ultra-violet region, silicon prisms, lenses and absorption cells are used.

(iii) **Sample container (cells or cuvettes):** The cell must be made of material that posses radiation in the spectral region of interest. This, quartz or fused silica is required for work in the uv region (below 350 nm); both these substances are also transparent in the visible region and to about 3000 nm in the infrared. Silicate glasses can be employed in the region between 350 to 2000 nm. Plastic containers have also found application in the visible region. Crystalline sodium chloride is the most common substance employed for cells in the infrared region.

The quality of spectroscopic data is critically dependent on the way the cell is handled. Fingerprints, grease or other deposits on the walls markedly alter the transmission characteristics of a cell. Thus, through cleaning before and after use is imperative; the surface of the windows must not be touched during handling.

(iv) **Detectors:** The photodetector gives response which varies with the radiant power reaching it. The less expensive photometers generally use photocells of the barrier-layertype. The more elaborate instruments use photoemmissive type receivers, photomultipliers, thermopiles, and bolometers. In each case, the radiant energy is converted to another form of energy (current, potential, heat etc.) which is ultimately measured.

(v) **Signal processors and Readouts:** The signal processor is ordinarily an electronic device that amplifies the electrical signal from the detectors and filters the unwanted ones. The signal processors may permit such mathematical operations on the signal as integration or conversion to a logarithm.

Several types of readout devices are found in modern instruments. Some of these include digital meters, the scales of potentiometers, recorders, computer, etc.

(B) TOXICOLOGY

Before entering into a brief discussion on Toxicology in the author's opinion it will be wise to give some definitions of some useful terms commonly met with the discussion.

DEFINITIONS :

Toxic, Toxicity and Toxicology: The word 'toxic' is derived from the Greek word toxon ('bow') and toxicon or pharmikon ('arrow poison'). Every chemical agent is inherently harmful, depending on form, dose administered, mode of entry and character of the organism. Toxicity is the inherent capacity of any chemical to affect adversely the activity of living organism. Toxicity is a relative term used to compare one chemical or metallic compound with another w.r.t. toxicity. Adverse effects due to toxicity include behavioural changes that affect collective populations. Early mortality, retardation of growth, impaired reproduction, neonatal mortality, neoplasms and varied diseases symptoms are common criteria for metal toxicity in mammals. Thus, 'Toxicology' is defined as basic science of poisons (where poison is defined as any agent that is capable of producing injury or death when ingested or absorbed). According to Paracelsus over 400 years ago "all substance are poisons"; there is none, which is not a poison. The dose differentiates a poison and a remedy.

Poisons may be administered orally, by injection, by inhalation, by application to a wound or by introduction into the rectum, vagina, and urethra.

CLASSIFICATION OF POISONS :

It is necessary to evolve a basis of classification of poisons. Poisons may be of synthetic, mineral, animal or vegetable origin, but such a classification, based on origin of poisons, is not helpful for their proper study. The best way to classify them would be on the basis of the chief symptoms they produce on the human body and in this way poisons can be studied in a scientific manner.

I. Corrosives :

(i) Strong acids, Mineral, e.g. Sulfuric acid, Nitric acid, Hydrochloric acid; Organic, e.g. Oxalic acid, Carbolic acid.

(ii) Strong alkalies, e.g. Caustic Soda or Sodium hydroxide, Caustic Potash or Potassium hydroxide, Ammonium Carbonate, Sodium Carbonate, etc.

II. Irritants:

(i) Inorganic, Non-metallic e.g. Phosphorus, Chlorine, Bromine, etc.
Metallic, e.g. Copper, Arsenic, Antimony, Lead, Zinc, Mercury, Aluminum, Vanadium etc.

(ii) Organic, Vegetable e.g. Castor oil seeds, Crouton seeds, Aloes, Abrus precatorius, etc.
Animal, e.g. Cantharides, Snake and insect bites etc.
Mechanical, e.g. Powdered glass, Diamond dust, Hair etc.

III. Neurotics:

(1) Cerebral (Affecting the brain),

(i) Somniferous, e.g. opium and its alkaloids.

(ii) Inebriant, e.g. Alcohol, Ether, Chloroform,

(iii) Deliriant, e.g. Dhatura, Belladonna, Hyoscyamus, Cannabis indica.

(2) Spinal (Affecting the spine), e.g. Nux Vomica, Gelsemium.

(3) Cardiac (Affecting the heart), e.g. Aconite, Digitalis, Oleander etc.

(4) Asphyxiants (Affecting the lungs), e.g. Carbon Monoxide, Carbon Dioxide etc.

(5) Peripheral (Affecting the peripheral nerves), e.g. Conium Curara etc.

IV. Miscellaneous Group: Food poisoning, botulism etc.

ACTION OF POISONS :

It is now important to understand the mode of action of poisons. Poisons may have local action, remote action or both.

(a) **Local Action**: This is due to direct action of the poison on the part or direct interaction with the tissues leading to:

(i) Corrosion as by strong mineral acids. Although corrosive substances cause lesions, the immediate cause of death may be due to indirectly related phenomenon, e.g. shock which of course should be considered as remote action.

(ii) Irritation and Inflammation, as by cantharides and tartaremetic or by arsenic which causes gastritis mainly due to local action.

(iii) Nervous Effects, i.e. effects on motor and sensory nerves, e.g. tingling followed by numbness produced by aconite, local anaesthesia due to cocaine, carbolic acid.

(b) **Remote Action:** The remote action of a poison should be described as (i) Non-specific and (ii) Specific.

(i) Non-specific remote action has already been referred to, e.g. shock produced reflexly by intense burning pain caused by corrosives.

(ii) Specific remote action is due to absorption of the poison into the system through the blood and subsequent specific action on certain organs, e.g. strychnine or nux vomica acting on the spinal cord produces tetanic convulsions, cantharides acting on the kidneys produces nephritis, phosphorus acting as a hepatotoxic poison.

(c) **Both local and Remote Action:** Certain poisons have both local action and remote action e.g. Oxalic acid acts locally as a corrosive and remotely by precipitating ionised calcium after absorption into the system, Carbolic acid acts locally as a corrosive and remotely as a narcotic poison.

(i) **Environmental Toxicology:** Environmental toxicology is the study of the unwanted effects of chemical environmental agents on living things.

(ii) **Industrial Toxicology or Occupational Toxicology**: Industrial toxicology deals with industrial chemicals in occupational health hazards and industrial hygiene. Occupational exposure to metals is restricted to 'safe' levels defined as the Threshold Limit Value (TLV) for an eight hour day, five-day work week. These levels are intended to provide a margin of safety between maximum exposure and minimum levels that will produce illness. For all these pollutants or toxicants, it is necessary to establish allowable concentration limits and reliable methods for analysis. These levels can be expressed either in terms of 'Maximum Allowable Concentrations' MAC or MAK (used by VDI committee of German Research Association) or 'Threshold Limit Value' TLV (used by American Conference of Governmental Industrial Hygienist), the values being published on the basis of known data on the toxic effect of a contaminant. Also in terms of permissible biologic levels for the chemical or their metabolites (biologic TLV). MAC or TLV of a substance (or pollutant) is the value at which a worker can be exposed for 8 hours a day without showing any adverse effect on health and is expressed in units mg/m^3 or $\mu g/m^3$ and mg/litre (for air and water respectively). The values are applicable only for pure substances and not for mixture of toxicants. Permissible levels very widely and the differences reflect, in a sense, the toxicologic potency of the metal. As a general rule, the metals that are most abundant in the environment have lesser potential for toxicity as evidenced by the prevailing standard for permissible occupation exposure.

(iii) **Synergism and Antagonism:** Interactions between metal compounds potentiate or decrease the toxicity of metals. Thus in the presence of mixtures of toxicants, the toxic effects are greatly influenced, enhanced or attenuated. When the toxic effects by the combination of contaminants is greater than the effect of individual contaminant it is called synergism or potentiation. Synergism possesses a special problem for aquatic and terrestrial species

because it is possible that a certain combination by relatively harmless substances may result in an unpredictable high level of toxicity that would seriously threaten the existence of one or more species.

When toxic effect of substance is reduced on the addition of a substance, the phenomenon is referred to 'antagonism' antagonistic substance may or may not be toxic when present by itself. The toxicity of cyanide and of mercury in presence of nickel and selenium affect antagonistically. There occurs the reduction in toxicity of vanadium by chromium, cadmium by zinc, selenium by thallium and mercury, arsenic, silver, cadmium and copper by selenium (Frost*, 1972). Since each pair involves one essential metal a stoicheiometric antagonism may be envisioned.

(iv) **Carcinogens and Carcinogenicity:** Carcinogens or oncogens are biologic, chemical and physical agents capable of producing uncontrolled cell proliferation in organs and tissues. The capacity to induce cancer by carcinogens is the carcinogenicity. Carcinogenicity varies with different routes of administration, exposure time, dose and physical state of the material as well as with host specific factors. Tumours are abnormal masses of tissue that grow and persist independent of surrounding structures. They have not physiologic function. Tumours that spread to other tissues (metastasize) or are transplantable to other tissues, are called malignent tumours or cancers. Tumours that are usually incapsulated and do not metastasize are benign. Since benign tumours may develop into malignant tumours, the U. S. Environmental Protection Agency (Gibney,** 1976) classified that oncogens are those substances capable of inducing either type of tumour. Carcinogens cause permanent damage and a biologic modification of the cell, making them more susceptible to further carcinogenic effect. Metals such as beryllium,

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* D. V. Frost, *CRC Critical Review in Toxicology*, **1** (4) 467(1972).

** L. Gibney, *Chemical and Engineering News*, **53** 15(1976).

chromium, cobalt, nickel, cadmium and zinc are proven carcinogens. Special organic complexes of titanium iron, nickel, rhodium and palladium are established carcinogens, e.g. titanocene and iron dextran. Scandium, arsenic, manganese, selenium yttrium, aluminium, zirconium, silver and lead are reported to possess carcinogenicity, while copper, zinc and tin may possess recondite carcinogenicity. Some metals are primary carcinogens, others are cocarcinogens. Metal carcinogens may enhance or potantiate the carcinogenicity of organic compounds by inhibiting the detoxifying mechanism, e.g. copper potentiates the tumourigenesis of N-hydroxy-2-acetyl-amino-fluorene (Stanton*, 1967).

(v) **Genotoxicity or mutagenicity:** Chemical carcionogens are a type of toxic agent that exhibits a specific, defining adverse effect–the production of cancer in animals or humans. Chemical carcinogenesis is classified into two general categories: DNA – reactive (genotoxic) and epigenetic. The DNA reactive (genotoxic) category comprises carcinogens that chemically interact with and alter DNA. These carcinogens are of course mutagenic. Some metals have displayed genotoxic effects suggestive of DNA interaction, these have been placed in this occurring and industrially produced chemicals, including metallic compound may constitute genetic hazard [20]. Among the inorganic chemicals, chromium, titanium, nickel, selenium, cobalt, manganese, lead, beryllium and certain of their derivatives have been found carcinogenic under specific experimental conditions [21].

(vi) **Essential elements or micronutrients and metabolism:** Essential elements or micronutrients serve their biological function satisfactorily and can be regarded like vitamins, as normal dietary constituents without which healthy life and growth are not possible e.g. iron (haemoglobin), iodine (thyroid function) selenium (glutathione-peroxidase). Chromium (glucose tolerance factor), manganese (pyruvate carboxylase). It is only in the last two decades cadmium, chromium, selenium, manganese, silicon and tin each has been

* M. F. Stanton, *Cancern Res.*, **28** 1000(1967).

proposed an essential nutrient for humans, though classically they have long histories as toxic elements. Even the well-known toxic elements arsenic, lead and cadmium are required in trace quantities for the growth of animals. It will be safe to state that nontoxic means a low toxicity. Many metals listed as environmental hazards are essential dietary trace elements required for normal growth and development of animals and human beings. These elements are Ag, Al, As, Ba, Be, Bi, Cd, Co, Cu, Ce, Cr, Fe, In, Mn, Mo, Pb, Se, Sn, Te, Tl, Ti, U, V, W, and Zn.

Nutrients are elements essential to the growth and reproduction of plants and animals and aquatic species depend on the surrounding water to provide their nutrients. Although a wide variety of minerals and trace elements can be classified as nutrients, those required in most abundance by aquatic species are carbon, nitrogen phosphorus. Carbon is readily available from many sources. Carbon dioxide from the atmosphere, alkalinity and decay products of organic matter all supply carbon to the aquatic system. In most cases, nitrogen and phosphorus are the nutrients that are the limiting factors in aquatic plant growth.

Schwartz* used the term 'concentration window' to draw the arbitrary lines of demarcation: (a) essential at trace level for substance of life processes, (b) 'deficient' at lower level than (a) causing metabolic disorder (c) 'toxic' at higher level than (a) causing adverse effects. Many carcinogenic metals are essential nutrients. They induce acute toxicity at high concentration. Metabolism is defined as the chemical changes in molecule within living organisms. In other-words, the sum of anabolism and catabolism processes can be shortened as metabolism.

* K. Schwartz, 'Clinical Chemistry and Toxicology of Metals, *Elsevier,* 1977, P.3.

(a) Classification of Toxicology:

Toxicology embraces different scientific disciplines such as chemistry, biology, physiology, nutrition, pharmacology, pathology, immunology and medicine. Toxicology comprises many areas of service and research. Environmental toxicology is that branch of toxicology that deals with the incidental exposure of man and other animals to harmful contaminants of the environment. Forensic toxicology deals with the medical and legal aspects of the adverse effects of chemicals on humans. Clinical toxicology deals with the study of the diagnosis and treatment of diseases resulting from adverse effect of chemicals. Experimental toxicology studies the effect of toxic levels of chemicals and drugs. Industrial toxicology deals with materials involved in occupational health hazards and industrial hygiene. Economic toxicology is the study of such agents as insecticides, herbicides defoliants and their effects on pests, domestic animals and humans. Behavioral toxicology is a new concept [N. K. Mello, *Fed. Proc.*, **34** (1975) 1832; J. M. Spyker, ibid, **34** (1975) 1845].

(b) Heavy Metal Toxicity:

The heavy metals are among the most dangerous and yet least understood of contaminants. Because they exist in nature as part of earthcrust, so they occur in all soils, rivers and oceans. Perhaps mercury shares the unique undesirable characteristics of being not only deadly but entirely without any useful compensating satisfactory function in biological systems when they turn up as contaminants. Some heavy metals on the other hand, serve their biological function satisfactorily only when they are present within fairly specified limits and in particular form, so that either the deficiency or the over abundance of an essential heavy metal can lead to disorder or to toxic effects.

Further similar metals tend to interfere with each other biologically, some lose their biological activity in the presence of abnormal level of other elements. With the exception of need of iron (hemoglobin) selenium (glutathione-

peroxidase), chromium (glucose tolerance factor), manganese (pyruvate carboxylase) and iodine (thyroid function), a growing understanding of the biological effects and role of heavy metals has led to the growth of a parallel concern for their effects, even in small amounts, on the patterns of health. The number of cancer causing agents is large but in terms of controllable environmental contaminatns the heavy metals comprise a significant proportion of them. The capacity of heavy metals to form stable and irreversible co-ordinated complexes with O, S, and N donor atoms of the ligands of biologically active macromolecules present in the living systems may be responsible for their toxicity. Increased electropositivity and inherent toxicity are associated with increasing atomic number or weight. The heavier metals in each group have the capacity to form irreversible and stable complexes with biologic macromolecules, hence these heavy metals are toxic. The inherent toxicity of heavy metals is enhanced if the solubility of salts of these metals is increased. The toxicity of some heavy metals can be associated with their state of oxidation.

The higher oxides of manganese, chromium, vanadium, molybdenum, lead and barium and polyvalent oxyacid salts such as MoO_4^{2-}, MnO_4^-, CrO_4^{2-} and VO_4^{2-} are more toxic than the corresponding lower oxides or lower oxysalts. The higher oxides may undergo spontaneous reduction to lower forms, disrupting the delicate mechanism of cellular electron transport systems. There are also lot of examples where lower valents states of certain metals (As, Sb, etc.) more toxic than these of higher valents ones.

ESSENTIAL ELEMENTS WITH POTENTIAL FOR TOXICITY

Eight metals generally accepted as essential are: cobalt, copper, cadmium, chromium, nickel, lead, zinc and molybdenum. Each of these eight essential elements has three levels of biologic activity, trace levels required for optimum growth and development, homeostatic levels (storage levels) and toxic levels. For these elements, environmental accumulations are generally less important routes of excess exposure than accidents or occupation.

These essential metals are being investigated for their toxicity in excessive amount. The complete dose-response curve for essential metals shows a general complex activity spectrum comparable to that of Fig. 4.

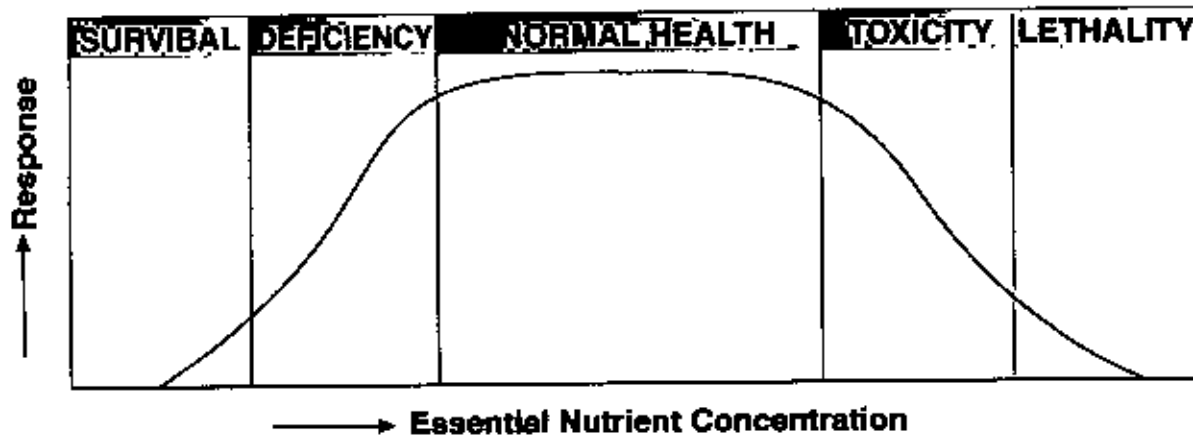

Fig.-4 : Activity spectrum of an essential metal.

[Source: "*Metal Toxicity in Mammals*, 1"; T. D. Luckey and B. Venugopal (Eds.) Plenum press, New York, 1977, p. 7]

Discussion made so far is of general in nature, the following discussion will be restricted solely to the metal (cadmium) as embodied in thesis.

CADMIUM :

Cadmium is the heaviest metal among the post transition elements. It is not essential in human and animal nutrition but its toxicity is tremendously dangerous. So we should be very careful about its toxicity.

Sources :

Cadmium does not occur free state in nature and there are no specific ores from which it is mined. It occurs in nature in association with zinc and lead. Extraction involves separation and recovery of either zinc or cadmium or of all three metals in a single refinery plants. Later it came to be used extensively in the manufacture of alkali storage batteries and plastics. Most early recorded cases of cadmium poisoning were due to inhalation of cadmium fumes or dusts. Cadmium sulfide greenockite (78% Cd), occurs as a coating on sphalerite a ZnS ore and other ore's of Zn, Fe and Cu. Cadmium is obtained as an important by product from the refining of zinc and copper. The earth's crust contains about 0.05 ppm Cd and sea water contains 0.3 ppb. The ratio of Cd to Zn in the soil varies from 1 : 500 to 1 : 5000, in sea water it is 1 : 168. Cadmium is present in trace amounts in plants and marine animals. The middle-aged human adult contains about 50 mg Cd in his body, one-third is in the kidneys, and the liver, lungs, and pancreas are the other sites of cadmium storage. Oysters contain about 3.75 μg Cd g^{-1} (wet weight), wheat and rice protein also contain appreciable Cd. Cadmium may be stimulatory in mammals, but it is not considered to be essential. It is carcinogenic. Cadmium is becoming an ever more widely used metal in industry. Cadmium metal is used in protective coatings for iron, copper and steel. Cd-electroplated parts are used in radios and television sets. Telephone wires are made of Cu-Cd alloys and Ni-Cd rechargeable batteries are extensively used in electronic equipment. Metallic Cd and CdF_2 act as good neutron absorbers in oxide

which is used in storage batteries, Cd-Ag alloys, semiconductors, phosphors and ceramic glazes. Cadmium chloride and bromide are used in photography, lithography, calico printing and dyeing and cadmium tungstate in X-ray screens, scintillation counters and phosphors. Cadmium salts were used in some parts of the world as antihelminthies, ascaricides, nematocides and antiseptics in veterinary medicine, but these uses are obsolete. Cadmium sulfide is used in treating scborrheic dermatities.

Cadmium intoxication is caused mainly by environmental contamination, accumulation of Cd-containing scrap and commercial phosphate fertilizers. Cigarette smoke inhalation is another source of exposure. The total Cd in cigarette smoke varies from 15 to 18 μg per 20 cigarettes. This represents 70% of the Cd content of cigarette tobacco [22]. A dietary source of Cd intoxication is sea food, especially oysters. Extensive food processing and refining raise Cd levels in wheat and rice flour. Cadmium is an industrial health hazard, because cadmium dust, fumes and mists pollute the atmosphere in zinc, copper, lead and cadmium refinery processes. The industrial waste from an upstream cadmium mine was responsible for the contamination of food and drinking water.

An event occurred shortly after world war II that stimulated interest in cadmium because it involved relatively low-level exposure of the general population through contamination of food. In 1946, Dr. Hagino, a general practitioner, returned to Fuchu, Japan, from the army to reopen his medical practice. He was visited by numerous patients aged 40 to 70 who complained of severe rheumatic and myalgic pains. He gave this mysterious disease the name 'Itai-itai' (pain-pain, or ouch-ouch). Gradually it came to be accepted that cadmium in the local rice played an etiologic role in this disease. The source of the cadmium was the effluent from a Pb-Zn-Cd mine upstream from the rice fields.

Interest in cadmium was further stimulated when Schroeder published a provocative epidemiologic study in 1965 linking dietary cadmium to hypertension in the general population [23]. Because of the large number of people potentially affected by hypertension, a great deal of effort has since been expended investigating the effects of cadmium on the cardiovascular system.

The leading Cd ore producers in 1974 were the United States, Canada, Australia, Belgium-Luxembourg, Mexico and Peru, with production ranging from around 400 to 140 short tons (Peru) annually. The United States and Japan led the world in smelter production of Cd followed by the former Soviet Union, Germany, Canada, Belgium and other countries. World smelter production in 1974 totaled 1780 short tons, compared with 10,000 in 1958.

Disposition :

Cadmium, like mercury is easily vaporizable, and Cd^{2+} is similar to Cu^{2+} in ionic size and charge. Since Cd is a post transition metal. The electronic build up is in the inner orbital positions, while the number outer valance electrons remains constant. Normally Cd exhibits a maximum valance of + 2 and forms stable cationic salts. However, with its large number of inner electrons. Cd has a tendency to from outer orbital complexes with less electronegative elements involving covalent bonds. Cadmium forms tetrahedral complexes with a coordination number of 4. It forms halogen complexes such as $[CdX_4]^{2-}$ and $[CdX_6]^{4-}$. Cd is also amphoteric and forms stable salts such as sodium cadmate. Na_2 [Cd $(OH)_4$], in which the hydroxyl group can be replaced by water and monovalent groups. Cadmium resembles zinc in its electronic configuration and affinity toward organic ligands, but it has greater affinity than zinc to thiol groups and will replace zinc from some metal enzyme complexes.

However, Zn is bound more lightly than Cd to O-and N-containing ligands. The binding of Cd with S is stronger than that of any essential metals except Cu, among the toxic metals only Hg and Pb bind more strongly with S ligands than Cd. Cadmium has a high affinity toward hemoglobin and metallothionein, a protein present in mammalian kidney and liver. Cadmium binds to nucleotides in vitro and can presumably bind with nucleic acids. It forms stable chelates with some of the common chelating agents in vitro but not in vitro. Cadmium could not be removed from tissues with chelating agents which can mobilize zinc from tissues, apparently it is bound very firmly in the tissues.

Metabolism/ Essentiality :

Cadmium is not essential in human and animal nutrition. The biochemistry, metabolism and toxicology of Cd have been studied extensively, and excellent reviews are available [24-26]. The daily dietary intake of Cd by human adults is about 215 μg, Cd intake by inhalation is about 2 μg by non-smokers and about 20 μg by smokers. Cadmium is not required for enzyme although it can activates some enzymes. In general, it is inhibitory and acts as an antimetabolite for Zn.

The valence state of inorganic mercury profoundly influences the degree of absorption and even the pattern of distribution in the body. Cadmium occurs only in one valence state, +2 and does not form stable alkyl compounds or other organomettalic compounds of known toxicologic significance. The solubility of cadmium salts is highly variable. The halogen salts, sulfate, and nitrate are relatively soluble while the oxide, hydroxide and carbonate are insoluble in water.

The mammalian gastrointestinal absorption of Cd is low : 20% in rats [27] and goats [28], 5% in swine [29], and lambs [30], and 16% in cows [31]. In humans, Cd absorption was computed to be 3–8% [26]. It is influenced by the dietary levels of Zn and the solubility of the Cd salts.

Studies of cadmium absorption in man are limited but are consistent with animal studies. Tracer doses of radioactive cadmium administered with food to human volunteers were absorbed to the extent of 4.7 to 7 percent [32]. Numerous dietary factors enhance cadmium absorption, notably deficiencies in calcium, iron and protein. Calcium is actively absorbed by the small intestine. This process requires a low-molecular-weight calcium binding protein (CaBP), the synthesis of which is stimulated by dietary calcium deficiency. Recent evidence suggests that the increased CaBP activity induced by Ca deficiency may serve to enhance cadmium absorption as well as calcium absorption [33]. The enhancing effect of CaBP probably is counterbalanced by the influence of metallothionein, a low-molecular-weight protein whose synthesis is induced by cadmium, zinc and mercury. It has a repressor role in limiting the intestinal absorption of zinc and probably exerts a similar effect in regard to cadmium.

The absorption of Cd ions from the sites of parenteral injection into the blood is rapid and complete [34]. In the blood Cd^{2+} penetrates erythrocytes and is also distributed in blood plasma, Cd binds to serum proteins, especially α-globulins, and is readily distributed to other tissues [35]. The absorption of Cd^{2+} through the skin is very limited. The absorption from the lungs following inhalation of Cd mists is rapid and complete, and only insoluble salts such as CdS remains in the lung unabsorbed, these cause local inflammation and ulceration.

Most cases of acute Cd poisoning among industrial workers are owing to Cd absorption form the lungs. Retention of Cd in small quantities has been demonstrated in all animals tissues, greater amounts accumulate in the kidneys, liver, reproductive system and lungs, but the pancreas, aorta, esophagus and omentum also accumulate Cd under certain circumstances.

Irrespective of the mode of administration, Cd crosses the placental barrier in pregnant rats and hamsters, as shown by detectable amounts in the liver, brain and digestive tract of the newborn. More than 2.5 times the amount was found in the livers of the young born of test animals dosed with Cd while pregnant than in control animals [36, 37]. However, there is an efficient placental barrier against Cd in goats [38].

Cadmium is widely distributed elsewhere in the body at low concentrations relative to the liver and kidney. With in kidney there is a substantial gradation in concentration, progressing downward from outer cortex to inner medulla. Cadmium is highly cumulative. This is suggested by human autopsy data showing concentration rising to a peak in kidney at the age 50 and in other oranges somewhat earlier in life. This progressive accumulation of cadmium in the body over major fraction of the lifespan has also been demonstrated experimentally in animals. Beyond age 50 a decrease in the amount of cadmium in the kidney has been reported by several investigations. Steady-state concentrations of cadmium in blood occur relatively early in life under reasonably constant conditions of exposure. In workers newly exposed to a cadmium-contaminated environment, a new steady-state blood cadmium concentration was attained with in one year [39].

Excretion of Cd in mammals is slow and is predominantly fecal, however, excretion in the urine can be appreciable [40]. Using radioactive Cd in tracer quantities in goats, it was found that only 6% of an injected does was excreted in the first two weeks, most of it in the first three days and the rest was excreted over a long period of time [28]. The unabsorbed Cd (80%) on ingested dose excreted with in five days in the feces. The retention of inhaled

doses of Cd salts varies with the species 10-20% in mice and about 40% in dogs [41]. The slow excretion and prolonged retention of Cd in the tissues suggest that no homeostatic mechanism exists for Cd in animals [31, 34, 42]. The major route of cadmium excretion in man is generally stated to be the urine. This conclusion is based on a study of five volunteers who received single oral doses of radioactive cadmium [32.]

The urinary excretion of cadmium is of special interest because there is need for a biologic monitoring process whereby the degree of body contamination with cadmium can be assessed. It has already been pointed out that the concentration of cadmium in the blood fails in this regard. Blood cadmium equilibrates with any given level of exposure with in a year, while the total amount in the body keeps accumulating over a period of decades. Much the same situation has been noted in regard to the urinary excretion of cadmium. In the general population, there is practically no increase in cadmium excretion with age in spite of strong evidence that the body burden notably in the kidneys, increases markedly to age 50. By contrast in heavily exposed population groups urinary excretion does increase with age. A reasonable explanation for this difference has been proposed [43].

Toxicology :

As with mercury cadmium is a very toxic metal to all systems studies in man and animals, and has been responsible for a number of deaths. The major toxic phenomenon in man are respiratory and renal toxicity, seen principally in industrial workers, the "Itai Itai" disease complex reported from Japan, involving primarily elderly multiparous women, and finally the highly controversial hypertensive effect suspected to involve a large number of people in the general population. The major effects of cadmium poisoning are experienced in the lungs, kidneys and bones.

The principal toxic effects of cadmium inhalation are attributable to local irritation of the respiratory tract. Death is usually due to massive pulmonary edema. Signs and symptoms are delayed a few hours and consist mainly of irritation of the upper respiratory tract, chest pains, nausea and dizziness. Gastrointestinal effects e. g. nausea and diarrhea, may also occur. Acute effects of inhalation are bronchitis and pneumonitis and toxemia in the liver [44, 45]. Effects can be fatal in the dose, such as 8 mg m^{-3} of CdO fume, is inhaled for five hours [46]. In the case of oral intake the manifestations are nausea, vomiting, salivation diarrhea, abdominal cramps, vertigo and for large doses, loss of consciousness [47]. Death may occur with in 24 hours due to shock and dehydration or may be delayed one or two weeks following onset of various systemic effects, notably renal and cardiopulmonary failure. A lethal dose of cadmium would be > 350 – 500 mg [47].

Chronic inhalation of cadmium compounds as fumes or dust produce pulmonary emphysema, where the small airsacs of the lungs become distended and eventually destroyed reducing lung capacity. The effect becomes apparent after a number of years of occupational exposure [48-51]. Cadmium induced emphysema was first discovered in 1948 [44] and appears to be less common since the late 1970's [47].This is probably because of improved working conditions.

Both the chronic inhalation and oral intakes of cadmium affect the kidneys producing in the first instance proteinuria, similar to proximal tubule proteinuria [52, 53, 54]. The renal damage, which is first seen by the appearance of low molecular weight (MW 12,000 – 30,000) proteins in the urine, is caused by the impaired re-adsorption function of the proximal tubules. The tubules are part of the filtering system that separates waste materials, such as urea, creatinine and sulphate from necessary materials which are reabsorbed back into the blood stream. The low molecular weight proteins excreted are α_2^-, β_2^- and γ globulins, such as β_2 – micro globulin (MW ~ 11,800) retinal binding protein (MW ~ 21,000) lysozyme and γ- globulin L– chains [55, 56]. This type of

proteinuria is not specific to cadmium, and care is needed in population studies to have adequate controls and matched for age [57]. The most common measure of the renal effect is the amount of β_2^- micro globulin in the urea, and its presence is said to represent an adverse health effect. Retinal binding protein can also be used as a measure of the toxicity. A later, and may be independent effect, is the appearance of high molecular weight proteins, such as albumin and transferring from a glomerular dysfunction of the kidneys [44, 55]. Later effects of further renal damage is aminoacid uria, phosphate uria glucosuria and calcium in urine [37, 38]. The appearance of Ca^{2+} and PO_4^{3-} indicates that as a consequence of the damage, there is interference in the metabolism of the two ions [44] and this shows up in an increased incidence if kidney stones for people with cadmium poisoning [51, 54]. The critical level of cadmium in the kidneys is 100 – 300 $\mu g\ g^{-1}$ (ww) and a mean of 200 $\mu g\ g^{-1}$ (ww). In addition to dose the exposure time is also important [44, 55].

The dramatic toxic effect of cadmium is the development of "Itai-Itai" disease, where the outcome is osteomalacia, which is a softening of bones usually produced by a deficiency of vitamin-D. The early sings of the problem is pain in the joints, lumbago pains and pseudo-fracturing of the bones. It is an intensely painful disease leading to deformity of the bones [50, 58].

In the Jintsu river area of Japan, where the disease was first recognized in the 1950's and 1960's, it was the older women, who had been through a number of pregnancies, and had nutritional and vitamin-D deficiency, contracted the disease. Among the people of the Jintsu river valley who all consumed similar amounts of cadmium contaminated rice, middle-aged to elderly multiparous women were mainly affected.

The most prominent effects, osteomalacia with attendant spontaneous multiple bone fractures, have seldom been reported in cadmium poisoning of industrial origin. Despite this fact, the role of cadmium in the etiology of this disease is reasonably certain. For one thing cadmium in the food supply grown in the

area was extremely high. Further, the disease featured, in common with the industrial disease, both proteinuria and glycosuria. Finally, the disease has been reproduced experimentally in rats by combining dietary excess of cadmium with calcium deficiency [59]. The problem has been recognized elsewhere in the world, and cadmium is a contributing factor. Its intervention is probably adversely affecting the Ca^{2+}, PO_4^{3-} and vitamin-D metabolic in the body [44, 46, 52, 58] Administration of vitamin-D relieves the symptoms [58].

The estimated intake of cadmium by the women in the jintsu area, was 600 μg d^{-1} over periods as long as 20 years, more than 10 times typical intakes [44, 53]. Levels of cadmium in the rice were around 1 μg g^{-1}, and sometime as high as 3 μg g^{-1}. The close match between the incidences of the disease and levels of cadmium in the soil, used to grow the rice, is quite stricking [58]. Up to early 1981, the number of deaths reported numbered 66 with many more diagnosed or suspected to have the disease [60]. Other influences cadmium can have on human health are less well defined. Its effect on enzymes is to replace essential elements, such as zinc and therefore render the enzyme biologically ineffective. This takes place because of the competition between cadmium and zinc for the binding site on the enzyme, and where these are sulpher cadmium has a distinct chemical advantage being a softer acid than zinc [56.]

Perhaps the most controversial issus of all concerning human health effects of cadmium is the suggestion, first put forth in 1965, that cadmium has a significant role in the etiology of hypertension in the general population [23]. The initial study was purely epidemiologic persons dying from hypertension were found to have significantly higher concentrations of cadmium and higher cadmium to zinc ratios in their kidneys than people dying of other causes. Some people with hypertension have been found with elevated cadmium in their kidneys and arterial walls and an elevated Cd/Zn concentration ratio, but

whether this is causative is not known [46, 61]. Slight anemia has been associated with cadmium toxicity. This may occur because of competition between cadmium and iron in the body, giving the appearance of iron deficiency [44, 51]. The carcinogenic effect of cadmium has been established in animals. The situation of human beings is less clear, but there has been found a relationship between cadmium exposure in industry and incidence of prostatic cancer. A large scale epidemiological study seems warranted [47, 62]. Cadmium sulphide may have some mutagenic effects [48]. Testicular destruction has been induced in animals by cadmium, but there is no evidence that this occurs for human beings. The cadmium levels in the bonds of still births has been reported as being higher than in normal people. Whether cadmium is implicated is not clear [63.]

The main protein that cadmium is associated with is metallothionein, which has a stoichimetry of seven cadmium atoms per protein molecule [48, 51, 56]. Cadmium like some other metals induced the synthesis of metallothionein in the liver. It is likely that the metallothionein-cadmium complex is then transported to the kidney where it is absorbed by the proximal tubule cells. The acute effects of cadmium may arise from the metal not being bound to the metallothionein and chronic effects when the capacity of the metallothionein to bind cadmium becomes exceeded [56]. It is at the stage that cadmium becomes more evident in the urine. Chronic feeding of Cd at low levels to rats rabbits, lambs, pigs, claves and poultry causes diminished growth and feed consumption. Rats tolerate 10 ppm Cd as $CdCl_2$ in their drinking water, and show no visible symptoms of toxicity, but their longevity is reduced [64]. Loss of weight was observed in rabbits, which were fed 40 – 40 mg Cd kg-1 as $CdCl_2$ [65]. Growth retardation was observed in lambs fed 60 ppm Cd, in pigs fed 450 ppm Cd [29], and in calves fed 640 ppm Cd [66], dietary Cd at 1350 ppm caused complete cessation of growth in pigs, and 2560 ppm caused heavy mortality in calves.

Dietary Cd affects the intracellular distribution of Zn and Cu in rats [67]. Cadmium inhabits enzymes associated with Zn by competing with Zn and displacing it from metalloenzyme such as alkaline phosphatases in the kidney and prostate of guinea pigs are inhabited by Cd [68]. Dietary Cd inhabits Zn uptake by the prostate, tastes and other tissues [69]. There are resemblances among the symptoms of Cd in toxication and Zn deficiency in several species, dietary Zn supplements decrease the severity of Cd intoxication and in some instance, prevent Cd toxicity [67, 70, 71]. In rats 50 ppm Cd in diet causes depletion of Fe in the liver [72], cadmium induced anemia in chicks, due to defective intestinal absorption of iron [73]. Cadmium interferes with the metabolism of copper by reducing its absorption [38] and by increasing its urinary excretion. Reduced ceruloplasmin activity was observed in rats fed 1.5 μg Cd g^{-1} diet with normal Cu content, 3μg Cu g^{-1} diet, increased Cd intake 6 and 18 μg Cd g^{-1} diet, considerably reduced plasma and liver Cu concentration and serum ceruloplasm activity [74]. Bone malformations from simple Cu deficiency were also noted. Similar effects of Cd intoxication or Cu were observed in pregnant ewes and lambs [75].

Cadmium intoxication in rets fed 100 μg Cd g^{-1} diet inhibited Fe absorption and hemoglobin formation leading to anemia, growth failure and poor bone mineralization [67] and similar Cd and Fe interaction with occur in chicks and Japanese quail. In birds dietary supplementation with Fe^{2+} or ascorbic acid reverse the effects of Cd intoxication. The inverse relationship beween the Cd and Fe contents of duodenal mucosa, following Cd administration, suggests that the interaction involves competition between Fe and Cd for mucosal binding sites [76]. The antimetabolite of activity of Cd^{2+} causes destruction of microvilli of the duodenal mucosa and extensive cytoplasmic vacuolation in the gastrointestinal tract. Bone disease is a recognized symptom of industrial exposure to Cd [77]. Serum Ca decreases following intravenous injection of $CdCl_2$, Cd concentration in mice fed dietary Cd are greater when the Ca intake is low [78].

In lactating cows fed 3g Cd as $CdCl_2$ daily, Cd accumulated in the mammary gland and milk production was decreased drastically, but Cd was not incorporated into milk protein and could be found only in trace amounts, < 0.1 ppm, in the milk [31]. Generally, ruminants absorb very little ingested Cd, and only trace amounts of absorbed Cd are found in the milk, but in rats ingested Cd accumulates in the mammary tissue, and part of it is expressed in the milk.

Excess of Cd causes gonadal tissue damage in experimental animals and sterility in both sexes. Cd also causes testicular antrophy, cessation of spermatogenesis, and vascular changes in the ovary lead to sterility, irrespective of the mode of administration. Intratesticular injection of Cd damages the male gonads in all species and permanently stops spermatogenesis [79], this chemical castration was studied for possible use in practical animal husbandry.

The mechanism of Cd toxicity in mammals is complex and is yet to be understood. Changes in membrane permeability leading to abnormal transport of metabolites and minerals, antimetabolite effects, derangement of cellular energy metabolism, and binding to cellular respiratory components are considered to be some of the mechanisms of Cd toxicity in mammals [80]. Confirms that the primary action of Cd is on tissue endothelium.

Cadmium inhabits ATPase of myosin [81], pulmonary alveolar macrophages and cell membranes [82]. In mice dietary Cd increased the liver and hard tissue levels of malic dehydrogenase and glucose-6-phosphate dehydrogenase [83]. Cadmium sulfate at 0.5 mg mL^{-1} of blood causes invitor multiple cytophagy or phagocytosis of the erythrocytes and thrombocytes by the leukocytes and alteration in cellular consistency, especially karyoplasmatic alterations of absorbing elements [84]. In massive Cd doses, multiple cytophagy could also occur invivo. Cadmium chloride significantly increased cAMP–syathesizing enzyme in the hepatic tissue of rats [85]. Changes in the cAMP levels can attect carbohydrate metabolism in the various tissue that are largest of Cd intoxication.

Hygienic Standards of Permissible Exposure :

In 1977, Fairhall recommended TLV for CdO production is 0.05 mg Cd m^{-3} with an A_2 notation classifying this operation as presenting industrial substances suspect of carcinogenic potential for workers. For CdO fume, the ceiling value is 0.05 mg Cd m^{-3}. The NIOSH criteria document for Cd (1976), recommended a limit of 40 μg Cdm^{-3} determined as a time – weighted average exposure concentration for up to a 10 hr work day, 40 hr work week, or at a ceiling concentration of 200 μg Cd m^{-3} for any 15 min period. Other countries former Czechoslovakia, Japan, Poland, Rumania, Hungary, Bulgaria and Russia have adopted 1 μg Cd m^{-3} as Cd or CdO. Finland (1972) set 0.01 μg Cd m^{-3} for the fume.

Treatment and Therapy :

There is surprisingly little information concerning the management of cadmium poisoning. In the ease of Itai-Itai, large doess of vitamin-D given over a period of months are effective in relieving painful symptoms and, in some instances at least, therapy reduces the incidence of spontaneous fracture [86]. There is no therapeutic approach being utilized in the management of industrial cadmium poisoning. Chelating agents have been studied in regard of their efficacy in the mobilization of cadmium. Dimercaptopropanol (BAL) has been shown to increase the uptake of cadmium by the kidney and to increase its nephrotoxicity. A similar effect has been noted regarding Ethelenediamin tetraacetic acid (EDTA).

Ethylenediamintetraacetic acid (EDTA [87, 88, 89, 90] and diethylenetriamin-penta acetic acid (DTPA) [91] have been shown to reduce acute experimental poisoning but actually to worsen chronic poisoning [87, 88, 89, 90]. More

recently it has been shown [92] that simultaneous oral administration of nitrilotriacetic acid (NTA) can reduce rat mortality from orally administered Cd (64 and80 mg kg^{-1} as $CdCl_2$). NTA also increases urinary and fecal excretion and reduces Cd deposition in liver, kidney and muscle. The simultaneous administration requirement however, considerably reduces the practical usefulness of this procedue.

Pyrindoxine (vitamin B_6) administered to young femal rats with hypochromic, macrocytic anemia from dietary Cd at 1000 ppm resulted in an exaggeration of the Cd induced anemia [92]. The unexpected finding supported the conclusion that Cd toxicity impairs Fe metabolism, making the rats Fe deficient, a finding demonstrated by others [93, 94]. Therapy for cadmium poisoning is not readily available. For example removal of cadmium by a complexing agent takes the metal through the kidneys, which may add to the renal effects of the element [49, 50].

(C) ENVIRONMENTAL POLLUTION

Before entering into a brief discussion of Environmental pollution author's opinion it will be wise to give some definition of some useful terms commonly met with the discussion.

(a) **Definitions :**

(i) **Environmental Pollution** : "Environmental pollution is partly rapicity and partly a conflict of interest between the individual multimillions of individuals and the commonwealth, but largely, in our generation it is the exaggerated effects of specialization with no sense of ecology i. e. the balance of nature".

····· G. G. McClellan.

Environmental pollution is any degree of contamination of air, water, soil or food which is likely to produce a significant adverse health effect to a significant number of persons in a forseeable period of time.

(ii) **Pollutant :** A substance present in nature, is greater than natural abundance due to human activity, which ultimately has a detrimental effect on the environment and therefrom on living organisms and mankind.

Example : Lead, chromium, mercury, sulphur dioxide, carbon dioxide etc.

(iii) **Contaminant :** A material which does not occur in nature, but is introduced by human activity into the environment, affecting its composition. A contaminant is classified as a pollutant when it exerts a detrimental effect.

Example : Chlorine gas, Bromine gas, etc.

(iv) **Receptor :** The medium which is affected by a pollutant. Man is the receptor of photochemical smog causing irritation of the eyes and respiratory tract. Trout fingerlings are receptors of dieldrin in water which causes their death.

(v) **Speciation** : The different chemical forms or species of inorganic, organic or organo-metallic compounds present in the environment. It is important to identify the chemical species of a pollutant since some species are more toxic than others. Thus, chromium (VI) is much more toxic than chromium (III).

(vi) **Dissolved Oxygen (DO)** : Oxygen is a vitally important species in water. It is consumed by oxidation of organic matter/reducing agents etc. It is an important water quality parameter. The optimum value for good water quality is 4-6 mg L^{-1} of DO, which ensures healthy aquatic life in a water body. Lower DO values indicate water pollution.

(vii) **Threshold Limit Value (TLV)** : This indicates the permissible level of toxic pollutant in atmosphere to which a healthy industrial worker is exposed during an eight-hour day without any adverse effect. TLV values for Cd, Cr, Be, Al and Zn are 0.05, 0.05, 0.002, 10.0 and 1.00 mg m^{-3}, respectively.

(viii) **Tolerance Limit** : Tolerance is defined as ability to endure the continued and for increasing administration of a toxicant. Tolerance is also the capacity of an organism to exhibit less response to a test dose of a chemical than it did previously to the same dose.

(b) **Sources and Distribution of the Contaminants :**

The main sources of contaminants in the atmosphere can broadly be divided into natural and anthropogenic. The former includes windborne dust, forest fires, volcanic eruptions, sea mist plant decomposition products etc. The anthropogenic source are mines, factories where the metals or contaminants are processed and factories where different metal compounds are manufactured. Modern industrialization has introduced harmful metals into the environment by redistributing them immobilized ones and minerals. Thus main entnropogenic sources of contamination of the environment arise from manufacure from their ores from which industrial waste airborne emission and industrial products take the leading role in contaminating the biosphere. This can be illustrated with the following typical diagram.

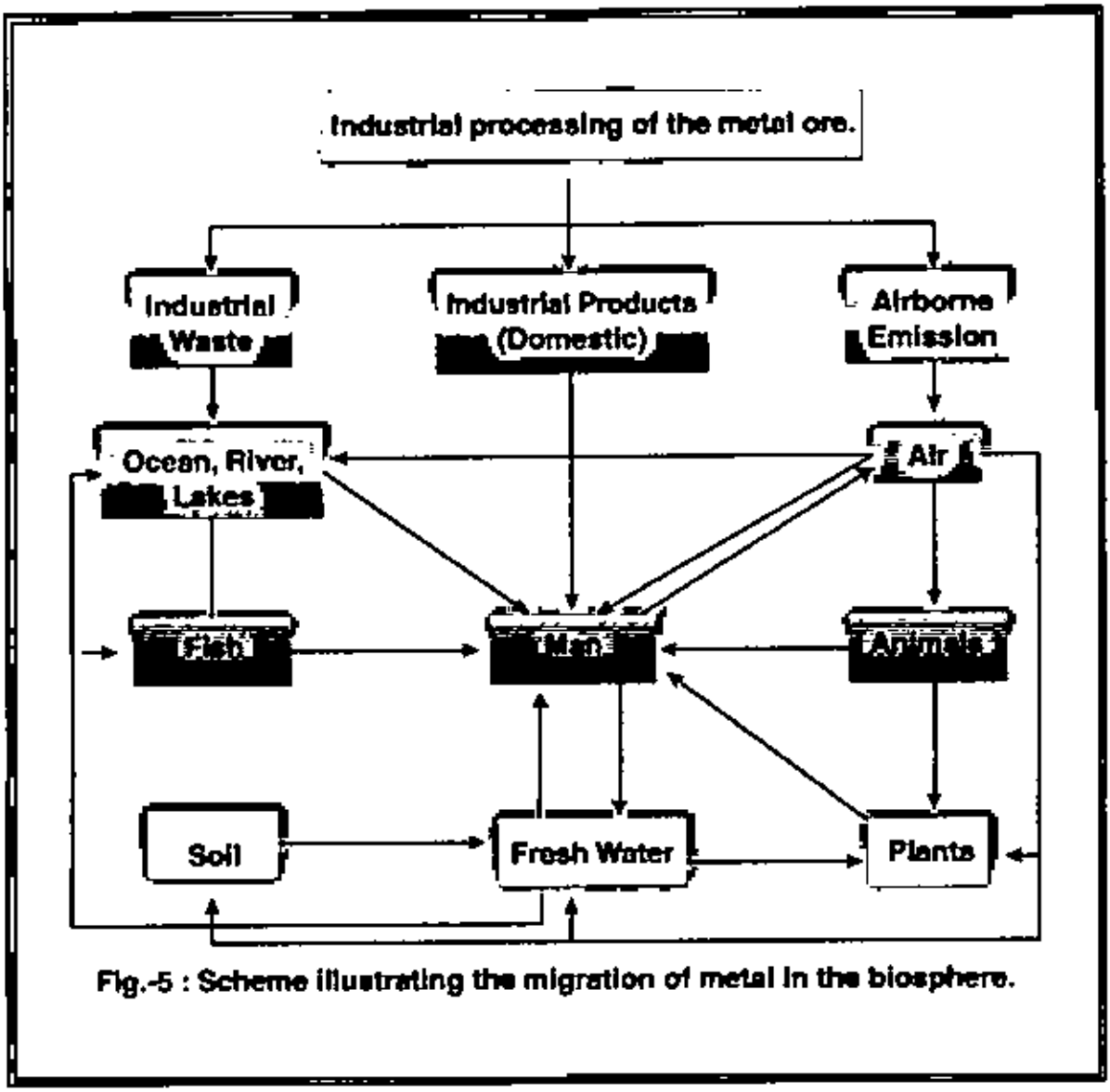

Fig.-5 : Scheme illustrating the migration of metal in the biosphere.

(c) **Public Health and Pollution :**

Mankind has been confronted with pollution problems since early times. Until the end of the 19th century, it was universally accepted that health was equivalent to the absence of disease. It was only at the beginning of the present century that, thanks to achievements in the social field, a more positive concept of health began to crystallize. It came to be recognized as a state of physical, mental and social wel-being, a definition which is in fact embodied in the constitution of WHO adopted in 1948.

The general public has become increasingly concerned about the pollution of the environment and in number of countries the problems caused by pollution have been met by a whole range of statutory and regulatory provisions aimed at protecting of public health. The term pollution is generally defined as the presence in the ambient environment of chemical, physical or biological factors capable of inducing disturbances in the normal physiology and functioning of human organs. If we bear in mind that the respiratory system and digestive tract are merely extensions (without the body) of the external environment, the tendency to associate the pollution of foodstuffs and drugs with that of air, water and soil will be readily understood.

The fields in which pollution can occur are manifold, since no activity can be preformed without entailing pollution. It is precisely this linkage between human activities and the resultant pollution that constitutes the nub of the problem. It is at this juncture that we begin to reflect on the protection of basic human rights.

Worker's demands during the last century and especially in the last 50 years, have lead to the recognition of a large number of occupational diseases associated with the presence of harmful agents in the working environment. Measures to protect workers against occupational hazards have shown a remarkable expansion in recent years.

The effects of pollution on individual depends on various factors. These include the toxicity or harmfulness of the pollutants involved, their concentration and the conditions under which they exert their effect. Having in mind that the human being has a remarkable capacity for adaptation and recovery following exposure to external agents, one can judge how complexing the problems are.

The rising incidence of bronchial diseases among the workers and the populations of certain large cities is certainly connected with the increase in the emission of sulfur dioxide from factories, plants and heating installations.

The development of lung tumors in cities could be the consequence of air pollution caused by motor vehicles or from certain domestic sources.

Pollution of the sea was responsible for the notorious outbreak of mercury poisoning among the population living around Minimata Bay in Japan. Prior to "the epidemic intoxication" in 1971/2 which was one of the most catastrophic with 6530 cases of poisoning with methylmercury in farmers and their families in Iraq, about 1000 cases had been ascribed in the world as methyl and ehtylmercury poisoning.

Cadmium and poisoning with cadmium between workers and Itai-Itai disease caused by cadmium in general population are also known in Literature.

A Public Health Service in USA study of the chromateproducing industry indicates that the incidence of a whole service of ill effects ranging from dental caries to bronchiogenic cancer, was abnormally high.

(d) The Growing Hazards :

The increasing demand of chemicals in day-to-day life and the residue of these compounds are likely to change the composition of air, water, soil, food chain and living tissues. The persistence of DDT, bis-chloroisopropyl ether, polyvinyl chloride, trace elements, etc, is an alarming concern and hence needs a through investigation of their impact on the total environment.

In this content the disastrous Bhopal gas tragedy needs a worthy mention. The leakage of methylisocynate gas claimed the lives of several thousand people. People are still suffering from its after affects. The dangerous gas did not even spare the plant kingdom. Ammonia gas escaped from a tank car which burst at Ghorasal Fertilizer near Dhaka in August, 1991 and killed eight persons working in a nearby room. The release of waste water from Ghorasal and Polash Fertilizer claimed the lives of fishes and aquatic animals and polluted the water of river Shitalakaya. The release of carbon monoxide gas from automobile exhaust, dust particles from Cement Facory at Chittagong and

chlorine gas from different industries of Bangladesh, show the negligence of the governing bodies. Evidence of contamination of products used in food packing and pipes for drinking water [95] by unpolymerised vinylchloride monomer have also been reported.

An examination of the Location of industries show that Paper Mills are situated on the bank of rivers Karnaphuli, Surma, Padma and Bhairab. These mills are established long ago and do not have elaborate effluent processing systems. They discharge alkali hypochlorite, chlorinated/ sulphonated lignin compounds, etc in the rivers. Urea and TSP fertilizer factories are situated on the banks of the river Karnaphuli, Kushiyara, Maghna and Shitalakaya. These industries too were established at a time when awareness for preserving the environment was not much. As a result these industries too have only limited effluent processing arrangement. Steel and Oil refinery industries have scarcely and effluent treatment systems. Effluents from Tannery industries, mostly located near cities of Chittagong and Dhaka, find its way to the adjoining water systems. Tannery industries use chromium salts which are toxic even in low doses. No measure worth the name have so far been taken to regulate discharge of these toxic materials in the rivers. Sugar mills, dotted around North West Part of the country, do not have any effluent processing system.

Hence there is a great need of regulation of environmental protection act of banning the use of hazardous compounds recklessly in Bangladesh.

Elemental contents in the human body and environmental water quality standard for Bangladesh are summarized in the Table 1 and 2, respectively

TABLE-1 : ELEMENTAL CONTENT IN THE HUMAN BODY[a].

Element	Serum, ppm	Urine	Tissues ppm[b]
Li	0·01		
Na	3200	1000-5000 mg/day	0·07 g/gN
K	120-214		
Rb			20-200 (dry)[c]
Be			0·00012 (liver)
Mg	18-29(ave 22)	60-120 mg/day	300-500
Ca	90-100	96-800 mg/day	60-90
Sr		0·4 mg/day	0·1-0·5 (dry)
Ba			0·02-0·10 (dry) 1·0 in lung
Ti			0·3-0·6 (dry) 10 in lung
V	0·005 ± 0.008		<0·02-0·03 (dry)[d] 0·6 in lung
Cr	0·03		0·01-0·13[e] 0·36 in spleen
Mo	0·10-0·16[e]	0·01 - 0·03 mg/day	0·1-0·2 (dry)
Mn	0·01-0·02	0·04 - 0·07 mg/day	0·2-1·7
Fe	0·80-1·6 (ave 1·25) men	0·1 - 0·3 mg/day	
	0 65-1·3(ave·0·90) women		
Co	0 00007-0·017 (Whole blood)	0·001-0·007 ppm	0·1-0·2 (dry)
Ni	0·025(range 0·001-0.08)	0·025 mg/day (range 0·007-0·04)	
Cu	1·05-1·10		5-20(dry), 10-15 in liver
Ag			<0·01-0·2 (dry)
Au			<0·1-1 (dry) (occurrence < 20%)
Zn	1·2	0·3-0·6 mg/day	12-100
Cd	**0·0033-800 ± 0·0024**	**0·002-0·02 ppm**	**0·2-0·8, 2·0-6·0 in kidney**
Hg		<0·03 ppm	
B			0·5-1 (dry)

Element	Serum, ppm	Urine	Tissues ppm[b]
Al	0·13-0·17	0·05 mg/day	0·2-0·6, 20-60 in lung
Tl[1]	3-17	>0·35 ppm	
Si			20-40 (dry), 400 in lung
Sn			5-30 (ash)
Pb	0·3-04[9]	0·01-0·07 mg/day	1-10 (dry)
As	0·04-0·2	≤0·1 ppm	0·2-0·3
Bi	0·02		<1 (ash)
Se	0·14		0·2-0·6
P	0·3-0·65	0·4-1 3 g/day	0·2-0·45
$N(asNO_1^-)$	0·5-1·0		0·2-0·6

Source : [a]G.D. Christian, *Analytical Chemistry*, 4th Edn. John Wiley and Sons, New Yourk, 1986, P, 531.

[b]Fresh weight, [c]Rats,[d]Organs, [e]Sheep and Cattle, [f]Concn, during thallium poisoning, [g]Whole blood.

TABLE-2 : STANDARD VALUES FOR WATER.

Standard value									
Parameters	**Unit**	**Drinking Water**		**Recreational**	**Fishing**	**Industrial**	**Irrigation**	**Livestock**	**Coastal**
Determinants		EQS[a]	WHO[b]	Water	Water	Water	Water	Water	Water
pH		6–8	6–8·5	NYS	NYS	NYS	NYS	NYS	NYS
Aldehyde	mg/L	NYS	NYS	< 20	NYS	NYS	NYS	NYS	NYS
Aluminium	mg/L	NYS	NYS	NYS	20–100	NYS	1	NYS	NYS
Ammonia (NH_3)	mg/L	0·5	0·5		0·2-5	NYS	3	NYS	NYS
Elemental Nitrogen (as N)	mg/L	NYS		NYS	1·2	NYS	15	NYS	60
Arsenic	mg/L	0·05	0·05	0·2	NYS	NYS	1	1	1
Barium	mg/L	0·5		NYS	NYS	NYS	NYS	NYS	NYS
Benzene	mg/L	0·01	10	NYS	NYS	NYS	NYS	NYS	NYS
Bicarbonate	mg/L	NYS	339	NYS	NYS	NYS	NYS	500	NYS
BOD	mg/L	0·2	6·0	3	6	10	10	NYS	NYS
Boron	mg/L	1·0	1·0	NYS	NYS	NYS	not <1	NYS	NYS
Cadmium	**mg/L**	**0·005**	**0·01**	**NYS**	**NYS**	**NYS**	**0·01**	**0·5**	**0·3**
Carbondioxide	mg/L	NYS	NYS	NYS	6	NYS	NYS	NYS	NYS
Chloride	mg/L	150–600	500	600	600	NYS	600	2000	NYS
Calcium	mg/L	75	750	NYS	NYS	NYS	NYS	700	NYS
Carbon tetrachloride	mg/L	0 01	5	NYS	NYS	NYS	NYS	NYS	NYS

Standard value									
Parameters	**Unit**	**Drinking Water**		**Recreational**	**Fishing**	**Industrial**	**Irrigation**	**Livestock**	**Coastal**
1, 1-Dichloro-ethylene	mg/L	0·001		NYS	NYS	NYS	NYS	NYS	NYS
1, 2-Dichloro-methylene	mg/L	0·03	NYS	NYS	NYS	NYS	NYS	NYS	NYS
Tetrachloroethylene	mg/L	0·03		NYS	NYS	NYS	NYS	NYS	NYS
Trichloroethylene	mg/L	0·09		NYS	NYS	NYS	NYS	NYS	NYS
Pentachlorophenol	mg/L	0·03	0·001	NYS	NYS	NYS	NYS	NYS	NYS
2, 4, 6-Tri-chlorophenol	mg/L	0·03		NYS	NYS	NYS	NYS	NYS	NYS
Chlorine (residul)	mg/L	0·2	1·0	0·3	<0·01	NYS	NYS	NYS	2
Chloroform	mg/L	0 03	10	NYS	NYS	NYS	NYS	NYS	NYS
Chromium (Cr^{6+})	mg/L	0·05	0·05	0·05	NYS	0 5	NYS	NYS	NYS
Chromium (Total)	mg/L	0·05	0·05	NYS	0·05	NYS	NYS	NYS	NYS
COD	mg/L	4	4	4	NYS	3-10	NYS	NYS	8
Coliform (Faocal)	n/100	n/	0		NYS	NYS	10	NYS	NYS
Coliforms (Total)	n/100	n/	2'	200	5000	NYS	1000	100	1000
Color	Hazen Unit	15		Clear	Normal	Normal	Normal	Normal	Normal
Copper	mg/L	1	1·0	NYS	<0·4	NYS	0 2	NYS	0·3
Cyanide (as CN)	mg/L	0·1	0·05	0·1	NYS	NYS	NYS	NYS	0·2
Detergente	mg/L	0·2		NYS	NYS	NYS	NYS	NYS	NYS

Standard value									
Parameters	**Unit**	**Drinking Water**		**Recreational**	**Fishing**	**Industrial**	**Irrigation**	**Livestock**	**Coastal**
DO	mg/L	6	4–6	4-5	4-6	5	5	4-6	6
Fluoride	mg/L	1	1 5	1·5	NYS	NYS	NYS	4	NYS
Formaldehyde	mg/L	NYS		NYS	NYS	NYS	NYS	NYS	NYS
Hardness ($CaCO_3$)	mg/L	200-500	500	NYS	80-120	250[b]	NYS	NYS	NYS
Hydrogen Sulfide	mg/L		10			1-5[c]			NYS
Iron	mg/L	0·321[c]	0 3	NYS	NYS	0·5[d]	NYS	NYS	NYS
Kjeldahl nitrogen (Total)	mg/L	1	1	1	1	NYS	NYS	NYS	NYS
Lead	mg/L	0·05	0·05	NYS	0·05	2·01	0·1	0·05	0·2
Magnesium	mg/L	30-50	30	NYS	NYS	NYS	NYS	NYS	NYS
Manganese	mg/L	0 1	NYS	NYS	0·1-1[f]	2	NYS	NYS	NYS
Mercury	mg/L	0·001	0·001	NYS	0 001	NYS	NYS	NYS	NYS
Nickel	mg/L	0·1	0 2	NYS	NYS	NYS	0·5	NYS	0 2
Nitrate (as N)	mg/L	10	13	NYS	NYS	NYS	NYS	250	NYS
Nitrate (as NO_2)	mg/L	0·1	0·1	NYS	0·03	NYS	NYS	None	NYS
Odour		Odour		unobjectionable	Normal	Normal	Normal	Normal	Normal
Oil and Greas	mg/L	0 01	0·01	0·1	0·1	NYS	NYS	NYS	NYS
Phosphate (as P)	mg/L	0·01	0·8	0·05	0·8	0 8	0·2	0·1	NYS

2 per 100 mL in two consecutive samples or in more than 100 of the samples examined for drinking water.

(a) For boiled feed water depending on boiler pressure.

(b) For boiler feed water 2-40 mg/L depending on boiler pressure, tanning 50-130 mg/L.

(c) For cooling water – 5 mg/L. For air conditioning water – 1 mg/L.

(d) Textile dyeing 0·25 mg/L, tanning 0·2 mg/L.

(e) 2 in some areas the maximum tolerable limit may be upto 5 mg/L in absence of better source for drinking water.

(f) For air conditioning water – 0·5 mg/L, for textile dyeing 0·2 mg/L.

*** NYS-Not yet sustainable.**

Source : "Environmental quality standard for Bangladesh, Department of Environment, People's Republic of Bangladesh, 1991.

WHO-World Health Organisation (International)

(D) AIM OF THE PROJECT

The choice of any analytical methods depends on the sensitivity, selectivity, accuracy, availability of reagents, cost effectiveness of instruments and the time required for analysis as well as safety and easeness of operation. Among various modern trace analysis techniques employed in solution, molecular absorption spectrophotometry has been rated to be one of the most usefuls powerful and successful tools recognized today. In some cases, it is the only suitable technique. Spectrophotometry is very sensitive so that sometimes picogram (10^{-12}g) per gram levels can be determined. It encompasses practically all the fields of chemical science and is so broad that it can be rated as a versatile technique. The key to the wide success of spectrophotometry in varied fields of chemical analysis lies in its manifold advantages, compared to any modern trace and ultratrace analytical technique.

Cadmium in trace amounts is industrially important. Cadmium is becoming an ever more widely used metal in industry. Cadmium metal is used in protective coatings for iron, copper and steel. Cd-electroplated parts are used in radios and television sets. Telephone wires are made of Cu-Cd alloys and Ni-Cd rechargeable batteries are extensively used in electronic equipment. Cadmium oxide is used in storage batteries, Cd-Ag alloys, semiconductors, photography, lithography, painting and dyeing and cadmium tungstate in X-ray screens, scintillation counters etc.

Cadmium is not essential in human and animal nutrition, but its toxicity is tremendously dangerous. Cadmium is a very toxic metal to all systems studies in man and animal, and has been responsible for a number of deaths. The most serious situation being the disease called "Itai-Itai" disease. The major effects of cadmium poisoning are experienced in the lungs, kidneys and bones. Acute effects of inhalation are bronchitis and pneumonitis and toxemia

in the liver. The acute effects of oral intakes of cadmium are excess salivation, nausea, vomiting, abdominal pains, diarrhea, vertigo and for large doses, loss of consciousness. Chronic inhalation of cadmium compounds as fumes or dust produce pulmonary emphysema. The industrial waste from an upstream cadmium mine was response for the contamination of food and drinking water. The carcinogenic effect of cadmium has been established in animals. Testicular destruction has been induced in animals by cadmium. Cadmium poisoning occur in animals manure, sea-food especially oysters and commercial phosphate fertilizers. Therefore, its accurate determination of trace level using simple and rapid method is of paramount importance.

Substances those do not absorb electromagnetic radiation in the visible range are colorless. These substances, hence not determinable, as such by visible spectroscopic methods. The project aims at the development of such a method for the quantitative determination of trace and ultra trace amount of cadmium in above spectral range.

The analysis of colorless substances by visible spectroscopy is not new, reacting the colorless analyte with a suitable reagent, a color product is produced and measured optically. As long as the product concentration is directly proportional to that of the analyte the measurement of the color intensity ultimately leads to the determinetion of the analyte. A method of calibration enable the estimation of the analyte. For the determination of cadmium only a few example of such method is cited in the literature, but these methods are limited by the complexity of the procedure, low sensitivity, less selectivity due to many interferences, temperature and pH dependent and unfavourable detection limit.

The Ultimate Aims of Present Dissertation are Primarily :

(a) To introduce a good spectrophotometric reagent through novel reaction techniques.

(b) To develop the non-extractive, direct spectophotometric method in very simple, rapid and highly selective and sensitive ways, particularly for some inorganic poisons such as cadmium for which either spectrophotometric methods are non-existence or scarce in literatures.

Finally, the aim af this study was to develop a simple spectrophotometric method for the determination of cadmium with 1, 2-dihydroxyanthra quinone - 3- Sulphonic acid, sodium salt (alizarin red s). The method was optimized individually and results of the measurements were checked by comparison with Convential analysis. Alizarin red S has been reported as spectrophotometric reagent for arsenic (v) but has not previously been used for determination of cadmium in spectrophotometic method. The present thesis deals with successful attempt toward the establishment of new type of spectrophotometric reagent. In the very sensitive procedure proposed here alizarin red S reagent complexed with cadmium.

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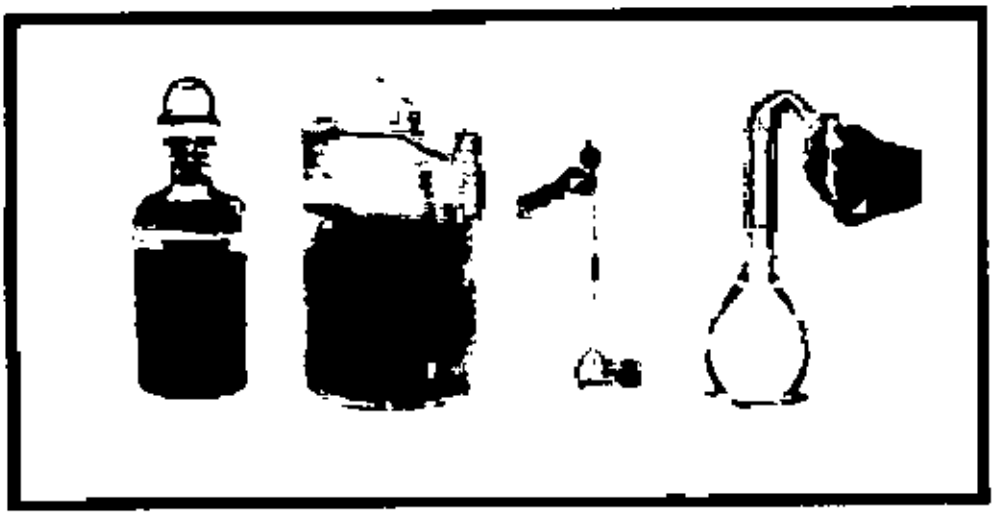
PART-II



EXPERIMENTAL SECTION

(A) REVIEW ON SPECTROPHOTOMETRIC METHOD OF CADMIUM.

(B) SPETROPHOTOMETRIC DETERMINATION OF TOXIC ELEMENTS IN AQUEOUS MEDIA.

(I) INTRODUCTION

(II) EXPERIMENTAL

(III) RESULTS & DISCUSSION

(IV) APPLICATIONS

(V) CONCLUSION

REFERENCES

(A) REVIEW ON SPECTROPHOTOMETRIC METHODS OF CADMIUM

Some principal physical properties of **cadmium** (Cd) are :

Discovery	: 1817 (Stromeyer, isolated in the free state from the Zinc ores.)
Atomic number	: 48
Electronic configuration	: $[Kr]\ 4d^{10}\ 5s^2$
Atomic Weight	: 112·40
Oxidation states chiefly	: + 2
Maximum allowable concentration (MAC)	: 0·05 mg Cd m^{-3} as CdO

Normally Cd exhibits a maximum valence of + 2, amphoteric and ionic character and forms stable cationic salts.

A few compounds of Cd exist in which the valence is + 1. Cadmium forms tetrahedral complexes with a co-ordination number of four. It forms halogen complexes such as $[CdX_4]^{2-}$ and $[CdX_6]^{4-}$; Cd is also amphoteric and forms stable salts such as sodium cadmate, $Na_2[Cd(OH)_4]$, in which the hydroxy groups can be replaced by water and monovalent groups. Cadmium is becoming an ever more widely used metal in industry.

The middle-aged human adult contains about 50 mg Cd in his body, one-third is in the kidneys and the liver, lungs, and pancreas are the other sites of Cd storage. Oysters contain about 3·75 μg Cdg^{-1} (wet weight), wheat and rice proteins also contain appreciable Cd. Cadmium may be stimulatory in mammals, but it is not considered to be essential. It is carcinogenic. The main symptoms following inhalations are persistent choking, coughing, leading to

pulmonary emphysema and bronchities, damage to renal tissues and olfactory nerves subsequently occurs. The major effects of cadmium poisoning are experienced in the lungs, kidney and bones. The acute effects of oral intakes of cadmium are excess salivation, nausea, vomiting, abdominal pains, diarrhea, vertigo and for large doses, loss of consciousness [1, 2]. Cigarette smoke inhalation is another source of exposure. The total cadmium in cigarette smoke varies from 15 to 18 μg per 20 cigarette, this represents 70% of the Cd content of cigarette tobacco [3].

Cadmium is an industrial health hazard, because cadmium dust, fumes and mists pollute the atmosphere. A dietary source of Cd intoxication is seafood, especially oysters. Extensive food processing and refining raise Cd levels in wheat and rice. The industrial waste from an upstream cadmium mine was responsible for the contamination of food and drinking water which caused "itai-itai" disease in Japan.

Cadmium is becoming an ever more widely used metal in industry. Cadmium metal is used in protective coatings for iron, copper and steel; Cd-electroplated parts are used in radios and television sets. Telephone wires are made of Cu-Cd alloys and Ni-Cd rechargeable batteries are extensively used in electronic equipments. Metallic Cd and CdF_2 act as good neutron absorbers in nuclear reactors. Cadmium oxides which is used in storage batteries Cd-Ag alloys, semiconductors, phosphors and ceramic glazes. Cadmium chloride and bromide are used in photography, lithography, calico printing and dyeing, and cadmium tungstate in X-ray screens, scintillation counters, and phosphors. Cadmium salts were used in some parts of the world as antihelminthics, ascaricides, nematocides and antiseptic in veterinary medicine, but these used are obsolete. Cadmium sulfide is used in treating seborrheic dermatitis.

Cadmium intoxication is caused mainly by environmental contamination accumulation of Cd containing scrap and commercial phosphate fertilizers.

At present few analytical techniques with sufficient sensitivity and selectivity are available for the determination of the trace levels of cadmium. Cadmium in the environmental and biological samples has been determined by NAA [57], ICP-atomic emission spectrophotometry [58], AAS [59] and solvent extraction spectrophotometry [4-32]. The first two methods are disadvantageous in terms of cost and instrumental used in the routine analysis. AAS is often lacking in sensitivity and affected by matrix conditions of samples such as salinity. Solvent extractive method are highly sensitive but are generally lacking simplicity. Although molecular spectrophotometry is one of the most powerful trace and ultra analytical techniques its application to the determination of cadmium has been practical barred due to other metal ion. Updated literature survey reveal that there is a few non-extractive spectrophotometric methods base on use of various reagents are reported for the determination and detection. Some of these methods are not sensitive or suffer from interference. The proposed method using Alizarin Red S not only is one of the most sensitive method for the determination of cadmium but also is excellent in terms selectivity and simplicity. Therefore this method will be successfully applied to the monitoring of trace amount of cadmium in environmental, biological and soil samples. This technique can also be used to determine trace concentration of cadmium in different samples matrics.

M. Jamaluddin Ahmed et al. [4] proposed a method for non-extractive spectrophotometric determination of cadmium by morin. A direct highly selective spectrophotometric method for the determination of cadmium with morin has been developed. Morin reacts in slightly acidic 50% ethanolic media (0·0001 – 0 0009 M H_2SO_4) with cadmium to give a deep-yellow chelate which has an absorption maximum at 436 nm. The average molar absorptivity and Sandell's sensitivity were found to be $2{\cdot}28 \times 10^3$ mol^{-1} cm^{-1} and 10 ng of Cd cm^{-2}, respectively. The reaction is instantaneous and absorbance remains stable for 48 hrs. The color system obeys Beer's law from 0·1–50 μg mL^{-1} of Cd, the stoichiometric composition of the chelate is 1 : 2 (Cd : morin). The

interference from over 50 cations, anions and complexing agents has been studied at 1·0 μg mL^{-1} of Cd. The method was applied successfully to some environmental waters (inland and surface), biological samples (human blood and urine), fertilizer samples (urea and T.S.P.), soils and complex synthetic mixtures.

F. Shaohua et al. [5] reported a method for the spectrophotometric determination of Cd. It was based on the color reaction of Cd(II) with a water insoluble reagent meso tetrakis (4– bromophenyl) porphyrin. A complex with the ratio of 1: 1 was formed by Cd(II) and the reagent in pH 10 forax-NaOH buffer solution in the presences of tween-80 and oxine. The absorption maximum of the complex was at 436 nm. The apparent molar absorptivity 4·52 × 10^5 and the linear range 0 – 0·36 μg mL^{-1}. Propanetriol and K-Na tartrate was used as masking agent. The mechanism of photosensitivity of the complex was studied. The method was used in the determination of Cd in tobacco, tea and environmental water samples with the RSD 2·46 – 3·67% and the results consistent with those by AAS.

G. jiang et al. [6] proposed a method for spectrophotometric determination of trace amount of cadmium in marine samples. The color reaction of Cd(II) with xylenol orange in the presence of hexamethylene triamine-KNO_3 – HNO_3 was studied. Cd(II) forms the complex at pH = 6·2–6·4 (λ_{max} = 578·4 nm) with an apparent molar absorptivity of 1·6 × 10^4L mol^{-1} cm^{-1}, Beer's law is obeyed for 0·5–6 μg mL^{-1} with the recovery of 90%–105%. The method is simple and highly sensitive, and was applied for the analysis of samples. The results were satisfactory.

M. Yang et al. [7] reported a method for synthesis of 1-(2-benzothiazole)-3-(4-nitrophenyl) triazene and studies on its color reaction with cadmium. This paper reports the synthesis of the new reagent 1-(2-benzothiazole)-3-(4-nitrophenyl) triazene (BTNPT) and the color reaction of BTNPT with cadmium. In the presence of Triton X-100, the reagent forms a yellow complex with

cadmium with a molar ratio of 1 : 2. The molar absorptivity is $2{\cdot}52 \times 10^5$L mol^{-1} cm^{-1} as being obtained by dual-wavelength spectrophoto-metry with reference wavelength of 435 nm and determination wavelength of 530 nm. Beer's law is obeyed in the range of 0 – 10 μg/25 mL. Trace cadmium in human hair and water has been determined by the method with satisfactory results.

L. Shutin et al. [8] proposed a method for color reaction of cadmium with a new chromogenic reagent quinolyldiazoaminoazobenzene with its application. A method for the spectrophotometric determination of Cd with a new chromogenic reagent quinolyldiazoaminoazobenzene was developed. An orange-red complex with the ratio of 1 : 2 was formed by Cd(II) and the reagent in borax buffer solution in the presence of OP. The absorption maximum of the complex was at 524 nm. The apparent molar absorptivity $1{\cdot}85 \times 10^5$, and Beer's law was obeyed at 0 – 10 μg/25 mL. NaF, thiourea, Na citrate, triethanolamine, and KI-MIBK can be used as masking agent. The method was ued in the determination of micro Cd in industrial waste water with the relative standard deviation 1·1 – 3·0% and the results were consistent with those by AAS.

X Li et al. [9] proposed a method for ion flotation of Cd with 2-(5-bromo-2 pyridylazo)-5-(diethylamins) phenol. The detection limit was 0·35 μg of Cd L^{-1} with a relative standard deviation < 5%, Recoveries were in the range of 95% – 106%.

G. Chen et al. [10] reported a method for cadmium inhibition of the oxidation of arsenazo-1 by H_2O_2. The detection limit was $2{\cdot}7 \times 10^{-3}$ μg of CdL^{-1} with linear response up to 40 μgL^{-1}.

S. Wang et al. [11] proposed a method for the spectrophotometric determination of Cadmium by 2, 4, 4'-tri-nitrodiazoaminobenzene. The absorption maximum of the complex was at 538 nm. Beer's law is obeyed at the range 0-540 $\mu gCdL^{-1}$.

The synthesis of O-hydroxybenzenediazoaminoazobenzene and its use in determining Cd spectrophotometrically has been described. The Cd complex absorbed at 520 nm with Beer's law being obeyed in the range 0 – 400 μgL^{-1} [12]. Cadmium and p-methoxyanilinodiazoazobenzene formed a complex in the presence of the surfactant Tween-80, which absorbed at 505 nm, with Beer's law obeyed in the range 0 – 400 μg of CdL^{-1} [13].

Cadmium was preconcentrated by precipitation as a 2-(5-bromopyridylazo)-5-(Diethylamino)-phenol complex, which was adsorbed on microcrystalline naphthalene. The solids were dissolved in acetone and Cd was determined spectrophotometrically at 570 nm. The linear range was 0 – 7 μg of Cd/10 mL of acetone solution [14]. In the presence of PAR, Cd(II) was reacted with α, β, γ, δ-tetrakis [4-trimethylammonium-phenyl]-prophyrin to form a complex that absorbed at 430 nm. Beer's law was adhered to over the range 0 – 0·28 mg CdL^{-1} [15]. A spectrophotometric method for determining Cd included forming a chelate with 4, 4'-diazo-benzenediazoaminobenzene in the presence of Triton X-100 and tetraborate. The absorbance was measured at 526 nm and was linear over the concentration range 0 – 0·4 ppm Cd [16]. The reaction of Cd, ethylrhodamine, B, KI, and poly (vinyl alcohol) formed a complex that absorbed at 605 nm and was suitable for determining Cd spectrophotometrically with a linear range of 4 – 60 μg CdL^{-1} [17]. The system Cd(II)-KI-Brilliant. Tween-60 in H_2SO_4 was used to determine Cd by measuring the absorbance at 670 nm. Beer's law was obeyed in the range 40 – 600 μg of CdL^{-1} [18].

A method for determining Cd based on the catalytic effect of Cd(II) and imidazole on the formation of the Co(III), α, β, γ, δ-tetrakis (4-sulfophenyl)-prophine complex was reported. Cadmium was determined in the range 0·5 – 16 μgL^{-1} by measuring absorbence at 432 nm and fluorescence at 644 nm [19].

Single sweep oscillopolarography was used to determine Cd by measuring the polarographic wave of the Cd(II) allylthiourea complex. The linear range was $8{\cdot}9 \times 10^{-8}$ to $8{\cdot}9 \times 10^{-6}$ M Cd [20].

The single sweep polarographic wave of the Cd(II)-3-hydroxy-1-(p-sulfophenyl)-3-phenyltriazine complex was used to determine Cd in the linear range $10^{-8} - 10^{-6}$ M, with a detection limit of 6×10^{-9} M [21].

Cadmium was determined by single sweep oscillopolarography using the adsorptive wave of the Cd(II)-decanohydroxamic acid complex. The peak height was proportional to Cd concentration in the range $1{\cdot}8 \times 10^{-6}$ to $3{\cdot}6 \times 10^{-6}$ M [22].

Spectrophotometric methods based on formation of ion associates of the anionic tetraiodocadmate(II) complex with basic dyes [23, 24] have been proposed. Some of them required liquid-liquid extraction with organic solvents [25, 26]. The solvent extraction step may be avoided when formation of a water soluble ternary compex results in a favourable spectral shift, allowing a simpler procedure carried out in aqueous medium to be developed [27, 28]. This happens with the interaction of $[CdI_4]^{2-}$ with Rhodamine B or 6G [28, 29], pyronine G [30], crystal violet [31].

Recently Neto-et al. [32] reported for the determination of cadmium in fertilizers by automated spectrophotometric method as ternary complex between cadmium, iodide and malachite green. Several masking agents and ion exchange separation were used for eleminating the interferences. The absorbance of the blue ternary complex was measured at 690 nm (ph 4·7). Beer's law was obeyed for 0 to 200 μg CdL^{-1}, the detection limit being 2 μg CdL^{-1}.

From above literature survey it revels those methods are lengthy, time consuming, temperature and pH-dependent and lack selectivity due to much interference.

It is needless to emphasize further that the direct spectrophotometric method in non-extractive way is more useful if it offers higher sensitivity and selectivity. Search should be directed to a new method in order to develop simpler and simple spectrophotometric method for non-extractive estimation of cadmium in very sensitive and selective way suitable for environmental chemical analysis. The present method [33] described here records for the first time the direct spectrophotometric determination of cdmium in aqueous media without recourse to any "clean up" step. The method [33] is far more selective (virtually specific) sensitive, non-extractive, simple and rapid than all the existing spectrophotometric method [4–32] and has been successfully tested upon some industrial, environmental, biological and soil samples and on various complex synthetic mixtures. The method is very reliable and concentration in the ng g^{-1} range in aqueous medium at room temperature (25°C) can be measured in a very simple and rapid way.

TABLE : Depicts the summary of comparative procedures layout for determination of cadmium reported by I. shutin et al [8] and present method [33].

TABLE : COMPARATIVE PROCEDURE LAYOUT FOR CADMIUM.

1 – 300 μg of cadmium (0·1 – 1 mL of $8{\cdot}89 \times 10^{-3}$M)	10 – 50 μg of cadmium
+ 0·5 – 1·8 mL (preferably 1 mL) of 0·05 M H_2SO_4 solution. + 1 mL of 0·05% Alizarin Red S solution.	+ 2 mL quinolyldi azoaminoazo-benzene + 1 ml borax buffer solution. An orange-red complex with the ratio of 1 : 2 was formed by Cd(II).
10 mL volumetric flask and the volume was made up to the mark with deionized water, a deep greenish yellow complex was formed.	10 mL volumetric flask and the volume was made up to the mark deionized water.
The absorbance was measured at 422 nm against a corresponding reagent blank.	The absorbance was measured at 524 nm against a corresponding reagent blank.
Interference : None.	Interference : Many such as Cu(II), Co(II), Sn(II), Ce(II).
M. Rafique ullah and M. Enamul Haque. Analytical Sciences, 2007 (Communicated).	L. Shutin and Z. Shutin. Jezin Fenxi, 19(3) (1999) 21. [Chem. abstr., 131 (1999) 2372006]

(B) SPECTROPHOTOMETRIC DETERMINATION OF TOXIC ELEMENTS IN AQUEOUS MEDIA.

INTRODUCTION

Different types of ligand were used with about 30 toxic metal ions to obtain color chelate through the novel reaction techniques. Finally Trace amount of toxic element cadmium was determined by spectrophotometric method using 1, 2-dihydroxy anthraquinone-3-sulphonic acid, sodium salt (Alizarin red S) as a new spectrophotometric reagent.

Cadmium in trace amounts is important industrially [34], as a toxicant [35] and biological non-essential [35], as an environmental pollutant [36] and as an occupational hazard [37] It is an extremely toxic metal, has been responsible for a number of deaths [38]. The symptoms of cadmium poisoning are instantaneous hypertension, shortening of life-span; Kidney damage, bronchitis, retardation of growth, gross abnormalities of the vital organs and the risk of prostatic cancer [39]. It also cause generalized cancers in laboratory animals and has been linked epidemiologically with certain human cancers [39]. The most serious situation being the disease called "Itai-Itai" disease which causes gradual weakening of the bone structure, diminution of stature and ultimately the total collapse of the entire skeletal system [40]. Its extreme toxicity towards marine and fresh water organisms is also well known [40]. Cadmium is a potential health hazard due to its presence in urban atmosphere and cigarette smoke [40]. The permissible limit of cadmium in drinking water is 0·05 mgL^{-1} according to EPA [41]. Increasing Cadmium pollution of the environment resulting from the growth of cadmium based industries and the use of fossil fuels makes the development of method for the trace and ultra-trace analysis of this toxic metal essential.

Spectrophotometry is essentially a trace-analysis technique and is one of the most powerful tools in chemical analysis. 1, 2-dihydroanthraquinone-3-sulphonic acid, sodium salt (Alizarin Red S) has been reported as a spectrophotometric reagent for Arsenic [42] but has not previously been used for spectrophotometric determination of cadmium. This paper reports its use in a very sensitive, highly specific spectrophotometric method for the trace determination of cadmium. The method possesses distinct advantages over existing methods [4-32] with respect to sensitivity, selectivity, range of determination, simplicity, speed, pH/acidity range, thermal stability, accuracy, precision and ease of operation. The method is based on the reaction of non-absorbent alizarin red S in slightly acidic solution (0·0005 – 0·05M H_2SO_4) with cadmium to produce a highly absorbent deep greenish yellow chelate product, followed by direct measurement of the absorbance in aqueous solution. With suitable masking, the reaction can be made highly selective.

EXPERIMENTAL

Apparatus :

A shimadzu (Kyoto, Japan) (Model–1601PC) double beam UV/VIS recording spectrophoto-meter and Jenway (England, U.K.) (Model–3010) pH-meter were used for the measurements of absorbance and pH, respectively. A Shimadzu (Model-AA 6200) atomic absorption spectrophotometer equipped with a micro computer-controlled nitrous oxide-acetylene flame was used for comparison of the results.

Reagents and Solutions :

All the chemicals used were of analytical-reagent grade or the highest purity available. Doubly distilled de-ionized water, which is non-absorbent under ultraviolet radiation was used throughout.

Glass vessels were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$ followed by washing with nitric acid (1 + 1) and rinsed several times with high-purity de-ionized water. Stock solutions and environmental water samples (1000 mL each) were kept in polypropylene bottles containing 1 mL of concentrated HNO_3. More rigorous contamination control was used when the cadmium levels in the specimens were low.

Alizarin Red S Solution, $1{\cdot}39 \times 10^{-3}$ M :

Prepared by dissolving the requisite amount of alizarin red S. (1, 2-dihydroxyanthraqui-none-3-sulphonic acid, sodium salt) (BDH chemicals) in a known volume of de-ionized water. More dilute solutions of the reagent were prepared as required.

Cadmium Standard Solutions :

A 100-mL amount of stock solution (1 $mgmL^{-1}$) of divalent cadmium was prepared by dissolving 0·2282mg of AR crystallized cadmium sulfate (3 Cd SO_4, 8 H_2O) (Merck) in doubly distilled de-ionized water. Aliquots of this solution were standardized by EDTA titration using xylenol orange as indicator. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with de-ionized water as and when required.

EDTA Solution :

A 100-mL amount stock solution of EDTA (0·01% W/v) was prepared by dissolving 10 mg of A.C.S.-grade (≥ 99%) of disodium dihydrogen ethylenediamine tetraacetate dihydrate in (100-mL) de-ionized water.

Potassium Permanganate Solution :

A 1% potassium permanganate solution (Merck) was prepared by disslolving in de-ionized water. Aliquots of this solution were standardized with oxalic acid. Sodium azide solution (2·5% W/v) (Fluka purity > 99%) was also used.

Tartarate Solution :

A 100-mL stock solution of tartarate (0·01% W/v) was prepared by dissolving 10 mg of A.C.S grade (99%) potassium sodium tartarate tetrahydrate in (100-mL) de-ionized water.

Aqueous Ammonia Solution :

A 100-mL solution of aqueous ammonia was prepared by diluting 10-mL concentrated NH_4OH (28 – 30%, A.C.S grade) to 100-mL with de-ionized water. The solution was stored in polypropylene bottle.

Other Solutions :

Solutions of a large number of inorganic ions and complexing agents were prepared from their analar grade or equivalent grade water soluble salts (or the oxides and carbonates in hydrochloric acid); those of niobium, titanium, zirconium and hafnium were specially prepared from their corresponding oxides (Specpure, Johnson Matthey) according to the recommended procedures of Mukharjee [43]. In the case of insoluble substances, special dissolution methods were adopted [44].

Procedure

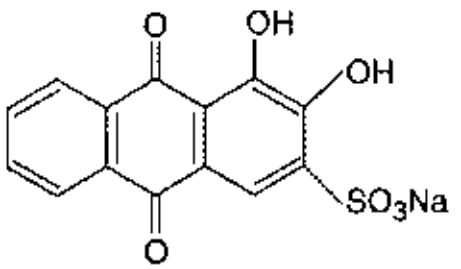
To 0·1 – 1·0 mL of a neutral aqueous (pH – 6) solution containing 1 – 300 μg of cadmium in a 10-mL calibrated flask was mixed with 1 : 5 – 1 : 110 fold molar excess of the alizarin red S. reagent solution (preferably 1·0 mL of 1·39 $\times 10^{-1}$M) followed by the addition 0·5 – 1·8 mL (preferably 1 mL) of 0·05 M sulfuric acid (or pH 5·5 – 6·1). The mixture was diluted to the mark with de-ionized water. The absorbance was measured at 422 nm against a corresponding reagent blank. The cadmium content in an unknown sample was determined using concurrently prepared calibration graph.

RESULTS AND DISCUSSION

Factors Affecting the Absorbance :

Absorption spectra :

The absorption spectra of the cadmium-alizarin Red S system in 0·05M H_2SO_4 medium was recorded using the spectrophotometer. The absorption spectra of the cadmium-alizarin Red S is a symmetric curve with the maximum absorbance co-efficient is shown in Fig-1. In all instances measurements were made at 422 nm against a reagent blank. The reaction mechanism of the present method is as reported earlier [45].



Structure of Alizarin red S (1, 2-dihydroxy anthraquinone-3-sulphonic acid, sodium salt).

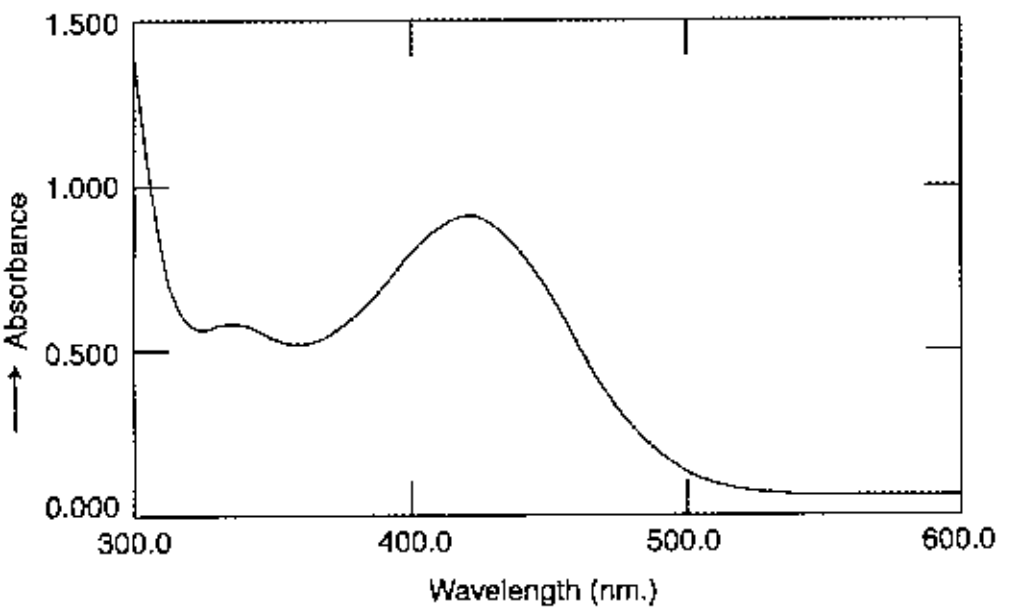


Fig.-1 : Absorption spectra of the cadmium- Alizarin red S system and the reagent blank (λ_{max} = 422 nm) in aqueous solutions.

Effect of Acidity :

Of the various acids (nitric, sulfuric, hydrochloric and phosphoric) studied. Sulfuric acid was found to be the best acid for the system. The absorbance was at a maximum and constant when the 10-mL of solution (1 μg mL^{-1}) contained, 0·5–1·8 mL of 0·05M sulfuric acid at room temperature (25 ± 5)°C. Outside this range of acidity, the absorbance decreased (Fig.-2).

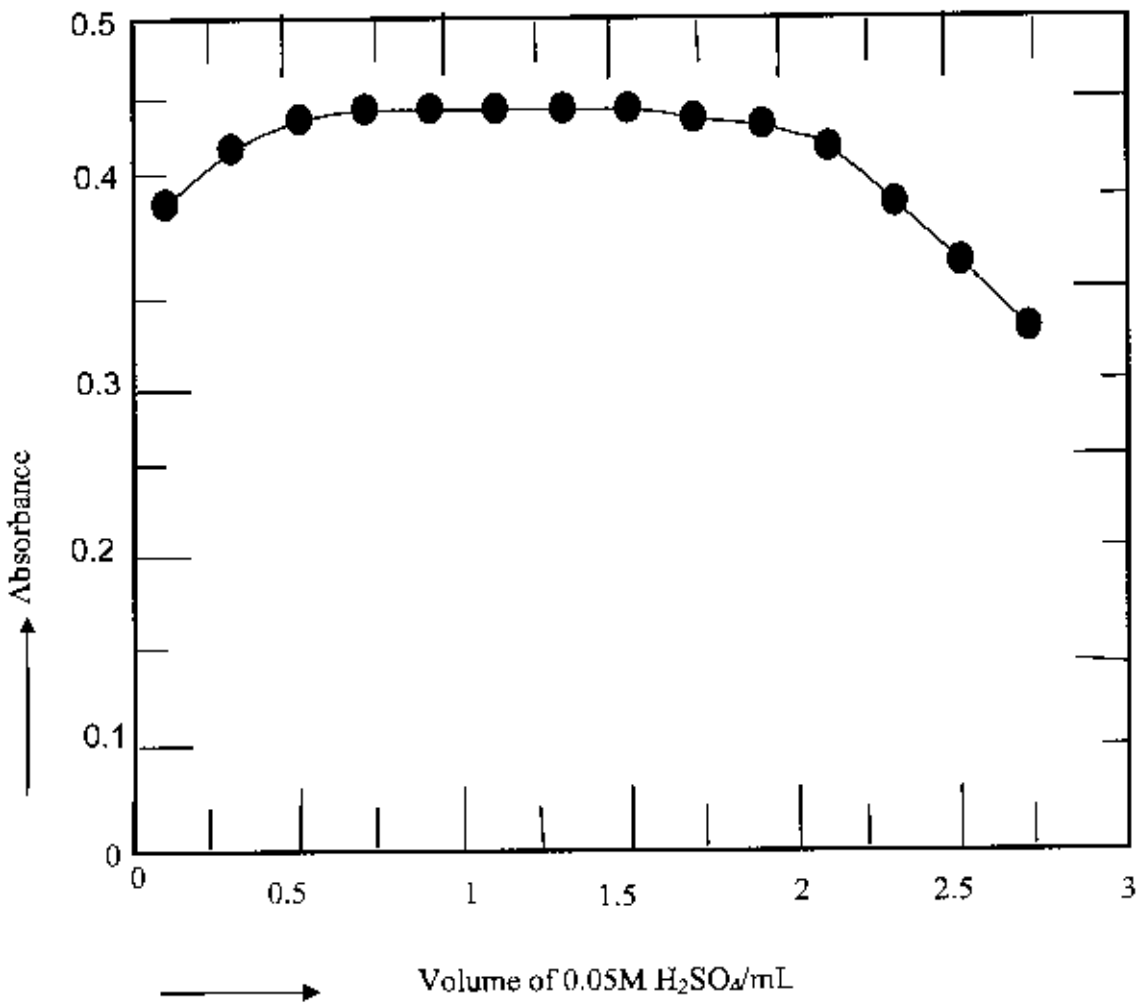


Fig.–2 : Effect of the acidity on the absorbance of Cd-Alizarin red S system.

Effect of Time :

The reaction is instantaneous. Constant maximum absorbance was obtained just after diluting to volume and remained strictly unaltered for 24h (Fig.-3).

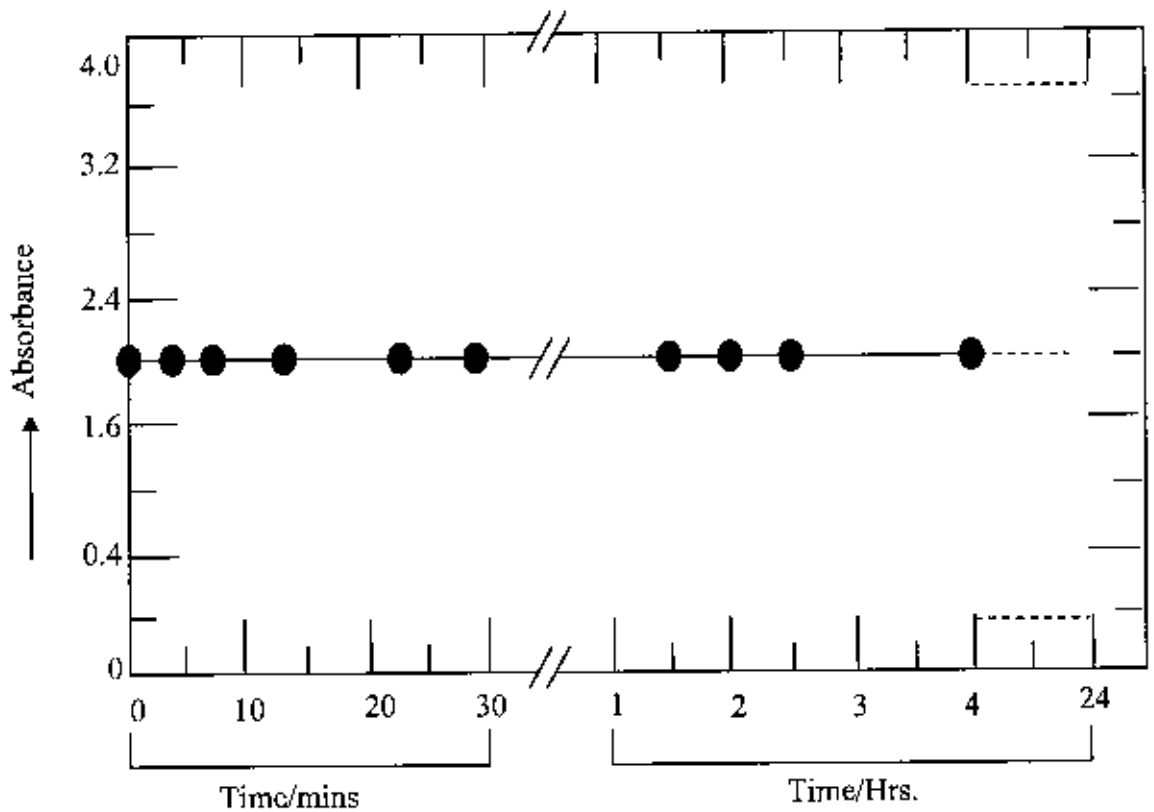


Fig.–3 : Effect of the time on the absorbance of Cd-Alizarin red S system.

Effect of Temperature :

The Cadmium-Alizarin Red S system obtained maximum and constant absorbance at room temperature (25 ± 5)°C. Outside this range of temperature, the absorbance decreased.

Effect of Reagent Concentration :

Different molar excesses of alizarin Red S were added to fixed metal ion concentration and absorbance were measured according to the standard procedure. It was observed that at the 1 μg mL^{-1} cadmium metal, the reagent molar ratios of 1 : 50 – 1 : 110 produce a constant absorbance of the Cd-chelate (Fig.-4). For all subsequent measurements 1 mL of 1·39 × 10^{-3}M Alizarin red S reagent was added.

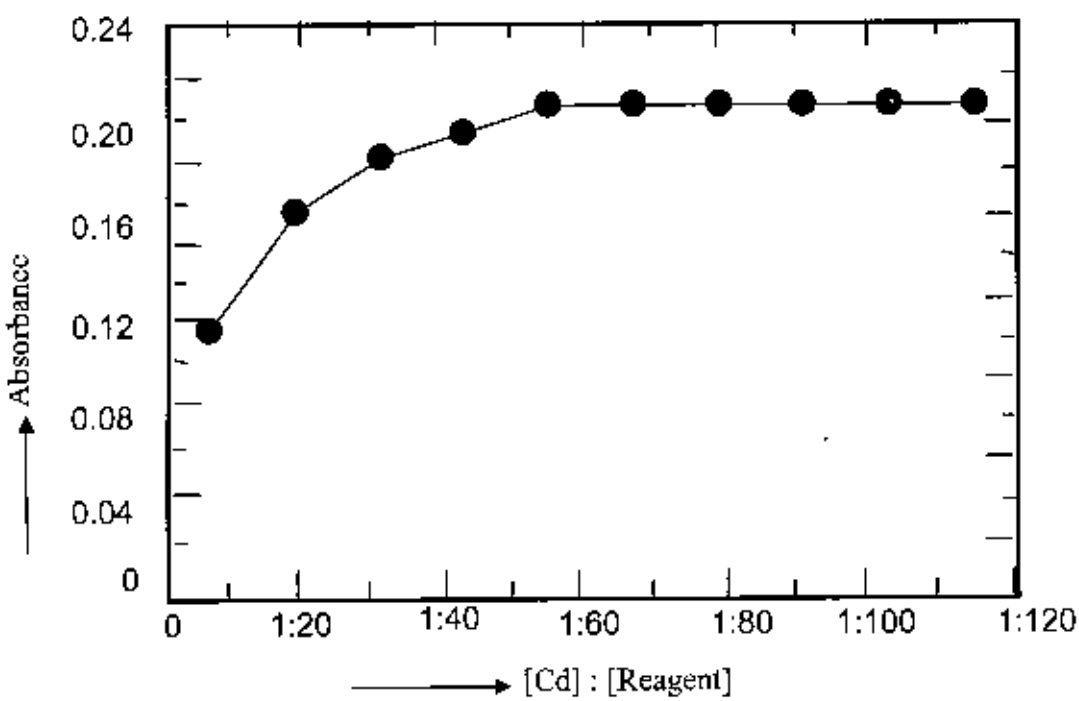


Fig.–4 : Effect of reagent (Cd : Alizarin red S molar concentration ratio) on the absorbance of Cd-Alizarin red S system.

Calibration Graph (Beer's Law and Sensitivity)

The well-known equation for spectrophotometric analysis in very dilute solution was derived from Beer's law. The effect of metal concentration was studied over 0·1 – 80 μg mL^{-1} distributed in three different sets (0·1 – 1, 0, 1 – 10 and 10 – 80 μg mL^{-1} for convenience of measurement. The absorbance was linear for 0·1 – 40 μg mL^{-1} of cadmium at 422 nm. The molar absorption co-efficient and the sandell's sensitivity [46] were found to be 2·24 × 10^3 L mol^{-1} cm^{-1} and 20 ng cm^{-2} of cadmium, respectively. Of the calibration graph which that showing the limit of linearity range is given in (Fig.-7). The next two was straight-line graphs passing through the origin (Fig.-5, 6).

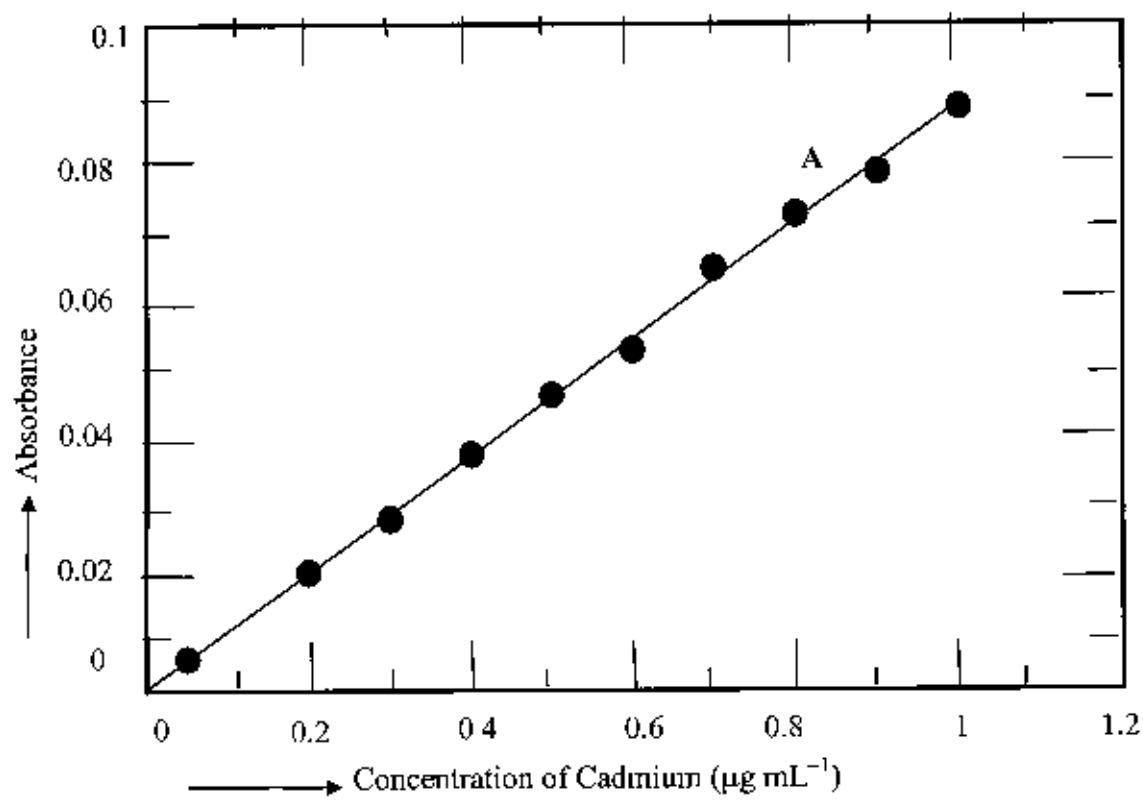


Fig.–5 : Calibration graph A : 0·1 – 1 μg mL^{-1} of cadmium.

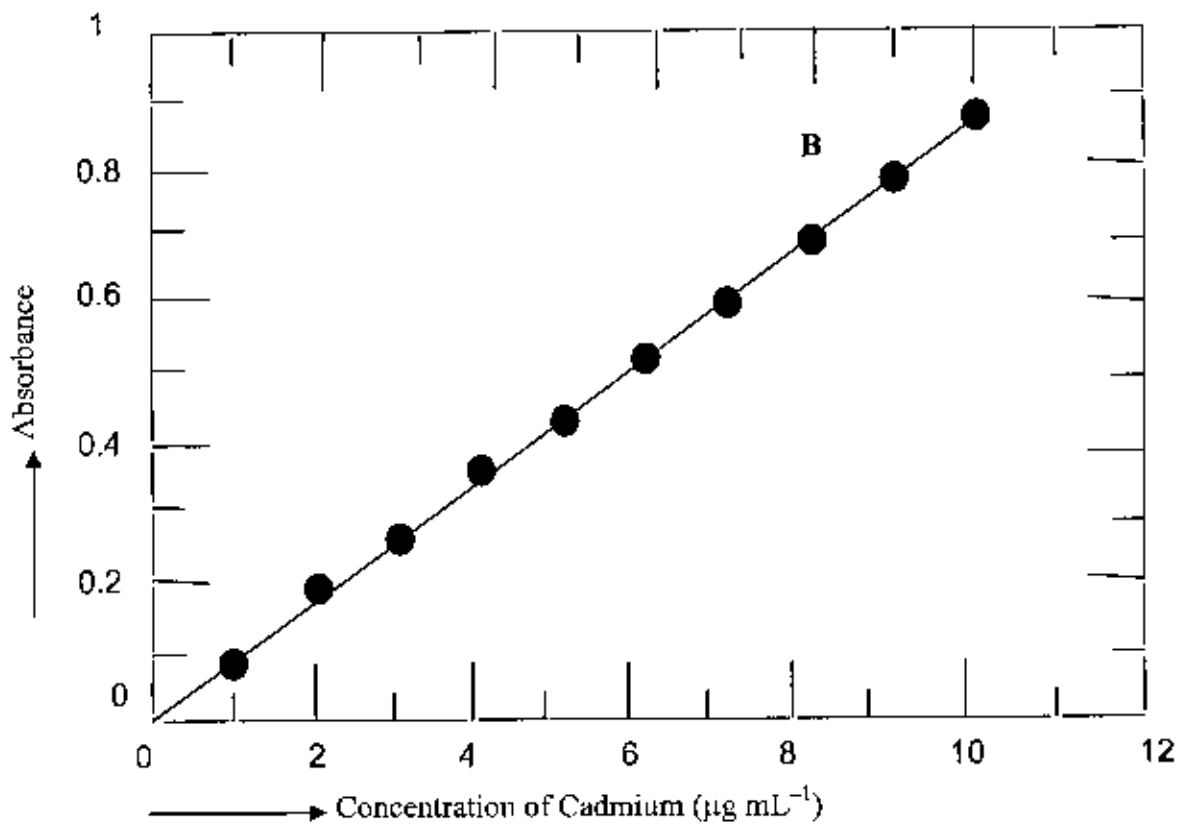


Fig.–6 : Calibration graph B : 1 – 10 μg mL^{-1} of cadmium.

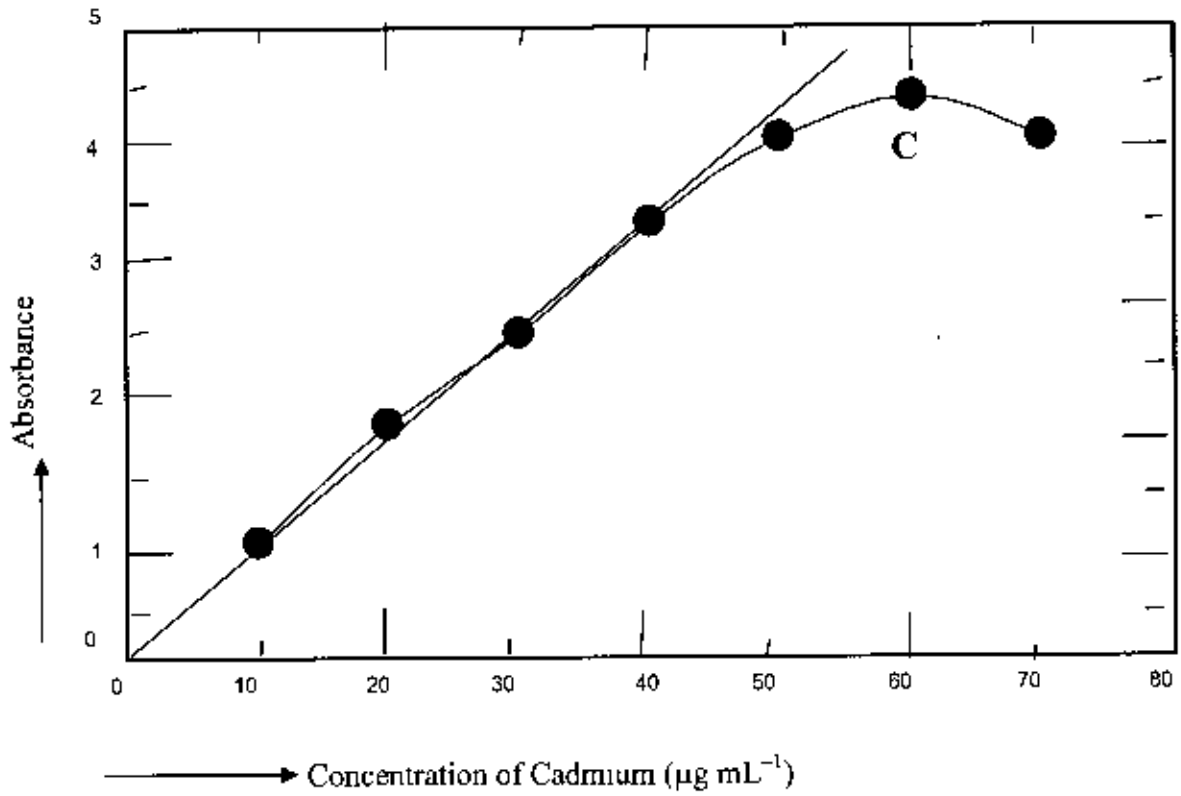


Fig.–7 : Calibration graph C : 10 – 40 μg mL^{-1} of cadmium.

The selected analytical parameters obtained with the optimization experiments are summarized in table–1.

TABLE-1 : SELECTED ANALYTICAL PARAMETERS OBTAINED WITH THE OPTIMIZATION EXPERIMENTS.

Parameter	Studied range	Selected Value
Wavelength/ λ_{max}(nm)	200 – 800	422
Acidity/M H_2SO_4	0·005 – 0·5	0·01 – 0·1
pH	4·0 – 7·0	5·5 – 6·2
Time/h	0 – 72	24
Temperature/°C	1 – 50	25 ± 5
Reagent (fold molar excess, M : R)	1 : 1 – 1: 110	1 : 50 – 1: 110
Linear range/ $\mu g\ mL^{-1}$	0·01 – 100	0·1 – 40
Detection limit/ng mL^{-1}	1 – 100	30
Reproducibility (% RSD)	0 – 2	0 –2

Precision and Accuracy :

The precision of the present method was evaluated by determining different concentrations of cadmium (each analyzed at least five times). The relative standard deviation (n = 5) was 2 – 0% for 1 – 300 μg of cadmium in 10-mL, indicating that this method is highly precise and reproduciable (Table-2). The detection limit (3 S of the blank) and Sandell's Sensitivity (Concentration for 0·001 absorbance unit) for cadmium were found to be 30 ng mL^{-1} and 20 ng cm^{-2}, respectively. Added cadmium was accurately recovered from the other metals (Table-5). The reliability of our Cd-Chelate procedure was tested by recovery studies. The average percentage recovery obtained for addition of a cadmium spike to some environmental water samples was quantitative as shown in (Table-6). The method was also tested by analyzing several synthetic mixtures containing cadmium and diverse ions (Table-4). The results of biological analysis by the spectrophotometric method were excellent agreement with those obtain by AAS (Table-7). Hence, the precision and accuracy of the method were found to be excellent.

TABLE–2 : STANDARD DEVIATION AND RELATIVE STANDARD DEVIATION OF CD(II)-ALIZARIN RED S SYSTEM.

Sample No.	Cd(II) taken $\mu g L^{-1}$	Cd(II) Found X_1 $\mu g\ L^{-1}$	Mean $\bar{X}$ $\mu g\ L^{-1}$	$X_1 - \bar{X}$	$(x_1 - \bar{X})^2$	Standard deviation (± s)	Relative standard deviation (s_r)%
1	100·0	99		1·14	1·29		
2	100·0	98 5		1·64	2 67		
3	100·0	101·		0·86	0·75		
4	100 0	100·5		0 36	0·13		
5	100·0	99·5		0·64	0·41		
6	100·0	101·5		1·36	1·85		
7	100·0	101	100·14	0·86	0·74	± 1·16	1·16
8	100·0	99·5		0·64	0·41		
9.	100·0	98 5		1·64	2·69		
10	100·0	101·5		1·36	1 85		
11	100	101		0 86	0·74		
N = 11		ΣX_1 = 1101 5		$\Sigma X_1 - \bar{X}$ = 11 364	$\Sigma (x_1 - \bar{X})^2$ = 13·53		

$$\text{Mean, } \bar{X} = \frac{\Sigma X_1}{N} = \frac{1101.5}{11} = 100.14$$

$$\text{Sandard deviation, } S = \sqrt{\frac{\Sigma (X_1 - \bar{X})^2}{N-1}} = \sqrt{\frac{13.53}{11-1}} = \sqrt{1.353} = \pm 1.16$$

$$\text{Relative standard deviation } (S_r)\ \% = \frac{S}{\bar{X}} \times 100.$$

$$= \frac{1.16 \times 100}{100.14}$$

$$= 1.16$$

Effect of Foreign Ions :

The effect of over 50 ions and complexing agents on the determination of only 1 $\mu g\ mL^{-1}$ of cadmium was studied. The criterion for an interference [47] was an absorbance value varying by more than ± 5% from the expected value for cadmium alone. The results are summarized, in (Table-3). As can be seen, A large number of ions have no significant effect on the determination of cadmium. The quantities of these diverse ions mentioned (Table-2) were the actual amounts added and not the tolerance limits. The most serious interferences were from V(V), Mo(VI) and Fe(III) ions. Interference from these ions are probably due to complex formation with alizarin Red S.

The greater tolerance limits for these ions can be achieved by using several masking methods. Inorder to eliminate the interference of V(V), Mo(VI) and Fe(III) ions. tartaric acid, EDTA, citric acid or chloride can be used as a masking agent [48]. A 10 fold excess of V(V), Mo(VI) or Fe(III) could be masked with EDTA, tartarate or chloride. During the interference studies, if any precipitate was formed, it was removed by centrifugation. Interference from these three metal ions V(V), Mo(VI) and Fe(III) have been effectively removed by a short single-step ion-exchange separation process, using an Amberlite XAD-8 resin (100 – 200 mesh) anion exchanger [49].

TABLE-3 : TABLE OF TOLERANCE LIMITS OF FOREIGN IONS*, TOLERANCE RATIO.

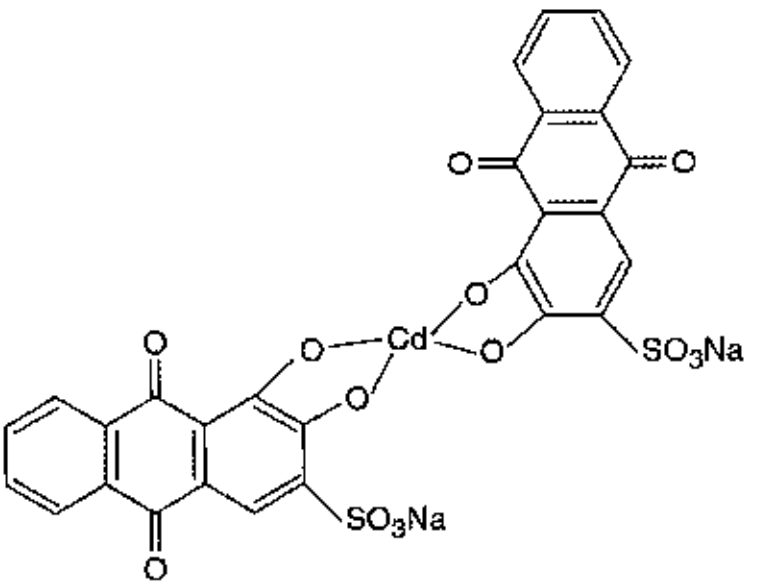
[SPECIES (X)]/ CD (W/W).

Species X	Tolerance ratio X/Cd	Species X	Tolerance ratio X/Cd
Ammonium (I)	100	Chromium (III)	50^{+}
Arsenic (III)	100	Chromium (VI)	25^{+}
Ascorbic Acid	100	Copper (II)	100^{++}
Azide	100	Vanadium (V)	10^{+}
Chloride	500	Selenium (IV)	50^{+}
Fluoride	1000	Selenium (VI)	25
Barium	200	Nickel (II)	25^{+}
Nitrate	500	Iodide	200
nitrite	100	Cesium	500
Bismuth (III)	100	Cerium	200
Citrate	500	Thiocyanate	100
Tartrate	200	Sodium	500
Bromide	100	Zinc	200
Cobalt (II)	50	Mercury (II)	25^{++}
Cobalt (III)	25	Calcium	1000
Iron (II)	50	Potassium	500
Iron (III)	10^{+++}	Molybdenum (VI)	10^{++}
Silver (I)	25^{+++}	Arsenic (V)	50
EDTA	100	Lead (II)	75
Oxalate	500	Thallium (I)	50
Phosphate	100	Gallium	25
Aluminium	100	Tungsten (VI)	50^{+}
Manganese (II)	200	Tungsten (VI)	50^{+}

* Tolerance limit was defined as ratio that causes less than 5 per cent interference.
'+' with 10 μgmL^{-1} tartrate
'++' with 10 μgmL^{-1} EDTA
'+++' with 10 μgmL^{-1} chloride.

Composition of the absorbent Complex :

Job's method [50] of continuous variation and the molar-ratio [51] method were applied to ascertain the stoichiometric composition of the complex. A cadmium-Alizarin Red S (1 : 2) complex was indicated by both methods.



Structure of the Cadmium-Alizarin red S complex.

APPLICATIONS

The present method was successfully applied to the determination of cadmium (II) in a series of synthetic mixtures of various compositions (Table-4) and also in number of real samples, e.g several Certified Reference Materials (CRM) (Table-5). The method was also extended to the determination of cadmium in a number of environmental, biological and soil samples. In view of the unknown composition of environmental water samples, the same equivalent portions of each such sample was analyzed for cadmium content, recoveries in both the 'spiked' (added to the samples before the mineralization or dissolution) and the 'unspiked' samples are in good agreement (Table-6). The results of biological analysis by spectrophotometric method were found to be in excellent agreement with those obtained by AAS (Table-7). The results of soil samples analysis by spectrophotometric method are shown in (Table-8). The precision and accuracy of the method were excellent.

Determination of Cadmium in Synthetic Mixtures :

Several synthetic mixtures of varying compositions containing cadmium and diverse ions of known concentrations were determined by the present method using tartarate or EDTA as a masking agent and the results were found to be highly reproducible. The results are shown in (Table-4). Accurate recoveries were achieved in all solutions.

TABLE-4 : DETERMINATION OF CADMIUM IN SOME SYNTHETIC MIXTURES.

Sample No.	Composition of Mixture/ μg mL^{-1}	Cadmium/μg mL^{-1}		Recovery ± SD[b]%
		Added	Found[a]	
A	Cd	0·50	0·49	98 ± 0·5
		1·00	0·99	99 ± 0·2
B	As in A + $Mn^{2+}_{(25)}$ + $Na_{(25)}$ + $EDTA_{(10)}$	0·50	0·49	98 ± 0·3
		1·00	1·01	101 ± 0·7
C	As in B + $Hg^{2+}_{(50)}$ + $Ni^{2+}_{(50)}$ + $EDTA_{(10)}$	0·50	0·53	106 ± 1·0
		1·00	1·02	103 ± 0·8
D	As in C + $Zn_{(25)}$ + $K_{(25)}$	0·50	0·54	108 ± 1·2
		1·00	1·04	104 ± 1·0
E	As in D + $Ba_{(25)}$ + $Br^-_{(50)}$	0·50	0·56	112 ± 1·3
		1·00	1·08	108 ± 1·5

[a]Average of five analyses of each semple.

[b]The measure of precision is the standard deviation (SD).

Determination of cadmium in alloys and Steels.

0·1 g amount of an alloy or steel sample was accurately weighed into a 50-mL flask following a method recommended by parker et al [52]. To it, 10-mL of 20% (V/V) sulfuric acid was added, carefully covering with a watch-glass until the brisk reaction subsided. The solution was heated and simmered gently after addition of 5-ml of concentrated HNO_3 until all carbides were decomposed. Then 2-mL of 1 : 1 (V/V) H_2SO_4 was added and the solution was evaporated carefully to dense white fumes to drive off the oxides of nitrogen and then cooled to room temperature (25 ± 5)°C. After suitable dilution with de-ionized water, the contents of the flask were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with dilute NH_4OH in the presence of 1 – 2 mL of 0·01% (W/V) tartarate solution. The resulting solution was filtered, if necessary, through a whatman No. 40 filter paper into a 50-mL calibrated flask. The residue was washed with a small volume of hot water and the volume was made up with de-ionized water. A suitable alliquot (0·1 – 1·0 mL) of the above solution was taken into a 10-mL calibrated flask and the cadmium content was determined as described under procedure using EDTA or fluoride as a masking agent. The results are shown in (Table-5). Added cadmium was recovered accurately from the other metals.

TABLE-5 : DETERMINATION OF CADMIUM IN STANDARD BRONZE, BRASS AND STEEL SAMPLE SOLUTIONS.

Sample No.	Certified Reference Material (Composition, %)	Cd Spiked		Recovery ± S[b] (%)
		Added (μg mL^{-1})	Found[a] (μg mL^{-1})	
1.	BAS – 32a, Al-Bronze Alloy Cu = 85·9, Zn = 0·94, Mn = 0·27 Fe = 2·67, Ni = 1·16, Al = 8·8	0·10 0·50	0·102 0·48	100 ± 0·2 96 ± 0·5
2.	BAS – 10g HT Brass Cu = 60·0, Fe = 1 56, Sn = 0·31 Pb = 3·34, Zn = 32·0. Mn = 1·36	0·10 0·50	0·103 0·49	103 ± 0·6 98 ± 0·5
3.	BAS – 646, High speed steel. Te = 0·90, Cr = 4·55 Mo = 4·95, V = 1·99	0·10 0·50	0·102 0·50	100 ± 0·2 100 ± 0·0
4.	Brass – 5f Cu = 70·8, Zn = 24·2, Sn = 1·85 Pb = 2·52, Fe = 0·31, P = 0·06	0·10 0·50	0·105 0·54	105 ± 1·6 108 ± 0·8

[a]Values given represent the average of triplicate determination.

[b]The measure of precision is the standard deviation (S).

Determination of Cadmium in Environmental Waters :

Each filtered (with whatman No.-40) environmental water sample (1000-mL) was evaporated nearly to dryness with a mixture of 5 mL of concentrated H_2SO_4 and 10-mL of concentrated HNO_3 in a fume cupboard following a method recommended by Greenberg et al [53], and was then cooled to room temperature. The residue was then heated with 10-mL of de-ionized water inorder to dissolve the salts. The solution was then cooled and neutralized with dilute NH_4OH in the presence of 1 – 2 mL of 0·01% (W/V) tartarate solution. The resulting solution was then filtered and quantitatively transferred into a 25-mL calibrated flask and made upto the mark with de-ionized water.

An aliquot (1 – 2 mL) of this preconcentrated water sample was pipetted into a 10-mL calibrated flask and the cadmium content was determined as described under procedure using EDTA or chloride as a masking agent. The analyses of environmental water samples from various sources for cadmium are shown .in (Table-6).

Most spectrophotometric method for the determination of cadmium in natural and sea water require preconcentration of cadmium [54] The concentration of cadmium in natural and sea water is a few ng mL^{-1}. A cadmium concentration of 200 $\mu g\ L^{-1}$ is toxic to certain fish. The concentration of cadmium found in U. S. drinking water is from 0·4 – 60 ng mL^{-1} [53].

TABLE-6 : DETERMINATION OF CADMIUM IN SOME ENVIRONMENTAL WATER SAMPLES.

Sample		Cadmium/$\mu g\ L^{-1}$		Recovery ± S (%)	S_r^b (%)
		Added	Found[a]		
Tap water		0	3 5	± 0·2	0·25
		100	105·0	99 ± 0·1	0·24
		500	504·0	100 ± 0 3	0·31
Pond water		0	5·0		
		100	107·0	100·9 ± 0·4	0·24
		500	508·0	100 ± 0·0	0 00
Rain water		0	5·5		
		100	105·5	99·4 ± 0·3	0·37
		500	504·0	100 ± 0 5	0·38
River water	(i) Burigonga (Upper stream)	0	12·0		
		100	120·0	99 ± 0·2	0·29
		500	522·0	100·2 ± 0·5	0·31
	(ii) Burigonga (Lower stream)	0	13 5		
		100	114·8	100·1 ± 0·3	0 21
		500	519·0	100 ± 0·5	0·00
Sea water	(i) Bay of Bengal (Upper)	0	15·0		
		100	113·0	98 ± 0·3	0 45
		500	515·0	100·3 ± 0·6	0·22
	(ii) Bay of Bengal (lower)	0	12·0		
		100	114·0	100·9 ± 0·3	0·25
		500	518·0	101 ± 0·6	0·17
Drain water	(i) Barger paints (Dhaka)	0	120		
		100	225	100·8 ± 0·5	0·28
		500	640	99·5 ± 0·8	0·34
	(ii) Asian paints	0	30		
		100	135	100·0 ± 0 00	0·26
		500	540	100·7 ± 0·1	0·32

[a]Average of five replicate determinations.

[b]The measure precision is the relative standard deviation (Sr).

Determination of Cadmium in Biological Samples :

Human Serum (5 – 10 mL) .or urine (10 – 20 mL) sample was taken into a 100-mL flask. A glass bead and 10-mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating. When the initial brisk reaction was over, the solution was removed and cooled following a method recommended by stalhr [55]. 1-mL of concentrated sulfuric acid was added carefully followed by the addition of 1–mL of 70% perchloric acid and heating was continued to dense white fumes, repeating nitric acid addition if necessary. Heating was continued for at least $\frac{1}{2}$h and then cooled. The content of the flask was filtered and neutralized with dilute NH_4OH in presence of 1 – 2 mL of 0·01% (W/V) tartarate solution. The resultant solution was then filtered and transferred quantitatively into a 10-mL calibrated flask and made upto the mark with de-ionized water.

Suitable aliquots (1 – 2 mL) were transferred into a 10-mL calibrated flask and the cadmium content was determined as described under procedure using EDTA or chloride as a masking agent. The results of biological analysis by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS. The results are shown in (Table-7).

TABLE-7 : CONCENTRATION OF CADMIUM IN BLOOD AND URINE SAMPLE.

Serial No.	Sample	Cadmium/μgL^{-1}		Sample Source
		AAS (n = 5)	Proposed method (n = 5)	
1	Blood	230·5	231 ± 1·3	Kidney disease patient (male)
	Urine	60	58 ± 1·0	
2	Blood	350	348 ± 1·5	Prostatic cancer Patient
	Urine	320	319 ± 0·8	
3	Blood	32	35 ± 1·0	Hypertension Patient (Female)
	Urine	25	23 ± 1·2	
4	Blood	4	3·2 ± 0·5	Normal Adult (Male)
	Urine	2	1·2 ± 0·4	

Determination of Cadmium in Soil Samples :

An air-dried homogenized soil sample (100g) was weighed accurately and placed in a 100-mL flask. The sample was digested in the presence of an oxidizing agent, following the method recommended by Jackson [56]. The content of the flask was filtered through a whatman No. 40 filter paper into a 25-mL calibrated flask and neutralized with dilute NH_4OH solution. It was then diluted upto the mark with de-ionized water.

Suitable aliquots (1 – 2 mL) were transferred into a 10-mL calibrated flask and a calculated amount of 0·05M H_2SO_4 (needed to give a final acidity of 0·0025M H_2SO_4) was added followed by 1 – 2 mL of 0·01% (W/V) tartarate or thiocyanide solution as a masking agent. Cadmium content was then determined by the above procedure and quentified from a calibration graph prepared concurrently. The results are shown in (Table-8).

TABLE-8 : DETERMINATION OF CADMIUM IN SOME SURFACE SOIL SAMPLES.[ab]

Serial No.	Cadmium ($\mu g\ g^{-1}$)	Sample Source
S_1^c	2·1 ± 0·7	Traffic Soil (Saidabad Bus Terminal Dhaka)
S_2	0·60 ± 0·2	Agriculture Soil (Kamrangi char, Dhaka)
S_3	1·2 ± 0·5	Road Side Soil (Chittagong–Dhaka Highway)
S_4	1·8 ± 0·8	Industrial Soil (Asian Paints (Bd) Ltd.)
S_5	4·0 ± 1·0	Contaminated Soil (Steel Mill Area)
S_6	0·35 ± 0·05	Marine Soil (Bay of Bengal)

[a]Average of five analyses of each sample.

[b]The measure of precision is the standard.

[c]Composition of the soil samples : C, N, P, K, Na, Ca, Mg, Cu, Pb, NO_3^-, Zn, SO_4, Mn, Mo, Co, etc.

CONCLUSION

In this Thesis a new simple, sensitive, selective and inexpensive method with Cd-Alizarin Red S complex was developed for the determination of cadmium in industrial, environmental, biological and soil samples for continuous monitoring. Although many sophisticated techniques such as pulse polarography, HPLC, AAS, ICP–AES, and ICP–MS, are available for the determination of cadmium at trace level in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement for consumables etc. have caused spectrophotometry to remain a popular techniques particularly in laboratories of developing countries with limited budgets. The sensitivity in terms of relative standard deviation of the present method are very reliable for the determination of cadmium in real samples down to ng g^{-1} levels in aqueous medium at room temperature (25 ± 5)°C.

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APPENDIX–1 : Abstract of the publication based on the present work

SPECTROPHOTOMETRIC DETERMINATION OF TOXIC ELEMENTS IN AQUEOUS MEDIA

Analytical Science, 2007 (communicated)

Trace amount of toxic element (Cadmium) was determined by spectrophotometric method using 1, 2-dihydroxy anthraquinone-3-sulphonic acid, sodium salt. (Alizarin red S) as a new spectrophotometric reagent. Alizarin red S reacts in slightly acidic solution (0·005 – 0·05M H_2SO_4) with cadmium to give a deep greenish yellow chelate which has an absorption maximum at 422 nm. The reaction is instantaneous and absorbance remains stable for over 24hrs. The average molar absorption co-efficient and sandell's sensitivity were found to he $2{\cdot}24 \times 10^3$L mol^{-1} cm^{-1} and 20 ng cm^{-2} of Cd respectively. Linear calibration graphs were obtained for 0·1 – 40 μg mL^{-1} of Cd. The stoichiometric composition of the chelate is 1 : 2 (Cd : Alizarin red S). Large excess of over 50 cations, anions, and some common complexing agents (e.g EDTA, oxalate, citrate phosphate, thio-urea, SCN^-) do not interfere in the determination. The method was successfully used in the determination of cadmium in Several Standard Reference Materials (alloys, steels and water) as well as in some environmental waters (In land and surface), biological samples (human blood and urine), soil samples and complex synthetic mixtures. The method has high precision and accuracy. (S = ± 0·01 for 0·5 μg mL^{-1}.