“DETERMINATION OF LEAD (Pb) IN TRACE AMOUNT USING ULTRAVIOLET-VISIBLE SPECTROPHOTOMETRIC METHOD.”

SUBMITTED BY

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EXAMINATION ROLL NO.: 100503201 F
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A DISSERTRATION SUBMITED IN PARTIAL FULFILMENT
OF THE REQUIREMENT FOR THE DEGREE OF
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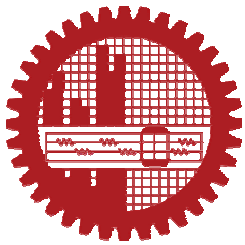

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DHAKA- 1000, BANGLADESH
APRIL, 2011

CERTIFICATE

This is to certify that the research work embodied in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any university or institution.

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Certification of Thesis

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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 on the field covered by this thesis in an oral examination held on 2nd April, 2011.

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DEDICATED
TO
MY PARENTS

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Author

…….
(MOHAMMAD SHAKIL HOSSAIN)

ABSTRACT

Trace amount of Lead (Pb) has been determined by spectrophotometric technique using 1-(2-pyridylazo)-2-naphthol [PAN], as a new spectrophotometric reagent. 1-(2-pyridylazo)-2-naphthol reacts in slightly acidic solution at pH 4.5 with Pb to give a pink chelate that has an absorption maximum at 548 nm. The reaction is instantaneous and absorbance remains stable for over 48 hrs. The average molar absorption co-efficient was found to be 6.32×10^{4} L mol^{-1} cm^{-1}. Linear calibration graphs were obtained for 0.1 – 3.0 ppm of Pb. The stoichiometric composition of the chelate is 1: 2 (Pb: PAN). Large excess of over 20 cations, anions, and some common complexing agents (e.g, oxalate, phosphate, tartarate, thio-urea) have been studied. The method was successfully used in the determination of Pb in some environmental and industrial waste water and made a comparison with those obtained by Atomic Absorption Spectrophotometer (AAS).

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1.1. SPECTROPHOTOMETRY

"Molecular absorption spectrophotometry is the backbone of modern analytical techniques 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. It is very widely used in clinical chemistry and environmental laboratories because many substances can be selectively converted to a colored derivative. [2] Spectrophotometry is extremely sensitive so much so that sometimes pictogram (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. 100 µg/gm). Thought the lower limit was not fixed at that time (neither as yet), perhaps it was originally indented 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 utramicrogram 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 ultra micro concentration ‘ultrace’ 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 fluorscence 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 limitation of absorptiometry. **[16-19]**

1.1.1. 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 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 of 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

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

Where λ is the wavelength in centimeters (cm.) ü 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 υ in cm^{-1}.

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

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}.

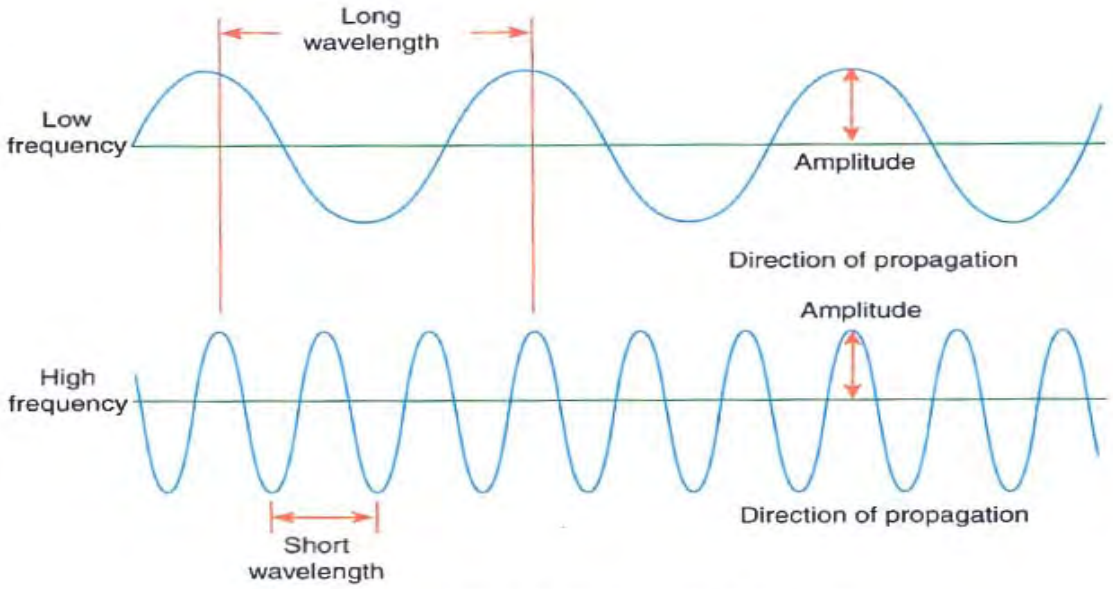

Fig.-1 : Wave motion of electromagnetic radiation.

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

$E = h\upsilon = {}^{hc}/\lambda$ ..... (3)

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

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 appreciable 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 (380nm) 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.

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.

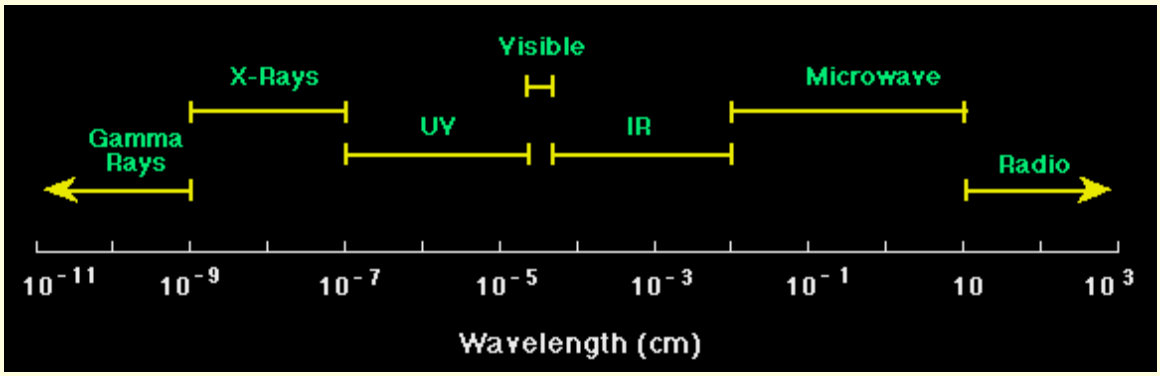

Fig-2: The electromagnetic spectrum

The following table gives approximate wavelengths, frequencies, and energies for selected regions of the electromagnetic spectrum.

Spectrum of Electromagnetic Radiation

Region	Wavelength (Angstroms)	Wavelength (centimeters)	Frequency (Hz)	Energy (eV)
Radio	$> 10^{9}$	> 10	$< 3 \times 10^{9}$	$< 10^{-5}$
Microwave	10^{9} - 10^{6}	10 - 0.01	3×10^{9} - 3×10^{12}	10^{-5} - 0.01
Infrared	10^{6} - 7000	0.01 - 7×10^{-5}	3×10^{12} - 4.3×10^{14}	0.01 - 2
Visible	7000 - 4000	7×10^{-5} - 4×10^{-5}	4.3×10^{14} - 7.5×10^{14}	2 - 3
Ultraviolet	4000 - 10	4×10^{-5} - 10^{-7}	7.5×10^{14} - 3×10^{17}	3 - 10^{3}
X-Rays	10 - 0.1	10^{-7} - 10^{-9}	3×10^{17} - 3×10^{19}	10^{3} - 10^{5}
Gamma Rays	< 0.1	$< 10^{-9}$	$> 3 \times 10^{19}$	$> 10^{5}$

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’.

1.1.2. 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_o which passes through a solution of an absorbing apecies 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,

$p = p_o 10^{-kb}$

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

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

$$\log T = \log \frac{p}{p_o} = -kb \text{.....(5)}$$

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

$$T = \frac{p}{p_o} = 10^{-k'c} \text{.....(6)}$$

or

$$\log T = \log \frac{p}{p_o} = -k'c \text{.....(7)}$$

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

$$T = \frac{p}{p_o} = 10^{-abc} \text{.....(8)}$$

Where 'a' is a combined constant of K and K'.

The logarithmic form of (8) is

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

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

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

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

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

This new quantity, ϵ is known as Molar Absorptivity. Since A is unitiless, 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 standardization 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 uncreative 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 absorptive. Discrepancies are usually found when the colored solute ionizes, dissociates or

associates in solution, since the nature of the species in solution will vary with 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 behavior 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 monocromator 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 of 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. It 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.

1.1.3. 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 ungraded state (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.

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

However, the term “forbidden” refers to rules set up 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 transition (low probability) give absorptions of very low intensity.

1.1.4. Absorption Instrument:

The quality and cost of uv-visible absorption instruments may differ tremendously 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 useable signal (usually electrical); and

(v) a signal processor and readout.

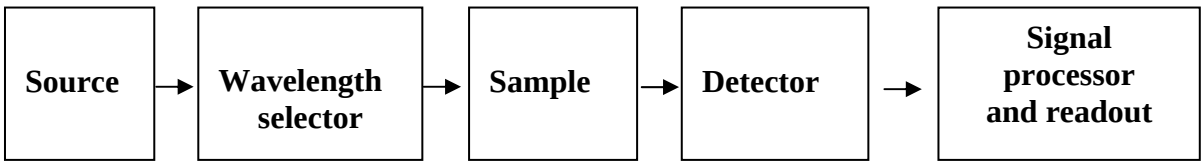

Fig.- 3: Shows a block diagram of uv-vis absorption instrument.

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:** The cell must be made of material that possesses radiation in the spectral region of interest. This, quartz or fused silica is 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.

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.

1.2. TOXICOLOGY

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

1.2.1. 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 behavioral 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 their is capable of producing injury of 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 does differentiates a poison and a remedy.

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

1.2.2. 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.

A. Corrosives:

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

Organic, e.g. Oxalic acid, Carbolic acid.

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

B. 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. Canthatides, Snake and insect bites etc.

Mechanical, e.f. Powdered glass, Diamond dust, Hair etc.

C. Neurotics:

(1) Cerebral (Affecting the barin),

(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.

D. Miscellaneous Group: Food poisoning, botulism etc.

1.2.3. 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 tartar emetic 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 following by numbness produced by aconite, local anesthesia 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 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 hours 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 be 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 in 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 toxicology potency of the metal. As a general rule, the materials 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 are 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 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 stoichiometric antagonism may be envisioned.

iv. Carcinogens and Carcinogenicity:

Carcinogens of 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 malignant tumours or cancers. Tumours that are usually encapsulated 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 sell, making them more susceptible to further carcinogenic effect. Metals such as beryllium,

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, aluminum, 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 co-carcinogens. Metal carcinogens may enhance or potentiate 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).

- ****D.V. Frost, CRC Critical Review in Toxicology, 1(4) 467 (1972).***
- ***** L. Gibney, Chemical and Engineering News, 53 15(1976).***
- ****** M.F. Stanton, Cancern Res., 28 1000 (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 displyed 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 (hemoglobin), 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 proposed an essential nutrient for humans, though classically have long histories as toxic elements. Even the well-known toxic elements arsenic, lead, copper, zinc 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.

.1.2.4. 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) 1945].

**** k. Schwartz, ‘Clinical Chemistry and Toxicology of Metals, Elsevier, 1977, P.3***

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 earth crust, 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 faction 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 contaminants 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 MnO_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 a lot of examples where lower valence states of certain metals (As, Sb, etc.) more toxic than these of higher valence ones.

1.3 ENVIRONMENTAL POLLUTION

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

1.3.1 Definitions:

(i) Environmental Pollution:

"Environmental pollution is partly rapacity 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 foreseeable 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 other. 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 does of a chemical than it did previously to the same does.

1.3.2 Public Health and Pollution:

Mankind has been confronted with pollution problems since early times. Until the end of the 19^{th} 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 well-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 performed 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 juncture that we begin to reflect on 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 depend 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 are 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 methyl mercury in farmers and their families in Iraq, about 1000 cases had been ascribed in the world as methyl and ethyl mercury poisoning.

1.3.3 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 tanker which burst at Ghorasal Fertilizer Factory near Dhaka in August, 1991 and killed eleven 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 Factory at Chittagong and chlorine gas from different industries in Bangladesh, show the negligence of the governing bodies. Evidence of contamination of products used in food packing and pipes for drinking water [22] by unpolymerised vinyl chloride monomer have also been reported.

An examination of the Location of industries shows 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 factory 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 measures 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. Environmental water quality standard for Bangladesh are summarized in Table-1.

TABLE-1: 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
Aluminum	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
Carbon dioxide	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-Dicloro-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
Pentachloropenol	mg/L	0.03	0.001	NYS	NYS	NYS	NYS	NYS	NYS
2,4,6-Tri-chlorrophenol	mg/L	0.03		NYS	NYS	NYS	NYS	NYS	NYS
Chlorine (residual)	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)	mg/L	n/	o		NYS	NYS	10	NYS	NYS
Coliforms (Total)	n/100	n/	2^t	200	5000	NYS	1000	100	1000
Color	Hazen	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

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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
lron	mg/L	0.321[c]	0.3	NYS	NYS	0.5[c]	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	1.1-1[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 Grease	mg/L	0.01	0.01	0.1	0.1	NYS	NYS	NYS	NYS
Phosphate	mg/L	0.01	0.8	0.05	0.8	0.8	0.2	0.1	NYS

* **NYS- Not yet sustainable.** Source: “Environmental quality standard for Bangladesh, Department of Environment, People’s Republic of Bangladesh, 1991.

1.4 ABOUT LEAD (Pb)

Lead is a main-group element with symbol **Pb** (Latin: *plumbum*) and atomic number 82. Lead is a soft, malleable poor metal. It is also counted as one of the heavy metals. Metallic lead has a bluish-white color after being freshly cut, but it soon tarnishes to a dull grayish color when exposed to air. Lead has a shiny chrome-silver luster when it is melted into a liquid. Some general properties of Lead (Pb) are follows:

General properties:	
Name, symbol, number	lead, Pb, 82
Group, period, block	14, 6, p
Standard atomic weight	207.2 g·mol^{-1}
Electron configuration	[Xe] 4f^{14} 5d^{10} 6s^{2} 6p^{2}
Electrons per shell	2, 8, 18, 32, 18, 4
Physical properties:	
Phase	solid
Density (near r.t.)	11.34 g·cm^{-3}
Liquid density at m.p.	10.66 g·cm^{-3}
Melting point	600.61°K (327.46°C, 621.43°F)
Boiling point	2022K (1749°C, 3180°F)
Heat of fusion	4.77 kJ·mol^{-1}
Heat of vaporization	179.5 kJ·mol^{-1}
Atomic properties:	
Crystal structure	cubic face centered
Oxidation states	4, 2 (Amphoteric oxide)
Electronegativity	2.33 (Pauling scale)
Ionization energies	1st: 715.6 kJ·mol^{-1}
(more)	2nd: 1450.5 kJ·mol^{-1}
	3rd: 3081.5 kJ·mol^{-1}

Atomic radius	180 pm
Covalent radius	147 pm
Van der Waals radius	202 pm
Miscellaneous:	
Magnetic ordering	diamagnetic
Isotopes	^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb

Lead (Pb) is used in building construction, lead-acid batteries, bullets and shots, weights, as part of solders, pewters, fusible alloys and as a radiation shield. Lead has the highest atomic number of all of the stable elements, although the next higher element, bismuth, has a half-life that is so long (much longer than the age of the universe) that it can be considered stable. Its four stable isotopes have 82 protons; a "magic number" in the nuclear shell model of atomic nuclei.

Lead is a poisonous substance to animals. It damages the nervous system and causes brain disorders. Excessive lead also causes blood disorders in mammals. Like the element mercury, another heavy metal, lead is a potent neurotoxin that accumulates both in soft tissues and the bones. Lead poisoning has been documented from ancient Rome, ancient Greece, and ancient China.

1.4 .1. HISTORY OF LEAD:

Lead has been commonly used for thousands of years because it is widespread, easy to extract and easy to work with. It is highly malleable and ductile as well as easy to smelt. Metallic lead beads dating back to 6400 BC have been found in Çatalhöyük in modern-day Turkey.[23] In the early Bronze Age, lead was used with antimony and arsenic. Lead is mentioned in the Book of Exodus (15:10).

The largest preindustrial producer of lead was the Roman economy, with an estimated output per annum of 80,000 t, typically won as a by-product of silver smelting. which was[24][25][26] Roman mining activities occurred in Central Europe, Roman Britain, the Balkans, Greece, Asia Minor; Hispania alone accounted for 40% of world production.

Roman lead pipes often bore the insignia of Roman emperors (see Roman lead pipe inscriptions). Lead plumbing in the Latin West may have been continued beyond the age of Theoderic the Great into the medieval period. Many Roman "pigs" (ingots) of lead figure in Derbyshire lead mining history and in the history of the industry in other English centers. The Romans also used lead in molten form to secure iron pins that held together large limestone blocks in certain monumental buildings. In alchemy, lead was thought to be the oldest metal and was associated with the planet Saturn.

Lead's symbol Pb is an abbreviation of its Latin name plumbum for soft metals; originally it was plumbum nigrum (literally, "black plumbum"), where plumbum candidum (literally, "bright plumbum") was tin. The English words "plumbing", "plumber", "plumb", and "plumb-bob" also derive from this Latin root.

1.4.2. HEALTH EFFECTS:

Lead is a soft metal that has known many applications over the years. It has been used widely since 5000 BC for application in metal products, cables and pipelines, but also in paints and pesticides. Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%).

Lead is a poisonous metal that can damage nervous connections (especially in young children) and cause blood and brain disorders. Lead poisoning typically results from ingestion of food or water contaminated with lead; but may also occur after accidental ingestion of contaminated soil, dust, or lead based paint. Long-term exposure to lead or its salts (especially soluble salts or

the strong oxidant PbO_2) can cause nephropathy, and colic-like abdominal pains. The effects of lead are the same whether it enters the body through breathing or swallowing. Lead can affect almost every organ and system in the body. The main target for lead toxicity is the nervous system, both in adults and children. Long-term exposure of adults can result in decreased performance in some tests that measure functions of the nervous system. It may also cause weakness in fingers, wrists, or ankles. Lead exposure also causes small increases in blood pressure, particularly in middle-aged and older people and can cause anemia. Exposure to high lead levels can severely damage the brain and kidneys in adults or children and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. Chronic, high-level exposure have shown to reduce fertility in males.[27] The antidote/treatment for lead poisoning consists of dimercaprol and succimer.

The concern about lead's role in cognitive deficits in children has brought about widespread reduction in its use (lead exposure has been linked to learning disabilities).[28] Most cases of adult elevated blood lead levels are workplace-related. High blood levels are associated with delayed puberty in girls.[29] Lead has been shown many times to permanently reduce the cognitive capacity of children at extremely low levels of exposure.[30] There appears to be no detectable lower limit below which lead has no effect on cognition.

During the 20th century, the use of lead in paint pigments was sharply reduced because of the danger of lead poisoning, especially to children. By the mid-1980s, a significant shift in lead end-use patterns had taken place. Much of this shift was a result of the U.S. lead consumers' compliance with environmental regulations that significantly reduced or eliminated the use of lead in non-battery products, including gasoline, paints, solders, and water systems. Lead use is being further curtailed by the European Union's RoHS directive. Lead may still be found in harmful quantities in stoneware, vinyl (such as that used for tubing and the insulation of electrical cords), and brass

manufactured in China. Between 2006 and 2007 many children's toys made in China were recalled, primarily due to lead in paint used to color the product.
Older houses may still contain substantial amounts of lead paint. White lead paint has been withdrawn from sale in industrialized countries, but the yellow lead chromate is still in use; for example, Holland Colours Holcolan Yellow. Old paint should not be stripped by sanding, as this produces inhalable dust.
Lead salts used in pottery glazes have on occasion caused poisoning, when acidic drinks, such as fruit juices, have leached lead ions out of the glaze.[31] It has been suggested that what was known as "Devon colic" arose from the use of lead-lined presses to extract apple juice in the manufacture of cider. Lead is considered to be particularly harmful for women's ability to reproduce. Lead(II) acetate (also known as sugar of lead) was used by the Roman Empire as a sweetener for wine, and some consider this to be the cause of the dementia that affected many of the Roman Emperors.
Lead as a soil contaminant is a widespread issue, since lead is present in natural deposits and may also enter soil through (leaded) gasoline leaks from underground storage tanks or through a wastestream of lead paint or lead grindings from certain industrial operations.
Lead can also be found listed as a criteria pollutant in the United States Clean Air Act section 108. Lead that is emitted into the atmosphere can be inhaled, or it can be ingested after it settles out of the air. It is rapidly absorbed into the bloodstream and is believed to have adverse effects on the central nervous system, the cardiovascular system, kidneys, and the immune system.[32]

1.4.3. LEAD POISONING:

Lead poisoning (also known as plumbism, colica pictonium, saturnism, Devon colic, or painter's colic) is a medical condition caused by increased levels of the heavy metal lead in the body. Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders.

Symptoms include abdominal pain, headache, anemia, irritability, and in severe cases seizures, coma, and death.

Routes of exposure to lead include contaminated air, water, soil, food, and consumer products. Occupational exposure is a common cause of lead poisoning in adults. One of the largest threats to children is lead paint that exists in many homes, especially older ones; thus children in older housing with chipping paint are at greater risk. Prevention of lead exposure can range from individual efforts (e.g. removing lead-containing items such as piping or blinds from the home) to nationwide policies (e.g. laws that ban lead in products or reduce allowable levels in water or soil).

Elevated lead in the body can be detected by the presence of changes in blood cells visible with a microscope and dense lines in the bones of children seen on X-ray. However, the main tool for diagnosis is measurement of the blood lead level; different treatments are used depending on this level. The major treatments are removal of the source of lead and chelation therapy (administration of agents that bind lead so it can be excreted).

Humans have been mining and using this heavy metal for thousands of years, poisoning themselves in the process. Although lead poisoning is one of the oldest known work and environmental hazards, the modern understanding of the small amount of lead necessary to cause harm did not come about until the latter half of the 20th century. No safe threshold for lead exposure has been discovered—that is, there is no known amount of lead that is too small to cause the body harm.

1.4.3.i. Classification

Classically, "lead poisoning" or "lead intoxication" has been defined as exposure to high levels of lead typically associated with severe health effects. Poisoning is a pattern of symptoms that occur with toxic effects from mid to high levels of exposure; toxicity is a wider spectrum of effects, including subclinical ones (those that do not cause symptoms).[33] However, professionals often use "lead poisoning" and "lead toxicity" interchangeably,

and official sources do not always restrict the use of "lead poisoning" to refer only to symptomatic effects of lead.

The amount of lead in the blood and tissues, as well as the time course of exposure, determines toxicity. Lead poisoning may be acute (from intense exposure of short duration) or chronic (from repeat low-level exposure over a prolonged period), but the latter is much more common. Diagnosis and treatment of lead exposure are based on blood lead level (the amount of lead in the blood), measured in micrograms of lead per deciliter of blood (µg/dL). The US Centers for Disease Control and Prevention and the World Health Organization state that a blood lead level of 10 µg/dL or above is a cause for concern; however, lead may impair development and have harmful health effects even at lower levels, and there is no known safe exposure level.[34] Authorities such as the American Academy of Pediatrics define lead poisoning as blood lead levels higher than 10 µg/dL.

Lead forms a variety of compounds and exists in the environment in various forms. Features of poisoning differ depending on whether the agent is an organic compound (one that contains carbon), or an inorganic one. Organic lead poisoning is now very rare, due to the fact that countries across the world have phased out the use of organic lead compounds as gasoline additives, but such compounds are still used in industrial settings. Organic lead compounds, which cross the skin and respiratory tract easily, affect the central nervous system predominantly.

1.4.3.ii. Signs and symptoms:

Lead poisoning can cause a variety of symptoms and signs which vary depending on the individual and the duration of lead exposure.[35] Symptoms are nonspecific and may be subtle, and someone with elevated lead levels may have no symptoms. Symptoms usually develop over weeks to months as lead builds up in the body during a chronic exposure, but acute symptoms from brief, intense exposures also occur. Symptoms from exposure to organic lead, which is probably more toxic than inorganic lead due to its lipid solubility, occur rapidly.[36] Poisoning by organic lead compounds has symptoms

predominantly in the central nervous system, such as insomnia, delirium, cognitive deficits, tremor, hallucinations, and convulsions.

Symptoms may be different in adults and children; the main symptoms in adults are headache, abdominal pain, memory loss, kidney failure, male reproductive problems, and weakness, pain, or tingling in the extremities.[37] The classic signs and symptoms in children are loss of appetite, abdominal pain, vomiting, weight loss, constipation, anemia, kidney failure, irritability, lethargy, learning disabilities, and behavior problems. Children may also experience hearing loss, delayed growth, drowsiness, clumsiness, or loss of new abilities, especially speech skills. Symptoms may appear in children at lower blood lead levels than in adults.[38]

Early symptoms of lead poisoning in adults are commonly nonspecific and include depression, loss of appetite, intermittent abdominal pain, nausea, diarrhea, constipation, and muscle pain. Other early signs in adults include malaise, fatigue, decreased libido, and problems with sleep. An unusual taste in the mouth and personality changes is also early signs. In adults, symptoms can occur at levels above 40 µg/dL, but are more likely to occur only above 50–60 µg/dL. Symptoms begin to appear in children generally at around 60 µg/dL. However, the lead levels at which symptoms appear vary widely depending on unknown characteristics of each individual. At blood lead levels between 25 and 60 µg/dL, neuropsychiatric effects such as delayed reaction times, irritability, and difficulty concentrating, as well as slowed motor nerve conduction and headache can occur. Anemia may appear at blood lead levels higher than 50 µg/dL. In adults, abdominal colic, involving paroxysms of pain, may appear at blood lead levels greater than 80 µg/dL. Signs that occur in adults at blood lead levels exceeding 100 µg/dL include wrist drop and foot drop, and signs of encephalopathy (a condition characterized by brain swelling), such as those that accompany increased pressure within the skull, delirium, coma, seizures, and headache. In children, signs of encephalopathy such as bizarre behavior, discoordination, and apathy occur at lead levels exceeding 70 µg/dL. For both adults and children, it is rare to be asymptomatic if blood lead levels exceed 100 µg/dL.

[A]. Acute poisoning:

In acute poisoning, typical neurological signs are pain, muscle weakness, paraesthesia, and, rarely, symptoms associated with encephalitis. Abdominal pain, nausea, vomiting, diarrhea, and constipation are other acute symptoms.[39] Lead's effects on the mouth include astringency and a metallic taste. Gastrointestinal problems, such as constipation, diarrhea, poor appetite, or weight loss, are common in acute poisoning. Absorption of large amounts of lead over a short time can cause shock (insufficient fluid in the circulatory system) due to loss of water from the gastrointestinal tract. Hemolysis (the rupture of red blood cells) due to acute poisoning can cause anemia and hemoglobin in the urine. Damage to kidneys can cause changes in urination such as decreased urine output. People who survive acute poisoning often go on to display symptoms of chronic poisoning.

[B]. Chronic poisoning:

Chronic poisoning usually presents with symptoms affecting multiple systems, but is associated with three main types of symptoms: gastrointestinal, neuromuscular, and neurological. Central nervous system and neuromuscular symptoms usually result from intense exposure, while gastrointestinal symptoms usually result from exposure over longer periods. Signs of chronic exposure include loss of short-term memory or concentration, depression, nausea, abdominal pain, loss of coordination, and numbness and tingling in the extremities. Fatigue, problems with sleep, headaches, stupor, slurred speech, and anemia are also found in chronic lead poisoning. A "lead hue" of the skin with pallor is another feature.[40] A blue line along the gum, with bluish black edging to the teeth is another indication of chronic lead poisoning. Children with chronic poisoning may refuse to play or may have hyperkinetic or aggressive behavior disorders.

1.4.3. iii. Exposure routes

Lead is a common environmental pollutant. Causes of environmental contamination include industrial use of lead, such as is found in plants that process lead-acid batteries or produce lead wire or pipes, and metal recycling and foundries. Children living near facilities that process lead, such as smelters, have been found to have unusually high blood lead levels. In August 2009, parents rioted in China after lead poisoning was found in nearly 2000 children living near zinc and manganese smelters.[41] Lead exposure can occur from contact with lead in air, household dust, soil, water, and commercial products.

A) Occupational exposure

Battery recycling workers are at risk for lead exposure. This worker ladles molten lead into billets in a lead-acid battery recovery facility.

In adults, occupational exposure is the main cause of lead poisoning. People can be exposed when working in facilities that produce a variety of lead-containing products; these include radiation shields, ammunition, certain surgical equipment, fetal monitors, plumbing, circuit boards, jet engines, and ceramic glazes. In addition, lead miners and smelters, plumbers and fitters, auto mechanics, glass manufacturers, construction workers, battery manufacturers and recyclers, firing range instructors, and plastic manufacturers are at risk for lead exposure. Other occupations that present lead exposure risks include welding, manufacture of rubber, printing, zinc and copper smelting, processing of ore, combustion of solid waste, and production of paints and pigments. Parents who are exposed to lead in the workplace can bring lead dust home on clothes or skin and expose their children.

B) Paint:

Some lead compounds are bright colors and are used widely in paints, and lead paint is a major route of lead exposure in children. Deteriorating lead paint can produce dangerous lead levels in household dust and soil.[42]

Deteriorating lead paint and lead-containing household dust are the main causes of chronic lead poisoning. Many young children display pica, eating things that are not food. Even a small amount of a lead-containing product such as a paint chip or a sip of glaze can contain tens or hundreds of milligrams of lead.[43] Eating chips of lead paint presents a particular hazard to children, generally producing more severe poisoning than occurs from dust. However, removing lead paint from dwellings, e.g. by sanding or torching, can create lead-containing dust and fumes. Therefore, special precautions must be taken when removing lead paint.

C) Soil:

A lead warning on a gas pump. Tetraethyl lead, which used to be added to gasoline, contributed to soil contamination. Residual lead in soil contributes to lead exposure in urban areas. Lead content in soil may be caused by broken-down lead paint, residues from lead-containing gasoline or pesticides used in the past, contaminated landfills, or from nearby industries such as foundries or smelters. Although leaded soil is less of a problem in countries that no longer have leaded gasoline, it remains prevalent, raising concerns about the safety of urban agriculture; eating food grown in contaminated soil can present a lead hazard.[44]

D) Water:

Lead from the atmosphere or soil can end up in groundwater and surface water. It is also potentially in drinking water, e.g. from plumbing and fixtures that are either made of lead or have lead solder. Since acidic water breaks down lead in plumbing more readily, chemicals can be added to municipal water to increase the pH and thus reduce the corrosivity of the public water supply. Chloramines, which were adopted as a substitute for chlorine disinfectants due to fewer health concerns, increase corrositivity.[42] In the US, 14–20% of total lead exposure is attributed to drinking water. In 2004, a team of seven reporters from The Washington Post discovered high levels of lead in the drinking water in Washington, D.C. and won an award for investigative reporting for a series of articles about this contamination.[45]

In Australia, collecting rainwater from roof runoff used as potable water may contain lead if there is lead contaminates on the roof or in the storage tank. The Australian Drinking Water Guidelines allow a maximum of .01 mg/L lead in water.

E) Lead-containing products:

Lead can be found in products such as kohl, a South Asian cosmetic, and from some toys. In 2007, millions of toys made in China were recalled from multiple countries due to safety hazards including lead paint.[46] Vinyl mini-blinds, found especially in older housing, may contain lead.ead is commonly incorporated into herbal remedies such as Indian Ayurvedic preparations and remedies of Chinese origin. There are also risks of elevated blood lead levels caused by folk remedies like azarcon and greta, which each contain about 95% lead. Ingestion of metallic lead, such as small lead fishing lures, increases blood lead levels and can be fatal. Ingestion of lead-contaminated food is also a threat. Ceramic glaze often contains lead, and dishes that have been improperly fired can leach the metal into food, potentially causing severe poisoning. In some places, the solder in cans used for food contains lead. People who eat animals hunted with lead bullets may be at risk for lead exposure. Bullets lodged in the body rarely cause significant levels of lead poisoning, but bullets lodged in the joints are the exception, as they deteriorate and release lead into the body over time.

1.4.3.iv. Pathophysiology:

Exposure occurs through inhalation, ingestion or occasionally skin contact. Lead may be taken in through direct contact with mouth, nose, and eyes (mucous membranes), and through breaks in the skin. Tetra-ethyl lead, which was a gasoline additive and is still used in fuels such as aviation fuel, passes through the skin; however inorganic lead found in paint, food, and most lead-containing consumer products is only minimally absorbed through the skin. The main sources of absorption of inorganic lead are from ingestion and inhalation. In adults, about 35–40% of inhaled lead dust is deposited in the

lungs, and about 95% of that goes into the bloodstream. Of ingested inorganic lead, about 15% is absorbed, but this percentage is higher in children, pregnant women, and people with deficiencies of calcium, zinc, or iron. Children and infants may absorb about 50% of ingested lead, but little is known about absorption rates in children.[47]

The main body compartments that store lead are the blood, soft tissues, and bone; the half-life of lead in these tissues is measured in weeks for blood, months for soft tissues, and years for bone. Lead in the bones, teeth, hair and nails is bound tightly and not available to other tissues, and is generally thought not to be harmful.[48] In adults, 94% of absorbed lead is deposited in the bones and teeth, but children only store 70% in this manner, a fact which may partially account for the more serious health impacts on children. The estimated half-life of lead in bone is 20–30 years, and bone can introduce lead into the bloodstream long after the initial exposure is gone. The half-life of lead in the blood in men is about 40 days, but it may be longer in children and pregnant women, whose bones are undergoing remodeling, which allows the lead to be continuously re-introduced into the bloodstream. Also, if lead exposure takes place over years, clearance is much slower, partly due to the re-release of lead from bone. Many other tissues store lead, but those with the highest concentrations (other than blood, bone, and teeth) are the brain, spleen, kidneys, liver, and lungs. It is removed from the body very slowly, mainly through urine. Smaller amounts of lead are also eliminated through the feces, and very small amounts in hair, nails, and sweat.

Lead has no known physiologically relevant role in the body, and its harmful effects are myriad. Lead and other heavy metals create reactive radicals which damage cell structures including DNA and cell membranes. Lead also interferes with DNA transcription, enzymes that help in the synthesis of vitamin D, and enzymes that maintain the integrity of the cell membrane. Anemia may result when the cell membranes of red blood cells become more fragile as the result of damage to their membranes. Lead interferes with metabolism of bones and teeth and alters the permeability of blood vessels and collagen synthesis. Lead may also be harmful to the developing immune system,

causing production of excessive inflammatory proteins; this mechanism may mean that lead exposure is a risk factor for asthma in children. Lead exposure has also been associated with a decrease in activity of immune cells such as polymorphonuclear leukocytes.[49] Lead also interferes with the normal metabolism of calcium in cells and causes it to build up within them.

a) Enzymes:

The primary cause of lead's toxicity is its interference with a variety of enzymes due to the fact that it binds to sulfhydryl groups found on many enzymes. Part of lead's toxicity results from its ability to mimic other metals that take part in biological processes, which act as cofactors in many enzymatic reactions, displacing them at the enzymes on which they act. Lead is able to bind to and interact with many of the same enzymes as these metals but, due to its differing chemistry, does not properly function as a cofactor, thus interfering with the enzyme's ability to catalyze its normal reaction or reactions. Among the essential metals with which lead interacts are calcium, iron, and zinc.

One of the main causes for the pathology of lead is that it interferes with the activity an essential enzyme called delta-aminolevulinic acid dehydratase, or ALAD, which is important in the biosynthesis of heme, the cofactor found in hemoglobin. Lead also inhibits the enzyme ferrochelatase, another enzyme involved in the formation of heme. Ferrochelatase catalyzes the joining of protoporphyrin and Fe^{2+} to form heme. Lead's interference with heme synthesis results in production of zinc protoporphyrin and the development of anemia. Another effect of lead's interference with heme synthesis is the buildup of heme precursors, such as aminolevulinic acid, which may be directly or indirectly harmful to neurons.[50]

b) Neurons:

Lead interferes with the release of neurotransmitters, chemicals used by neurons to send signals to other cells. It interferes with the release of glutamate, a neurotransmitter important in many functions including learning, by blocking NMDA receptors. The targeting of NMDA receptors is thought to

be one of the main causes for lead's toxicity to neurons.[51] A Johns Hopkins report found that in addition to inhibiting the NMDA receptor, lead exposure decreased the amount of the gene for the receptor in part of the brain. In addition, lead has been found in animal studies to cause programmed cell death in brain cells.

1.4.3.v. Complications:

Lead affects every one of the body's organ systems, especially the nervous system, but also the bones and teeth, the kidneys, and the cardiovascular, immune, and reproductive systems. Hearing loss and tooth decay have been linked to lead exposure, as have cataracts. Intrauterine and neonatal lead exposures promote tooth decay.[52] Aside from the developmental effects unique to young children, the health effects experienced by adults are similar to those in children, although the thresholds are generally higher.

[a] Renal system:

Kidney damage occurs with exposure to high levels of lead, and evidence suggests that lower levels can damage kidneys as well.[53] The toxic effect of lead causes nephropathy and may cause Fanconi syndrome, in which the proximal tubular function of the kidney is impaired. Long-term exposure at levels lower than those that cause lead nephropathy have also been reported as nephrotoxic in patients from developed countries that had chronic kidney disease or were at risk because of hypertension or diabetes mellitus. Lead poisoning inhibits excretion of the waste product urate and causes a predisposition for gout, in which urate builds up. This condition is known as saturnine gout.

[b] Cardiovascular system:

Evidence suggests lead exposure is associated with high blood pressure, and studies have also found connections between lead exposure and coronary heart disease, heart rate variability, and death from stroke, but this evidence is

more limited.[54] People who have been exposed to higher concentrations of lead may be at a higher risk for cardiac autonomic dysfunction on days when ozone and fine particles are higher.

[c] Reproductive system:

Lead affects both the male and female reproductive systems. In men, when blood lead levels exceed 40 µg/dL, sperm count is reduced and changes occur in volume of sperm, their motility, and their morphology.[55] A pregnant woman's elevated blood lead level can lead to miscarriage, prematurity, low birth weight, and problems with development during childhood. Lead is able to pass through the placenta and into breast milk, and blood lead levels in mothers and infants are usually similar. A fetus may be poisoned in utero if lead from the mother's bones is subsequently mobilized by the changes in metabolism due to pregnancy; increased calcium intake in pregnancy may help mitigate this phenomenon.[56]

[d] Nervous system:

Lead affects the peripheral nervous system (especially motor nerves) and the central nervous system. Peripheral nervous system effects are more prominent in adults and central nervous system effects are more prominent in children. Lead causes the axons of nerve cells to degenerate and lose their myelin coats.

The brain is the organ most sensitive to lead exposure.[57] Lead poisoning interferes with the normal development of a child's brain and nervous system; therefore children are at greater risk of lead neurotoxicity than adults are. In a child's developing brain, lead interferes with synapse formation in the cerebral cortex, neurochemical development (including that of neurotransmitters), and organization of ion channels. It causes loss of neurons' myelin sheaths, reduces numbers of neurons, interferes with neurotransmission, and decreases neuronal growth.

Lead exposure in young children has been linked to learning disabilities, and children with blood lead concentrations greater than 10 µg/dL are in danger of developmental disabilities. Increased blood lead level in children has been correlated with decreases in intelligence, nonverbal reasoning, short-term memory, attention, reading and arithmetic ability, fine motor skills, emotional regulation, and social engagement. The effect of lead on children's cognitive abilities takes place at very low levels. There is apparently no lower threshold to the dose-response relationship (unlike other heavy metals such as mercury). Reduced academic performance has been associated with lead exposure even at blood lead levels lower than 5 µg/dL. [58] Blood lead levels below 10 µg/dL have been reported to be associated with lower IQ and behavior problems such as aggression, in proportion with blood lead levels. Between the blood lead levels of 5 and 35 µg/dL, an IQ decrease of 2–4 points for each µg/dL increase is reported in children.

High blood lead levels in adults are also associated with decreases in cognitive performance and with psychiatric symptoms such as depression and anxiety.[59] It was found in a large group of current and former inorganic lead workers in Korea that blood lead levels in the range of 20–50 µg/dL were correlated with neuro-cognitive defects. Increases in blood lead levels from about 50 to about 100 µg/dL in adults have been found to be associated with persistent, and possibly permanent, impairment of central nervous system function.

Lead exposure in children is also correlated with neuropsychiatric disorders such as attention deficit hyperactivity disorder and antisocial behavior. Elevated lead levels in children are correlated with higher scores on aggression and delinquency measures. A correlation has also been found between prenatal and early childhood lead exposure and violent crime in adulthood. Countries with the highest air lead levels have also been found to have the highest murder rates, after adjusting for confounding factors. A May 2000 study by economic consultant Rick Nevin theorizes that lead exposure explains 65% to 90% of the variation in violent crime rates in the US. [60] A

2007 paper by the same author claims to show a strong association between preschool blood lead and subsequent crime rate trends over several decades across nine countries.[61]

1.4.3.vi. Prevention

In most cases, lead poisoning is preventable; the way to prevent it is to prevent exposure to lead. Prevention strategies can be divided into individual (measures taken by a family), preventive medicine (identifying and intervening with high-risk individuals), and public health (reducing risk on a population level).

Recommended steps by individuals to reduce the blood lead levels of children include increasing their frequency of hand washing and their intake of calcium and iron, discouraging them from putting their hands to their mouths, vacuuming frequently, and eliminating the presence of lead-containing objects such as blinds and jewellery in the house.[62] In houses with lead pipes or plumbing solder, these can be replaced. Less permanent but cheaper methods include running water in the morning to flush out the most contaminated water, or adjusting the water's chemistry to prevent corrosion of pipes. Lead testing kits are commercially available for detecting the presence of lead in the household.

Screening is an important method in preventive medicine strategies. Screening programs exist to test the blood of children at high risk for lead exposure, such as those who live near lead-related industries.

Prevention measures also exist on national and municipal levels. Recommendations by health professionals for lowering childhood exposures include banning the use of lead where it is not essential and strengthening regulations that limit the amount of lead in soil, water, air, household dust, and products. Regulations exist to limit the amount of lead in paint; for example, a 1978 law in the US restricted the lead in paint for residences, furniture, and toys to 0.06% or less. In October 2008, the US Environmental Protection Agency reduced the allowable lead level by a factor of ten to 0.15 micrograms per cubic meter of air, giving states five years to comply with the standards.[63]

The European Union's Restriction of Hazardous Substances Directive limits amounts of lead and other toxic substances in electronics and electrical equipment. In some places, remediation programs exist to reduce the presence of lead when it is found to be high, for example in drinking water. As a more radical solution, entire towns located near former lead mines have been "closed" by the government, and the population resettled elsewhere, as was the case with Picher, Oklahoma in 2009.[64]

1.5 LITERATURE REVIEW

There are a several methods for quantitative determination of Pb. Some of the established methods of quantitative determination of Pb are follows:

1.5.A. "DETERMINATION OF LEAD BY THE DITHIZONE METHOD." [65]

Discussion. Diphenylthiocarbazone (dithizone) behaves in solution as a tautomeric mixture of (C) and (D):

(C) (D)

It functions as a monoprotic acid (pK_Q = 4.7) up to a pH of about 12; the acid proton is that of the thiol group in (C). `Primary' metal dithizonates are formed according to the reaction:

$$M^{n+} + nH_2Dz \leftrightarrow M(HDz)_n + nH^+$$

Some metals, notably copper, silver, gold, mercury, bismuth, and palladium, form a second complex (which we may term `secondary' dithizonates) at a higher pH range or with a deficiency of the reagent:

$$2M(HDz)_n \longleftrightarrow M_2Dz_n + nH_2Dz$$

In general, the `primary' dithizonates are of greater analytical utility than the `secondary' dithizonates, which are less stable and less soluble in organic solvents.

Dithizone is a violet-black solid which is insoluble in water, soluble in dilute ammonia solution, and also soluble in chloroform and in carbon tetrachloride to yield green solutions. It is an excellent reagent for the determination of small (microgram) quantities of many metals, and can be made selective for certain metals by resorting to one or more of the following devices.

(a) Adjusting the pH of the solution to be extracted. Thus from acid solution (0.1-0.5M) silver, mercury, copper, and palladium can be separated from other metals; bismuth can be extracted from a weakly acidic medium; lead and zinc from a neutral or faintly alkaline medium; cadmium from a strongly basic solution containing citrate or tartrate.

(b) Adding a complex-forming agent or masking agent, e.g. cyanide, thiocyanate, thiosulphate, or EDTA.

It must be emphasised that dithizone is an extremely sensitive reagent and is applicable to quantities of metals of the order of micrograms. Only the purest dithizone may be used, since the reagent tends to oxidise to diphenylthiocarbadiazone, $S=C(N=NC_6H_5)_z$: the latter does not react with metals, is insoluble in ammonia solution, and dissolves in organic solvents to give yellow or brown solutions. Reagents for use in dithizone methods of analysis must be of the highest purity. De-ionised water and redistilled acids are recommended: ammonia solution should be prepared by passing ammonia gas into water. Weakly basic and neutral solutions can frequently be freed from reacting heavy metals by extracting them with a fairly strong solution of dithizone in chloroform until a green extract is obtained. Vessels (of Pyrex) should be rinsed with dilute acid before use. Blanks must always be run.

Only one example of the use of dithizone in solvent extraction will be given in order to illustrate the general technique involved.

Procedure. Dissolve 0.0079 g of pure lead nitrate in 1 L of water in a graduated flask. To 10.0 mL of this solution (containing about 50 µg of lead) contained in a 250 mL separatory funnel, add 75 mL of ammonia-cyanide-sulphite mixture (Note 1), adjust the pH of the solution to 9.5 (pH meter) by the cautious addition of hydrochloric acid then add 7.5 mL of a 0.005 per cent solution of dithizone in chloroform (Note 2), followed by 17.5 mL of chloroform. Shake for 1 minute, and allow the phases to separate. Determine the absorbance at 510 nm against a blank solution in a 1.0 cm absorption cell. A further extraction of the same solution gives zero absorption indicative of the complete extraction of the lead. Almost

the same absorbance is obtained in the presence of 100 µg of copper ion and 100 µg of zinc ion.

Notes. (1) This solution is prepared by diluting 35 mL of concentrated ammonia solution (sp. gr. 0.88) and 3.0 mL of 10 per cent potassium cyanide solution (caution) to 100 mL, and then dissolving 0.15 g of sodium sulphite in the solution.

(2) One millilitre of this solution is equivalent to about 20µg of lead. The solution should be freshly prepared using the analytical-grade reagent, ideally taken from a new or recently opened reagent bottle.

1.5.B. "DETERMINATION OF LEAD AND TIN IN A MIXTURE: ANALYSIS OF SOLDER." [66]

A mixture of tin(IV) and lead(II) ions may be complexed by adding an excess of standard EDTA solution, the excess EDTA being determined by titration with a standard solution of lead nitrate; the total lead-plus-tin content of the solution is thus determined. Sodium fluoride is then added and this displaces the EDTA from the tin(IV)-EDTA complex; the liberated EDTA is determined by titration with a standard lead solution.

Procedure. Prepare a standard EDTA solution (0.2M), a standard lead solution *(0.01 M),* a 30 per cent aqueous solution of hexamine, and a *0.2* per cent aqueous solution of xylenol orange.

Dissolve a weighed amount (about 0.4 g) of solder in 10 mL of concentrated hydrochloric acid and *2* mL of concentrated nitric acid; gentle warming is necessary. Boil the solution gently for about *5* minutes to expel nitrous fumes and chlorine, and allow to cool slightly, whereupon some lead chloride may separate. Add *25.0* mL of standard *0.2M* EDTA and boil for 1 minute; the lead chloride dissolves and a clear solution is obtained. Dilute with 100 mL of de-ionised water, cool and dilute to *250* mL in a graduated flask. Without delay, pipette two or three *25.0* mL portions into separate conical flasks. To each flask add *15* mL hexamine solution, 110 mL de-ionised water, and a few drops of xylenol orange indicator. Titrate with the standard lead nitrate solution until the colour changes from yellow to red. Now add *2.0* g sodium fluoride; the solution acquires a yellow colour owing to the

liberation of EDTA from its tin complex. Titrate again with the standard lead nitrate solution until a permanent (i.e. stable for 1 minute) red colour is obtained. Add the titrant dropwise near the end point; a temporary pink or red colour gradually reverting to yellow signals the approach of the end point.

1.5.C. "DETERMINATION OF LEAD AS CHROMATE" [67]

Discussion. Although this method is limited in its applicability because of the general insolubility of chromates, it is a useful procedure for gaining experience in gravimetric analysis. The best results are obtained by precipitating from homogeneous solution utilising the homogeneous generation of chromate ion produced by slow oxidation of chromium(III) by bromate at 90-95 °C in the presence of an acetate buffer.

Procedure. Use a sample solution containing 0.1-0.2g lead. Neutralise the solution by adding sodium hydroxide until a precipitate just begins to form. Add 10 mL acetate buffer solution [6M in acetic (ethanoic) acid and 0.6M in sodium acetate], 10 mL chromium nitrate solution (2.4g per 100 mL), and 10 mL potassium bromate solution (2.0 g per 100 mL). Heat to 90-95ºC. After generation (of chromate) and precipitation are complete (about 45 minutes) as shown by a clear supernatant liquid, cool, filter through a weighed sintered-glass or porcelain filtering crucible, wash with a little 1 per cent nitric acid, and dry at 120ºC. Weigh as $PbCrO_4$.

1.5.D. "DETERMINATION OF ANTIMONY, COPPER, LEAD AND TIN IN BEARING METAL (CONTROLLED-POTENTIAL PROCEDURE)." [68]

In this case the amounts of copper and antimony (which are deposited simultaneously) are small, and so the cathode potential can be set immediately to the limiting value, but with the higher proportion of tin it can be set initially to a value which is more positive than the limiting value so as to speed up the deposition process.

Procedure. Weigh accurately 0.2-0.4 g of the alloy (as drillings or fine filings) into a small beaker. Dissolve the alloy by warming with a mixture of 10 mL concentrated hydrochloric acid, 10mL water, and 1 g ammonium chloride (the last-named to minimise the loss of tin as tetrachloride). Solution may be hastened by the addition, drop by drop, of concentrated nitric acid. When all the alloy has dissolved, boil off the excess of chlorine and nitrous fumes, add 5 mL concentrated hydrochloric acid, dilute to 150 mL, and then add 1 g of hydrazinium chloride. Stir the solution efficiently and electrolyse, limiting the cathode potential to -0.36 volts vs S.C.E. (saturated calomel electrode); copper and antimony are deposited together. After 30-45 minutes the current becomes constant (usually at about 20 mA): remove the saturated calomel electrode, stop the stirrer, withdraw the electrodes from the solution while washing them with distilled water, and then break the electrolysis circuit. After the normal procedure, weigh the dried cathode.

Separate the copper and antimony by dissolving the deposit in a mixture of 5 mL concentrated nitric acid, 5 mL 40 per cent hydrofluoric acid (CARE), and 10 mL water: boil off the nitrogen oxides, dilute to 150 mL, and add dropwise a solution of potassium dichromate until the liquid is distinctly yellow. Deposit the copper by electrolysing the solution at room temperature and limiting the cathode Us S.C.E. potential to -0.36 volt. Evaluate the weight of antimony by difference.

To the solution from which the copper and antimony have been separated as above, add 5 mL concentrated hydrochloric acid and 1 g hydrazinium chloride. Electrolyse using a weighed copper-coated cathode after adding sufficient distilled water to cover the electrode. Set the potentiostat to give a cathode potential of - 0.6 volts vs the S.C.E. changing to -0.7 volt vs the S.C.E. over a period of 20 minutes; continue the electrolysis for a further 25 minutes to complete the deposition of lead and tin. Neutralise the electrolyte by adding dilute ammonia solution (1:1), otherwise some tin may re-dissolve during the washing of the electrodes, then remove the cathode, wash, dry and weigh to determine the weight of tin and lead.

Dissolve the deposit from the cathode in 15 mL nitric acid, sp. gr. 1.20, in a

400 mL beaker, and finally wash the cathode with water. Evaporate the resulting solution almost to dryness, cool, and add a further 15 mL nitric acid, sp. gr. 1.2. Digest hot for a time and then filter the hydrated tin(IV) oxide on a paper-pulp pack, and wash it four times with hot water. Dilute the resulting filtrate and washings to 100 mL, and heat to boiling. Electrolyse the hot solution with a small platinum gauze anode at 4-5 A until the deposition of PbO_2 is complete (about 5 minutes). Remove the anode, dry, and weigh as before. Calculate the percentage of lead from the weight of $Pb0_2$ using the empirical factor of 0.864. Evaluate the tin content by subtraction from the combined weight of tin and lead.

Calculate the percentages of antimony, copper, lead, and tin in the alloy.

In a similar determination described by Lingane and Jones," an alloy containing copper, bismuth, lead, and tin is dissolved in hydrochloric acid as described above, and then 100 mL of sodium tartrate solution *(0.1 M)* is added, followed by sufficient sodium hydroxide solution *(5M)* to adjust the pH to 5.0. After the addition of hydrazinium chloride (4 g), the solution is warmed to 70 °C and then electrolysed. Copper is deposited at -0.3 volt, and then sequentially, bismuth at - 0.4 volt, and lead at - 0.6 volt; all cathode potentials quoted are vs the S.C.E. After deposition of the lead, the solution is acidified with hydrochloric acid and the tin then deposited at a cathode potential of -0.65 volt vs the S.C.E.

1.5.E. "DETERMINATION OF LEAD AND COPPER IN STEEL." [69]

In the application of the polarographic method of analysis to steel a serious difficulty arises owing to the reduction of iron(III) ions at or near zero potential in many base electrolytes. One method of surmounting the difficulty is to reduce iron (III) to iron(II) with hydrazinium chloride in a hydrochloric acid medium. The current near zero potential is eliminated, but that due to the reduction of iron (II) ions at about - 1.4 volts vs S.C.E. still occurs. Other metals (including copper and lead) which are reduced at potentials less negative than this can then be determined without interference from the

iron. Alternatively, the Fe^{+3} to Fe^{2+} reduction step may be shifted to more negative potentials by complex ion formation. The following procedure may be used for the simultaneous determination of copper and lead in plain carbon steels. Dissolve 5.0 g of the steel, accurately weighed, in a mixture of 25 mL of water and 25 mL of concentrated hydrochloric acid: heat gently to minimise the loss of acid. Add a few drops of saturated potassium chlorate solution to dissolve carbides, etc., and boil the mixture until the solution is clear. Cool and dilute to 50 mL with water in a graduated flask. Pipette 2.00 mL of this solution into a polarographic cell and add: 1.0 mL of 20 per cent hydrazinium chloride solution to reduce any iron (III) to the iron (II) state, 1.0 mL of 0.2 per cent methyl cellulose to act as a maximum suppressor, and 5.5 mL of 2.0 M sodium formate solution to adjust the pH of the solution to that at which reduction of Fe(III) and Cu(II) ions takes place. Place the cell in a nearly boiling water bath for 10 minutes in order to complete the reduction. Cool. Analyse the solution polarographically: use a saturated calomel reference electrode. The first step in the polarogram is due to the reduction of copper (I) ions to the metal and has a half-wave potential of -0.25 volt vs S.C.E. The second step, which is due to lead, has a half-wave potential of -0.45 vs S.C.E. Carry out a calibration by adding known amounts of copper and lead to a solution of steel of low copper and lead content, and determine the increase in wave heights due to the additions.

Calculate the percentage of copper and of lead in the sample of steel.

1.5.F. "DETERMINATION OF LEAD WITH STANDARD POTASSIUM DICHROMATE SOLUTION." [70]

Both lead ion and dichromate ion yield a diffusion current at an applied potential to a dropping mercury electrode of - 1.0 volt against the saturated calomel electrode (S.C.E.). Amperometric titration gives a V-shaped curve. The exercise described refers to the determination of lead in lead nitrate; the application to the determination of lead in dilute aqueous solutions

(10^{-3} - 10^{-4}*M)* is self-evident.

Reagents. *Lead nitrate solution.* Dissolve an accurately weighed amount of lead nitrate in 250 mL water in a graduated flask to give an approximately *0.01 M* solution. For the titration, dilute 10 mL of this solution (use a pipette) to 100 mL in a graduated flask, thus yielding a *ca 0.001 M* solution of known strength.

Potassium dichromate, ca 0.05M solution. Use the appropriate quantity, accurately weighed, of the dry solid.

Potassium nitrate, ca 0.01 M solution. For use as the supporting electrolyte.

Procedure. Use the electrical equipment. Set up the dropping mercury electrode assembly and allow the mercury to drop into distilled water for at least 5 minutes. Meanwhile, place 25.0 mL of the *ca 0.001 M* lead nitrate solution in the titration cell, add 25 mL 0.01 *M* potassium nitrate solution, complete the cell assembly, and bubble nitrogen slowly through the solution for 15 minutes. Make the necessary electrical connections. Apply a potential of - 1.0 volt vs S.C.E.: at this potential both the lead and the dichromate ions yield diffusion currents. Turn the three-way tap so that the nitrogen now passes over the surface of the solution. Adjust the microammeter range so that the reading is at the `high' end of the scale. Do not alter the applied voltage during the determination. Add the *ca 0.05M* dichromate solution in 0.05 mL portions until within 1 mL of the end point, and henceforth in 0.01 mL portions until about 1 mL beyond the end point, and continue with additions of 0.05 mL. After each addition pass nitrogen through the solution for 1 minute to ensure thorough mixing and also de-oxygenation, turn the tap so that the nitrogen passes over the surface of the solution, and observe the current. It will be seen that a large initial current will decrease as the titration proceeds to a small value at the equivalence point, and then increase again beyond the equivalence point. Plot the values of the current as ordinates against the volume of reagent added as abscissae: draw two straight lines through the branches of the `curve'. The point of intersection is the

equivalence point. Calculate the percentage of lead in the sample of lead nitrate.

1.5.G. "DETERMINATION OF TRACE LEAD IN A FERROUS ALLOY" [71]

The procedure followed entails the removal of gross interferences by solvent extraction, and the selective extraction and concentration of the trace metal by use of a chelating agent. The alloy used should not contain more than 0.1 g of copper in the sample weighed out.

Preparation of solutions. The following solutions are required.

Ammonia solution (concentrated, `0.880', about 35 per cent NH_3). Preferably the special atomic absorption spectroscopy reagent grade should be used.

Hydrochloric acid, concentrated. Also a solution prepared by measuring 50 mL (measuring cylinder) of the concentrated acid into a 1 L graduated flask and making up with de-ionised water.

Nitric acid, concentrated. Analytical reagent grade.

Ammonium citrate*.* Dissolve 50 g tri-ammonium citrate in 50 mL of concentrated ammonia solution added with care. Cool, and make up to 100 mL with de-ionised water.

Ascorbic acid. Dissolve 20 g of the solid in 100 mL of de-ionised water. This reagent must be freshly prepared.

Potassium cyanide. Dissolve 25 g of the salt in 35 mL of de-ionised water to which has been added 5 mL of concentrated ammonia solution. Make up to 50 mL with de-ionised water and filter if necessary.

Sodium diethyldithiocarbamate *(NaDDC).* Dissolve 1 g in 50 mL of de-ionised water and filter if necessary. This reagent must be freshly prepared.

Lead caprate. Prepare a standard stock solution by dissolving 0.1323 g of the solid in 2 mL of naphthenic acid with warming. Add 20 mL of 4-methylpentan-2-one (methyl isobutyl ketone), cool and then make up to the mark in a 100 mL graduated flask with more of the ketone.

Procedure. Weigh accurately 1 g of the alloy and dissolve in 10 mL of

concentrated hydrochloric acid; warm gently, and if necessary add concentrated nitric acid dropwise (about 3 mL) to assist the dissolution. When the vigorous reaction is complete, digest the solution with gentle heat for about 15 minutes. Cool, if necessary filter through a Whatman No. 541 filter paper, washing the beaker and filter paper with small portions of concentrated hydrochloric acid so that a final volume of about 20 mL is attained. Transfer the solution to a 250 mL separatory funnel using a further 10 mL of concentrated hydrochloric acid to effect a quantitative transfer. Add 50 mL of butyl acetate, shake for one minute and allow to separate; iron and molybdenum are extracted into the organic layer. Separate the two layers, collecting the acid layer and transferring, with the aid of a further 10 mL of concentrated hydrochloric acid, to a clean 250 mL separatory funnel; extract with a 25 mL portion of butyl acetate. Again separate the two layers, collecting the acid layer in a 250 mL beaker.

Add cautiously**,** and with constant stirring, l0mL of the ammonium citrate solution; this will prevent the precipitation of metals when, at a later stage, the pH value of the solution is increased. Then add 10 mL of the 20 per cent ascorbic acid, and adjust to pH 4 (BDH narrow-range indicator paper), by the cautious addition of concentrated ammonia solution down the side of the beaker while stirring continuously. Then add 10 mL of the 50 per cent potassium cyanide solution and *immediately* adjust to a pH of 9-10 (BDH indicator paper) by the addition of concentrated ammonia solution.

Transfer the solution to a 250 mL separatory funnel, rinsing out the beaker with a little water. Add 5 mL of the 2 per cent NaDDC reagent and allow standing for one minute, and then adding a 10 mL portion of 4-methylpentan-2-one (methyl isobutyl ketone), shaking for one minute and then separating and collecting the organic layer. Return the aqueous phase to the funnel, extract with a further 10 mL portion of methyl isobutyl ketone, separate and combine the organic layer with that already collected. Finally, rinse the funnel with a little fresh ketone and add this rinse liquid to the organic extract. In these operations the lead is converted into a chelate which is extracted into the organic solvent.

In order to concentrate the lead extract, remove the lead from the organic solvent by shaking this with three successive 10 mL portions of the dilute hydrochloric acid solution, collecting the aqueous extracts in a 250 mL beaker. To the combined extracts add 5 mL of 20 per cent ascorbic acid solution and adjust to pH 4 by the addition of concentrated ammonia solution. Place the beaker in a fume cupboard, add 3 mL of the 50 per cent potassium cyanide solution and *immediately* adjust the pH to 9-10 with concentrated ammonia solution. Transfer the solution to a 250 mL separatory funnel with the aid of a little de-ionised water, add 5 mL of the 2 per cent NaDDC reagent, allow to stand for one minute and then add 10 mL of methyl isobutyl ketone. Shake for one minute and then separate and collect the organic phase, filtering it through a fluted filter paper. This solution now contains the lead and is ready for the absorption measurement.

Set up a double-beam atomic absorption spectrophotometer with a lead hollow cathode lamp and isolate the resonance line at 283.3 nm; adjust the gas controls to give a fuel-lean acetylene-air flame in accordance with the operating manual supplied with the instrument.

Prepare a blank solution by carrying through all the sequences of the separation procedures using a hydrochloric acid solution to which no alloy has been added, and then measure the absorption given by this blank solution, by a series of standard solutions containing from 1 to 10 µg Pb mL - ^{t} prepared by suitable dilution of the lead caprate stock solution (see Note), and finally of the extract prepared from the sample of alloy. Plot the calibration curve and determine the lead content of the alloy.

Note. If lead caprate is not available, standard lead solutions can be prepared from aqueous solutions containing known weights of lead nitrate and following through the extraction procedure as detailed for the final extraction of lead into methyl isobutyl ketone for the alloy. It should also be noted that steps should be taken to avoid excessive inhalation of the vapour of the methyl isobutyl ketone, which can cause a headache·

1.5.H. "ANALYTICAL CONDITIONS FOR QUANTITATIVE ANALYSIS OF LEAD IN STEELS IN DIRECT-CURRENT OR RADIO-FREQUENCY GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY."[72]

Synopsis: Optimum analytical lines as well as the discharge conditions for lead determination in steel samples were investigated in direct-current and radio-frequency glow discharge optical emission spectrometry (d.c. and r.f. GD-OES). Two emission lines: Pbl 405.784nm and Pb II 220.356 nm, were compared on their analytical performance in d.c. GD-OES, indicating that the Pb II 220.356-nm line should be selected as the analytical line because the emission intensity is much larger than that of the PbI 405.784-nm line. Several iron lines were also measured for correcting variations in the sampling amounts so that the emission intensities of Pb II 220.356nm can be estimated more accurately. Atomic and ionic iron lines, such as Fe I 344.374nm and Fell 254.874nm, having similar excitation energies to Pb II 220.356 nm, were suitable for the internal standard line, because their emission intensities well follow the intensity of the Pb II line when the sampling rate and the excitation conditions are changed. In r.f. GD-OES, a bias-current introduction method was employed for enhancing the emission intensity of the Pb I 405.784-nm line. By conducting of the bias-current of 33 mA at the r.f. power of 80 W, the emission intensities were 12 times larger than those obtained with the conventional plasma. This effect contributes to Pb determination with a higher detection ability in r.f. GD-OES.

1.5.I. CONDUCTOMETRIC METHOD FOR THE QUANTITATIVE ANALYSIS OF Pb(II) AND Cd(II) WITH 2-MERCAPTO-5-R-AMINO-1, 3, 4-THIADIAZOLE DERIVATIVES. [73]

The reactions of the cations with 2-mercapto-5-R-amino-1,3,4-thiadiazole derivatives were studied conductometrically with the purpose of establishing a new conductometric method for the quantitative analysis of Pb(II) and Cd(II). Aqueous solutions of $Pb(NO_3)_2$ and $Cd(CH_3COO)_2$ were titrated with hidroalcoholic solutions of 2-mercapto-5-amino-1,3,4-thiadiazole (MATD), 2-mercapto-5-allylamino-1,3,4-thiadiazole (MA1ATD) and 2-mercapto-5-acetylamino-1,3,4-thiadiazole (MAcATD) and 2-mercapto-5-phenilamino-1,3,4-

thiadiazole (MFATD) in different concentrations. The reactions takes place at pH 6.5 (realised with acetate buffer). A linear classical titration curves was obtained. In solutions more concentrated than $10^{(-2)}$ M just one equivalence point can be noticed, corresponding to 1:2 Me:R stoechiometries. For concentration less than $10^{(-2)}$ M two equivalence point was observed at 1:1 and 2:1 ratio of Me:R, indicating the step formation of the complex. Accurate conductometric determinations can be made using the second break points of the titration curves as equivalence points. The amounts of Cd(II) and Pb(II) taken and recovered are good, with an error less than 1%.

1.5.1 About 1-(2-Pyridylazo)-2-naphthol:

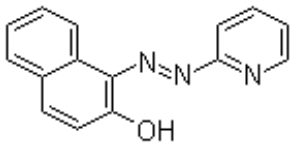
Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis. 1-(2-pyridylazo)-2-naphthol (PAN) has been reported as a spectrophotometric reagent for Cu, Co, Ni, Zn, Mn, Ca but has not previously been used for spectrophotometric determination of Lead (Pb) in aqueous media.

Identification of 1-(2-Pyridylazo)-2-naphthol:

1. Name: 1-(2-Pyridylazo)-2-naphthol,

Synonyms: PAN

2. Molecular Structure:



3. Molecular Formula: $C_{15}H_{11}N_3O$

4. Molecular Weight: 249.27

Physical Properties:

1. Appearance: Orange-red powder

2. Melting point: 138-141 ºC

3. Water solubility: Generally, water insoluble but soluble in organic solvent. In this research work, PAN has been soluble in water in acidic media.

1.6.1. Evidence for spectrophotometric reagent of PAN:

PAN previously has been used as a spectrophotometric reagent for several metals. Some special works are:

1.6.1. A **"Flame atomic absorption spectrometric determination of trace lead after solid-liquid extraction and preconcentration using 1-(2-pyridylazo)-2-naphthol."** [74]

An atomic absorption spectrometric method for the determination of trace amounts of lead after adsorption of its 1-(2-pyridylazo)-2-naphthol (PAN) complex on microcrystalline naphthalene has been developed. This complex was adsorbed on microcrystalline naphthalene in the pH range 8.4-11.5 from large volumes of aqueous solutions of various alloys and biological samples. After filtration, the solid mass consisting of the complex and naphthalene was dissolved with 5 ml of dimethylformamide and the metal was determined by flame atomic absorption spectrometry. Lead was alternatively quantitatively adsorbed on [1-(2-pyridylazo)-2-naphthol]-naphthalene adsorbent packed in a column and determined similarly. In this case, 0.5 µg of lead was concentrated in a column from 500 ml of aqueous sample, where its concentration was as low as 1.0 ng ml_{-1}. Eight replicate determinations of 4.0 µg ml_{-1} of lead gave a mean absorbance of 0.200 with a relative standard deviation of 1.5 %. The sensitivity for 1 % absorption was 88 ng ml_{-1}. The interference of a large number of anions and cations was studied and the optimized conditions developed were utilized for the trace determination of lead in various standard samples.

1.6.1. B **"Determination of trace amount of Cu (ii) ion in aqueous medium by using uv-vis spectrophotometer".** [75]

Trace amount of Copper has determined by spectrophotometric method using 1-(2-pyridylazo)-2-naphthol, as a new spectrophotometric reagent. 1-(2-pyridylazo)-2-naphthol reacts in highly acidic solution at pH 2.45 to 2.55 (HCl) with Copper to give a red chelate which has an absorption maximum at 550 nm. The reaction is instantaneous and absorbance remains stable for over 48 hrs. The average molar absorption co-efficient and sandell's sensitivity were found to be 2.0636×10^4 L mol^{-1} cm^{-1} and 30 ng cm^{-2} respectively. Linear calibration graphs were obtained for 0.1-2.5 µg mL^{-1} of Cu. The stoichiometric

composition of the chelate is 1 : 2 [Cu : 1-(2-pyridylazo)-2-naphthol]. Large excess of over 50 cations, anions, and some common complexing agents (e.g, oxalate, thio-urea) do not interfere in the determination. The method was successfully used in the determination of Copper in Several Standard Reference Materials (alloys, steels and water) as well as in some environmental and industrial waste water. The method has high precision and accuracy. (S = ±0.01 for 0.5 µg mL^{-1}).

1.6 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 easiness of operation. Among various modern trace analysis techniques employed in solution, molecular absorption spectrophotometry has been rated to be one of the most useful 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 spetrophotometry in varied fields of chemical analysis lies in its manifold advantages. Compared to any modern trace and ultra trace analytical technique.

Lead in trace amounts is industrially important. Lead is becoming an ever more widely used metal in industry.

Lead is a poisonous metal that can damage nervous connections (especially in young children) and cause blood and brain disorders. Lead poisoning typically results from ingestion of food or water contaminated with lead; but may also occur after accidental ingestion of contaminated soil, dust, or lead based paint. Long-term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO_2) can cause nephropathy, and colic-like abdominal pains.

Lead can cause several unwanted effects, such as:

- Disruption of the biosynthesis of haemoglobin and anaemia
- A rise in blood pressure
- Kidney damage
- Miscarriages and subtle abortions
- Disruption of nervous systems
- Brain damage
- Declined fertility of men through sperm damage

- Diminished learning abilities of children
- Behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity.

Lead can enter a fetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children.

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 lead in above spectral range.

The analysis of colorless substances by visible spectroscopy is not new, reacting the colorless analyte with a suitable regent, 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 determination of the analyte. A method of calibration enables the estimation of the analyte. For the determination of lead 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 unfavorable 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 lead for which either spectrophotometric methods are non-existence or scarce in literatures.

Finally, the aim of this study was to develop a simple spectrophotometric method for the determination of lead with 1-(2-pyridylazo)-2-naphthol (PAN). The method was optimized individually and result of the measurements was checked by comparison with congenital analysis. PAN has been reported as spectrophotometric reagent for Cu, Ni, Co, Zn, Mn, Ca, but has not previously been used for determination of lead in spectrophotometic method. The present thesis deals with successful attempt toward the establishment of new type of spectrophotometric reagent.

EXPERIMENTAL SECTION

- Spectrophotometric Determination Of Lead (Pb) In Aqueous Media
- Result And Discussion
- Conclusion

2.0 Spectrophotometric Determination Of Lead (Pb) In Aqueous Media

2.1 Introduction:

Different types of legend were used with about 30 toxic metal ions to obtain color chelate through the novel reaction techniques. Finally Trace amount of toxic element lead was determined by spectrophotometric method using 1-(2-pyridylazo)-2-naphthol (**PAN**) as a new spectrophotometric reagent.

Lead (Pb) in trace amounts is important industrially [76], as a toxicant [77] and biological non-essential [78] as an environmental pollutant [79] and as an occupational hazard [80] It is a toxic metal, has been responsible for a number of disease. Lead (Pb) is a highly toxic substance which can produce a wide range of adverse health effects. Both adults and children can suffer from the effects of lead poisoning, but childhood lead poisoning is much more frequent Lead poisoning is a medical condition caused by increased levels of the heavy metal lead in the body. Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders. Symptoms include abdominal pain, headache, anemia, irritability, and in severe cases seizures, coma, and death.

Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis. 1-(2-pyridylazo)-2-naphthol (PAN) has been reported as a spectrophotometric reagent for Cu, Co, Ni, Zn, Mn, Ca [81] but has not previously been used for spectrophotometric determination of lead in aqueous media. This paper reports its use in a very sensitive, highly specific spectro-photometric method for the trace determination of Lead. The method possesses distinct advantages over existing methods 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 1-(2-pyridylazo)-2-naphthol (PAN) in acidic solution with Lead to produce a highly absorbent pink chelate product, followed by direct measurement of the absorbance in aqueous solution. With suitable masking, the reaction can be made highly selective.

2.2 Experimental

2.2.1 Instruments:

A shimdzu (Kyoto, Japan) (Model-1601PC) double beam UV/VIS recording spectrophotometer and Jenway (England, U.K.) (Model-3010) pH-meter were used for the measurement 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.

2.2.2 Reagents and Solutions:

All the chemicals used were of analytical-reagent grade of 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 (1000mL each) were kept in polypropylene bottles containing 1 mL of concentrated HNO_3. More rigorous contamination control was used when the lead levels in the specimens were low.

1-(2-pyridylazo)-2-naphthol (PAN) Solution:

Prepared by dissolving the requisite amount of 1-(2-pyridylazo)-2-naphthol (PAN) (BDH chemicals) in a known volume of acidified (HNO_3) de-ionized

water. More dilute solutions of the reagent were prepared as required. PAN is insoluble in water but soluble in acidic water and organic solvent.

Lead Standard Solutions:

A 1000-mL of stock solution (100 ppm) of divalent lead was prepared by dissolving 0.159 g of AR crystallize lead nitrate [$Pb(NO_3)_2$]; (Merck) in doubly distilled de-ionized water.

EDTA Solution *:*

A 100-mL 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:

1% Potassium permanganate Solution (Merck) was prepared by dissolving in deionized water. Aliquots of this solution were standardized with oxalic acid. Sodium azide solution (5.5% W/v) (Fluka purity >99%) was also used.

Tartarate Solution :

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 :

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 [82] In the case of insoluble substances, special dissolution methods were adopted [83].

2.2.3 Procedure:

1-(2-pyridylazo)-2-naphthol (PAN) solution was taken in a calibrated flask with the Pb solution, the molar ratio of Pb: PAN was maintained in between 1: 2 → 1: 4 fold. The solution's pH was maintained at pH 4.50. The pH was controlled by HNO_3 as acid and NH_4OH as base as required. The solution was prepared with the double distilled de-ionized water. The absorbance was measured at 548 nm against a corresponding reagent blank. The lead content in an unknown sample was determined using concurrently prepared calibration graph.

3.0 Results and Discussion

Absorption spectra of PAN:

The absorption spectra of the PAN Solution system in pH=4.5 medium was recorded using the UV-Vis spectrophotometer. The absorption spectra of the PAN are a symmetric curve with the maximum absorbance co-efficient is shown in Fig-4 (table-2). The λ_{Max} is 440 nm found in different concentration of PAN (4.01 x 10^{-5}M to 3.20 x 10^{-3}M) at pH=4.5 in aqueous solution.

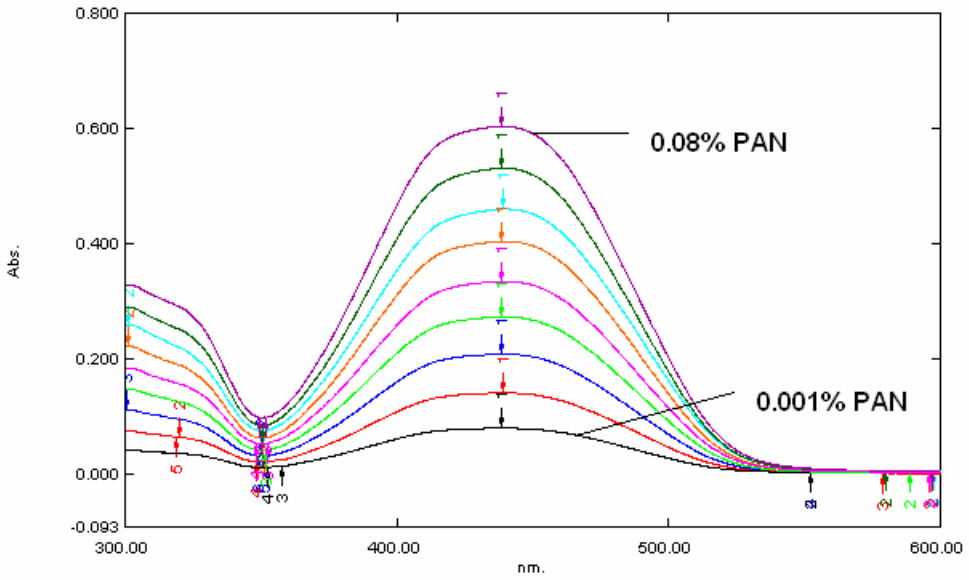


Fig. 4: Absorption spectra at different concentration of PAN (4.01 x 10^{-5}M to 3.20 x 10^{-3}M) at pH=4.5, λ_{Max}= 440 nm in aqueous solution.

Table-2: Absorbance data for different concentration of PAN system at pH= 4.5, λ_{max} =440 nm

Concentration of PAN (%)	Conc. of PAN ($molL^{-1}$)	Absorbance of PAN at pH= 4.5, λ_{max} =440 nm
0.001	4.01×10^{-5}	0.0310
0.015	6.01×10^{-4}	0.1150
0.025	1.00×10^{-4}	0.1975
0.035	1.40×10^{-3}	0.2765
0.045	1.80×10^{-3}	0.3548
0.050	2.00×10^{-3}	0.3950
0.060	2.40×10^{-3}	0.4740
0.070	2.80×10^{-3}	0.5530
0.080	3.20×10^{-3}	0.6320

It is observed in table-2 that the maximum absorbance has been occurred at λ_{Max}= 440 nm in aqueous solution. It has also been observed that, when the concentration of PAN increase then the absorbance also increase along with the λ_{Max} = 440 nm (Table-2). This is in favor of the Beer-Lambert's law.

Absorption spectra of Pb-PAN complex:

The absorption spectra of the Pb-PAN Solution system in pH=4.5 medium was recorded using the UV-Vis spectrophotometer. The absorption spectra of the Pb-PAN are a symmetric curve with the maximum absorbance co-efficient is shown in Fig-5. In all instances measurements were made at **548 nm** against a reagent blank.

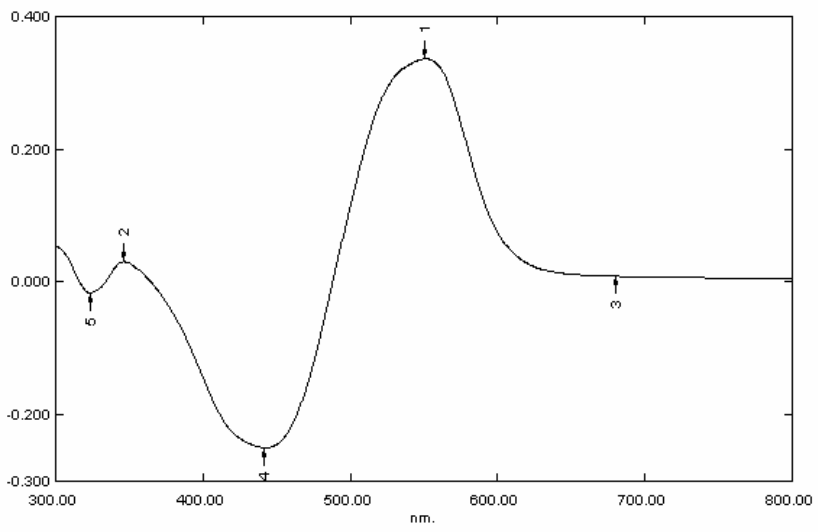


Fig.-5: Absorption spectra of Pb-PAN against the reagent blank in aqueous solution (at pH=4.5, λ_{Max}= 548 nm).

It is observed in fig. 5 that the maximum absorbance has been occurred at λ_{Max} 548 nm in aqueous solution. It has also been observed that, when the concentration of Pb increase then the absorbance also increase along with the λ_{Max} = 548 nm (Table-9). This is in favor of the Beer-Lambert's law.

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Comparison of absorption spectra of PAN and Pb-PAN in aqueous solution:

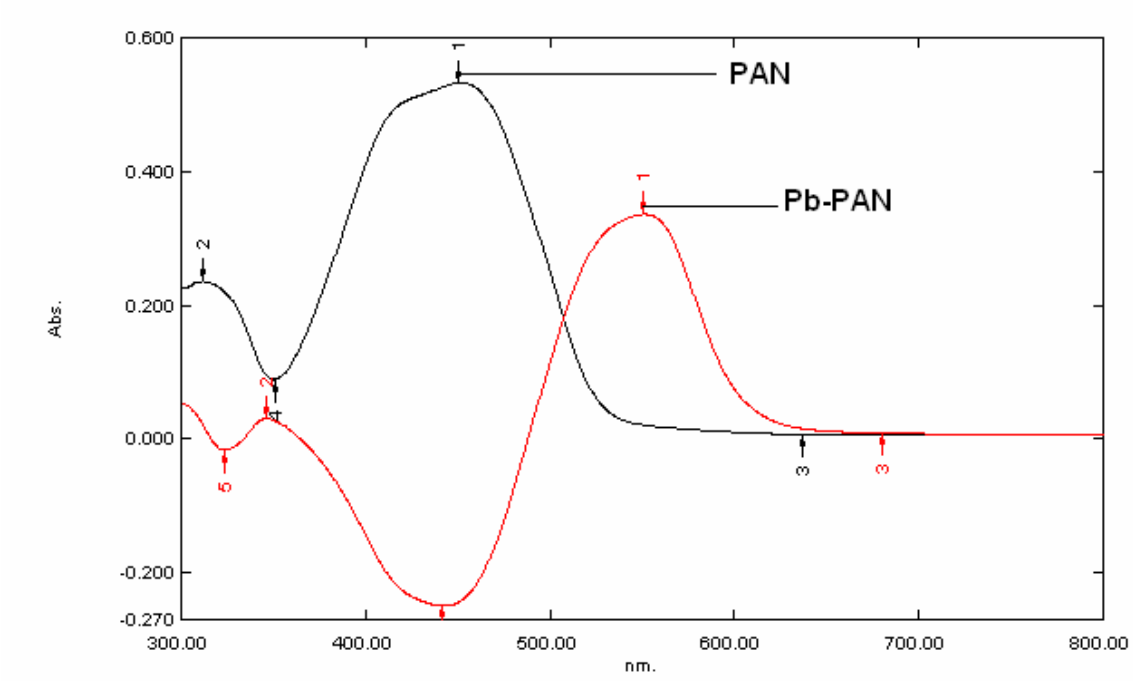

Fig.6: Absorption spectra of PAN and Pb-PAN in aqueous solution.

It is observed in the fig.6 that the λ_{Max} of PAN and Pb-PAN has been occurred in 440 nm and 548 nm respectively. The λ_{Max} shifted from 440 (PAN) to 548nm (Pb-PAN). This is due to formation of Pb-PAN complex.

3.1 Factors Affecting The Absorbance:

Factors Affecting the Absorbance are follows:

i. Effect of pH
ii. Effect of Time
iii. Effect of Temperature
iv. Effect of Reagent Concentration
v. Effect of foreign ions

[I] EFFECT OF pH (pH ADJUSTMENT):

To see the effect of different pH we have taken 1.1 ppm Lead solution. Of the various acids (nitric, sulfuric, and phosphoric) studied nitric acid was found to be the best acid for the system. The absorbances were measured at λ_{Max} 548 nm. For all subsequent measurement pH 4.50, PAN was 0.01% and Pb was 1.1 ppm. The results have been presented in table-3.

Table-3 Effect of various acids and base on the absorbance of Pb-PAN complex.

SL. No.	Name of acids & Base	Absorbance of Pb-PAN complex at λ_{Max}= 548 nm
01	**HNO_3**	**0.336**
02	$HClO_4$	0.201
03	H_2SO_4	0.185
04	Oxalic Acid	0.105
05	Citric Acid	0.095
06	H_3PO_4	0.075
07	CH_3COOH	0.050
08	NH_4OH	0.120

The results of table-3 indicate that the absorbance of Pb-PAN complex was low in the case of organic acids and high in the case of inorganic acids. More over the absorbance was highest in the case of HNO_3 acid.

Some samples of Pb-PAN complex of 1.1 ppm Pb and 0.01% PAN have been prepared with the continuous change of pH at 2.9, 3.1, 3.3, 3.5, 3.7, 3.9, 4.1, 4.3, 4.5, 4.7, 4.9, 5.1, 5.3, 5.5, 5.7 and 5.9 by the standard procedure. The absorbances were measured at λ_{Max} 548 nm and the results have been presented in table-4 and fig-7, 8.

Table-4 Absorbance data for different pH

pH of Pb-PAN complex solution	Absorbance of Pb-PAN complex at λ_{Max}= 548 nm
2.9	0.228
3.1	0.251
3.3	0.270
3.5	0.281
3.7	0.297
3.9	0.304
4.1	0.312
4.3	0.329
4.5	**0.336**
4.7	0.326
4.9	0.310
5.1	0.301
5.3	0.296
5.5	0.279
5.7	0.246
5.9	0.218

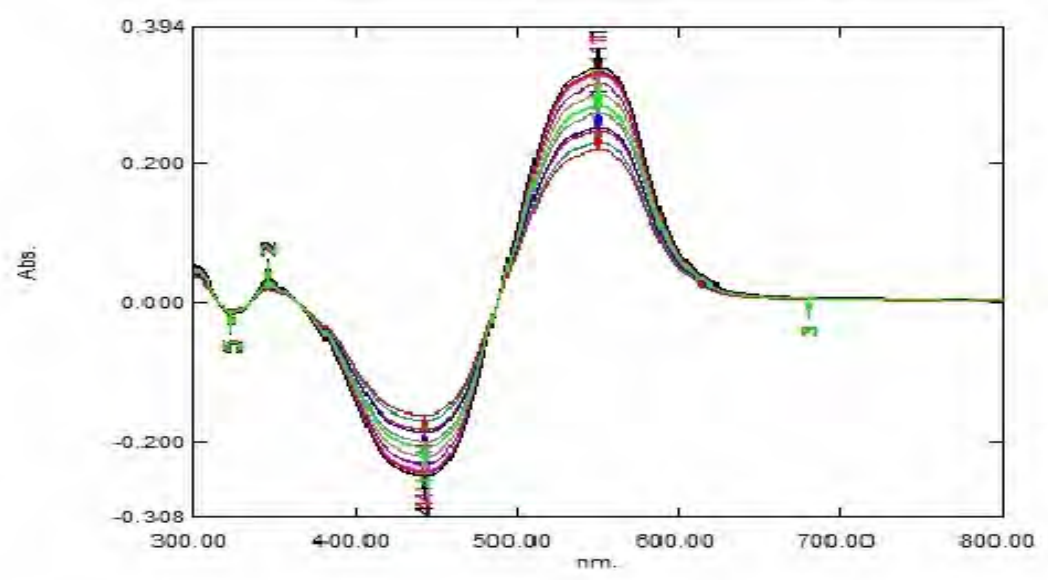

Fig. 7: The overlay of absorption spectra of Pb-PAN(1:2) at different pH(2.9-5.9).

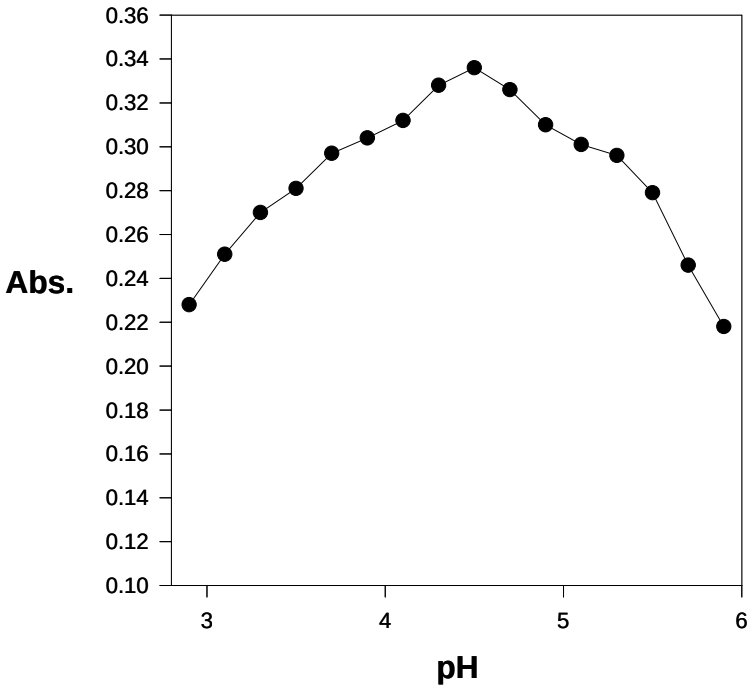

Fig.8: Effect of pH on the absorbance of Pb-PAN (1:2) complex.

The results of the table-4 indicate that the absorbance increased continuously from pH 2.9 to 4.5 at λ_{Max} 548 nm and decreased from pH 4.5. The maximum absorbance has been found at pH 4.5 (λ_{Max} 548nm, abs 0.336).

[ii] EFFECT OF TIME:

A standard sample of Pb-PAN complex at pH 4.50 was prepared to observe the effect of time. The absorbances were measured at λ_{Max} 548 nm with the time interval and the data obtained have been presented in table-5 & 6 and Fig. 9(a) & 9(b).

From the results it has been observed that for 48 hours the absorbance (0.336) remained constant at λ_{Max} 548 nm.

Table-5 Absorbance at different time interval in minute

Duration of Time (min)	**Absorbance of Pb-PAN complex at λ_{Max}= 548 nm**
0.0	0.336
05	0.336
10	0.336
15	0.336
20	0.336
25	0.336
30	0.336
60	0.336

Table -6 Absorbance at different time interval in hour

Duration of Time (hrs)	**Absorbance of Pb-PAN complex at λ_{Max}= 548 nm**
1	0.336
2	0.336
3	0.336
4	0.336
5	0.336
10	0.336
24	0.336
48	0.336

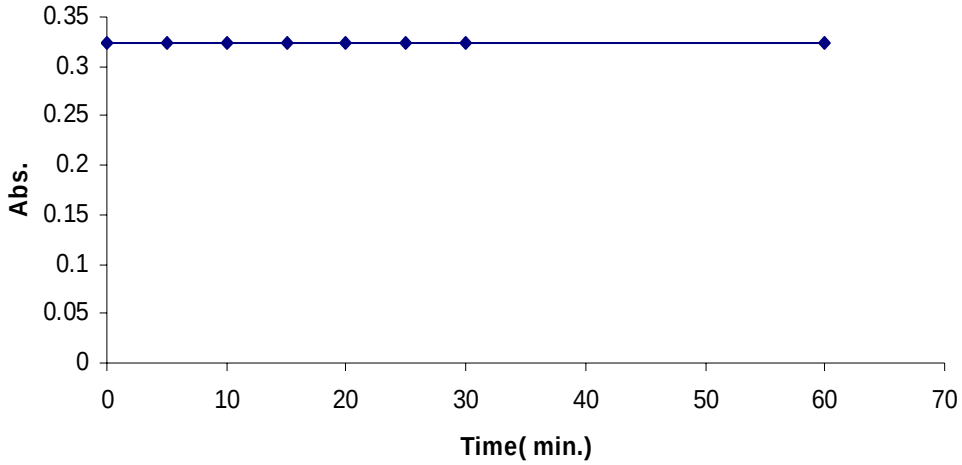

Fig. 9(a): Effect of the time (min) on the absorbance of Pb-PAN (1:2) system.

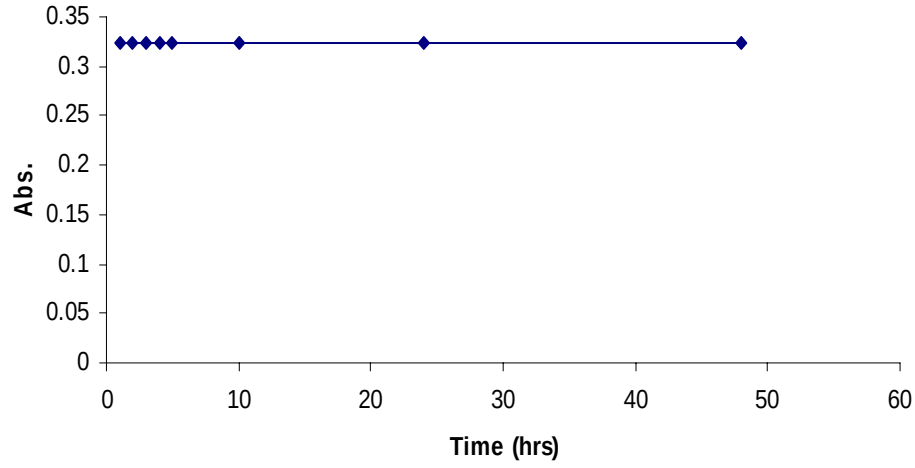

Fig.9 (b): Effect of the time (hrs) on the absorbance of Pb-PAN (1:2) system.

[III] EFFECT OF TEMPERATURE:

The effect of temperature on Pb-PAN complex has been studied over 15 °C to 40 °C at pH 4.5 and the absorbances were measured at λ_{Max} = 548 nm. The corresponding data have been presented in table-7.

Table-7: Absorbance at different temperature

Temperature(°C)	**Absorbance of Pb-PAN complex at λ_{Max}= 548 nm**
15±2	0.314
20±2	0.319
25±2	**0.336**
30±2	0.335
35±2	0.329
40±2	0.327

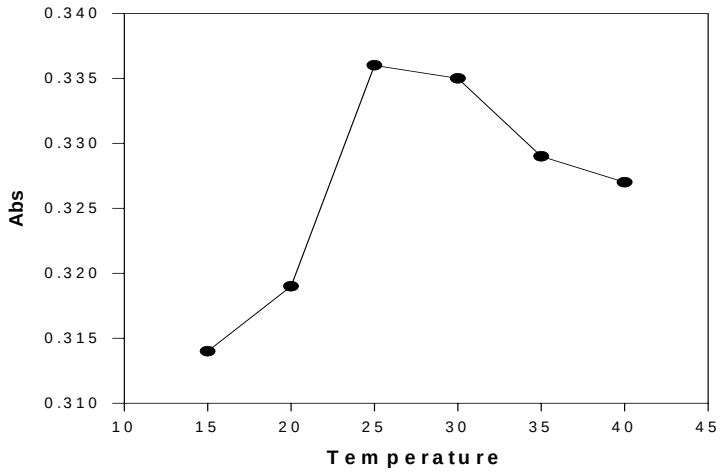

Fig.10: Effect of Temperature (°C)

It is observed, in the table-7, that the maximum absorbance (0.336) has been occurred at room temperature (25±2) °C. Outside this range of temperature, the absorbance decrease gradually.

[IV] EFFECT OF REAGENT CONCENTRATION:

Different molar excesses of PAN were added to fixed metal ion concentration and absorbance was measured according to the standard procedure. The different molar ratios were examined to find out the stoichiometric of Pb-PAN complex. In this research work, the molar concentration of Pb is 5.309 x 10^{-6} **M** is being used. The actual stoichiometric were observed by variation of molar concentration of PAN.

The absorbances have been measured at λ_{Max} = 548 nm. The corresponding data have been presented in table-8.

The results indicate that the absorbance increases with the increase of the ratio of PAN and remain constant after the molar ratio of Pb:PAN is 1:2.

Table-8 Absorbance data of different Pb-PAN molar ratio

Concentration of PAN (M)×10^6	**Molar ratio Pb:PAN**	**Absorbance of Pb-PAN complex at λ_{Max}= 548 nm**
2.654	1:½	0.068
5.309	1:1	0.172
10.618	**1:2**	**0.336**
15.927	1:3	0.336
21.236	1:4	0.336

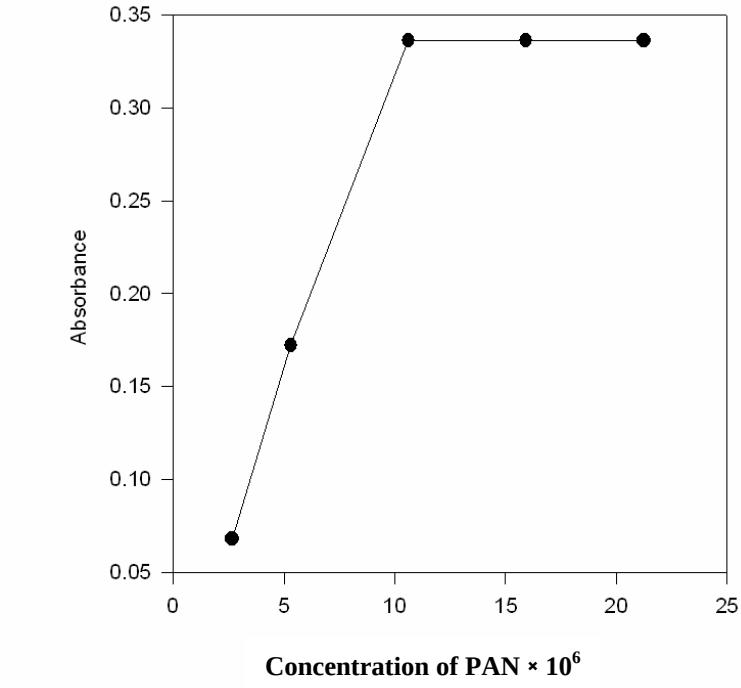

Fig.11: Absorbances of Pb-PAN complexes w.r.t. PAN Vs Molar ratio of Pb:PAN

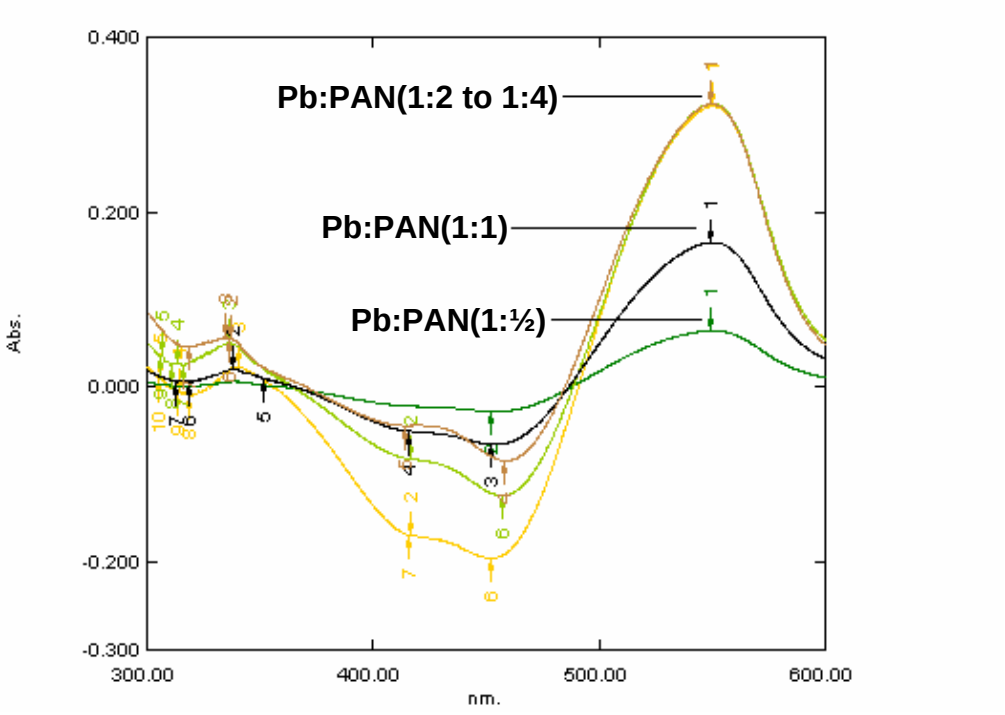

Fig.12: The overlay of absorption spectra of Pb-PAN w.r.t PAN at different molar ratio (Pb:PAN)

[V] EFFECT OF FOREIGN IONS:

The effect of over 20 ions and complexing agents on the determination of Pb was studied. The interference on an absorbance value varying not more than ± 5% are expected. [84] The results are summarized, in (Table-9).

From the results, it has been observed that a large number of ions have no significant effect on the determination of Pb. The most serious interferences were from Ni (II), Co (II), Cu (II) and Fe (III) ions. Interference from these ions were probably due to complex formation.

A greater tolerance limits for these ions can be achieved by using several masking methods.

TABLE-9: Table of Tolerance Limits of Foreign Ions[1].

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

Species X	Tolerance ratio X/Pb	Species X	Tolerance ratio X/Pb
Ammonium (I)	100	Iron (III)	10
Arsenic (III)	100	Chromium (III)	100
Ascorbic Acid	100	Chromium (VI)	100
Sodium	100	Cadmium (II)	100
Copper (II)	200	Nickel (II)	50
Barium	200	Zinc	100
Nitrate	250	Calcium	100
Nitrite	100	Potassium	100
Bromide	100	Phosphate	100
Cobalt (II)	50	Aluminum	100
Cobalt (III)	40	Manganese (II)	200
Iron (II)	60	Silver (I)	25

[1] Tolerance limit was defined as ratio that causes less than 5 per cent interference.

3.2 Verification of the Beer Lambert Laws for Pb-PAN complex at 548 nm, pH 4.5:

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 0.1-5.0 ppm distributed in two different sets (0.1 – 3.0 and 0.01 – 5.0 ppm) for convenience of measurement. The absorbance was linear for 0.1 – 3.0 ppm of Pb at λ_{max} 548 nm. The molar absorption co-efficient [85] was found to be **6.32×10^4** L mol^{-1} cm^{-1} or (30×10^{-2} ppm cm^{-1}). Of the calibration graph which that showing the limit of linearity range is given in table-10 and table-11.

Table-10: Absorbance data for different concentration of Pb-PAN system

Concentration of Pb (ppm)	**Conc. of Pb ($molL^{-1}$)$\times10^6$**	**Absorbance of Pb-PAN complex w.r.t. PAN at pH= 4.5, λ_{max} =548 nm**
0.1	0.483	0.031
0.5	2.413	0.153
1.0	4.826	0.305
1.5	7.239	0.458
2.0	9.652	0.611
2.5	12.065	0.763
3.0	14.478	0.916

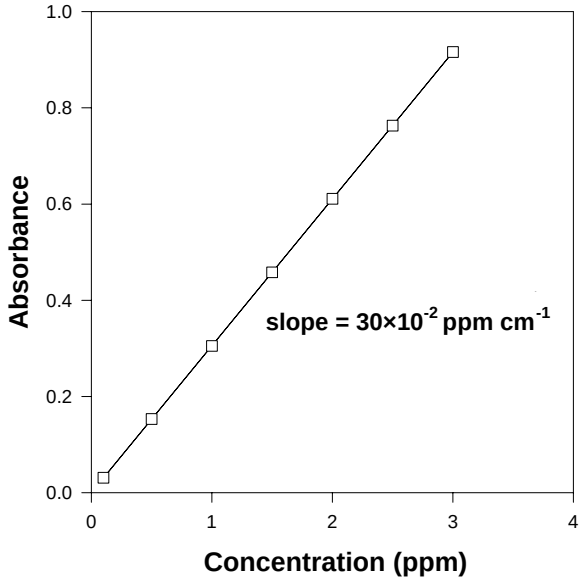

Fig: 13(a) Calibration graph of absorbance of Pb –PAN complex against the different concentration of Pb (0.1 to 3.0 ppm) at pH= 4.5, λ_{max} =548 nm.

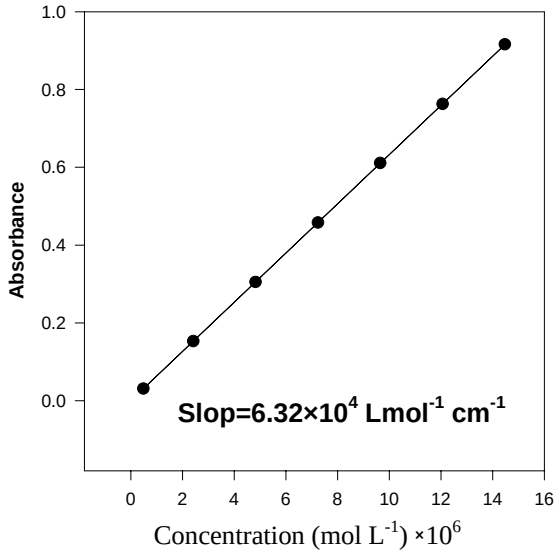

Fig: 13(b) Calibration graph of absorbance of Pb –PAN complex against the different concentration of Pb ($0.483\times10^{-6}$to 14.478×10^{-6} M) at pH= 4.5, λ_{max} =548 nm.

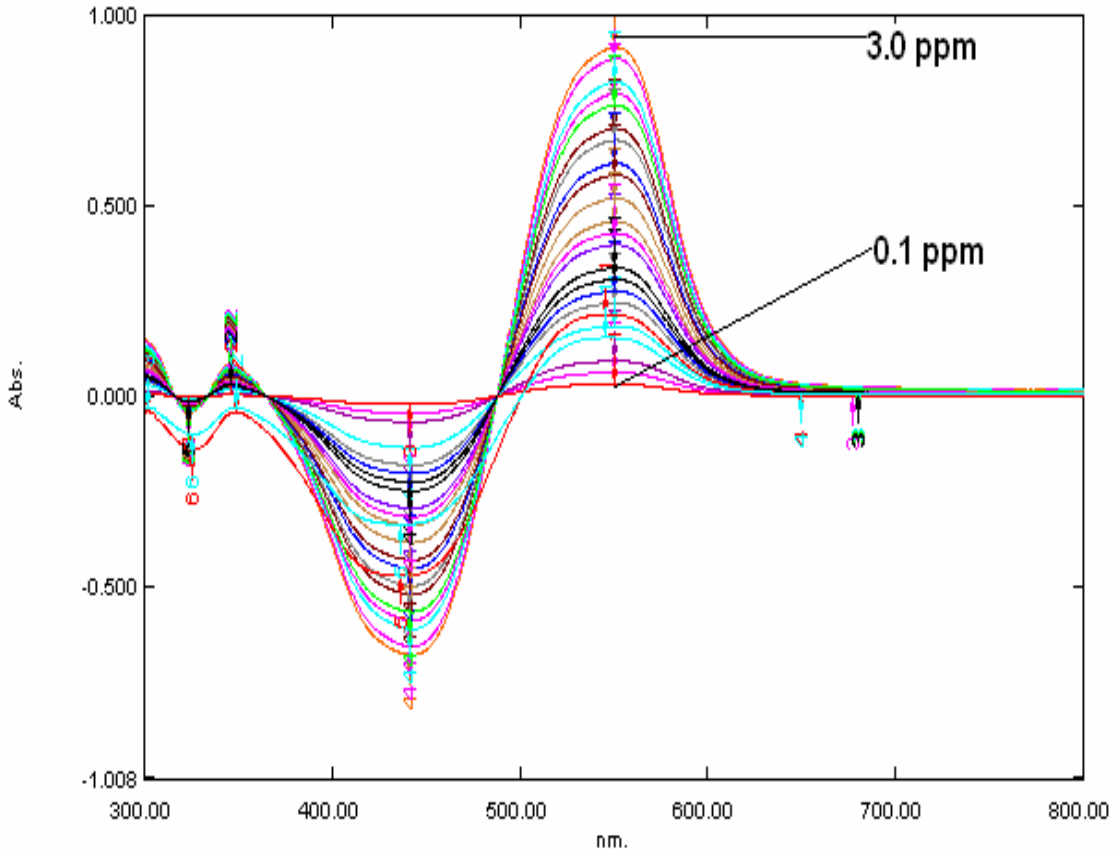

Fig: 14 The overlay of absorption spectra of Pb-PAN for 0.1 – 3.0 ppm of Pb at pH= 4.5, λ_{max} =548 nm.

Table-11: Absorbances of Pb –PAN complex w.r.t. PAN with the change of concentration of Pb (0.01 to 5.0 ppm) at pH= 4.5, λ_{max} =548 nm

Concentration of Pb (ppm)	**Absorbance of Pb-PAN complex w.r.t. PAN at pH= 4.5, λ_{max} =548 nm**
0.01	0.00101
0.05	0.0103
0.1	**0.031**
0.3	0.092
0.5	0.153
0.7	0.214
0.9	0.275
1.1	0.336
1.3	0.397
1.5	0.458
1.7	0.519
1.9	0.580
2.1	0.642
2.3	0.702
2.5	0.763
2.7	0.825
2.9	0.886
3.0	**0.916**
3.5	1.018
4.0	1.131
4.5	1.202
5.0	1.259

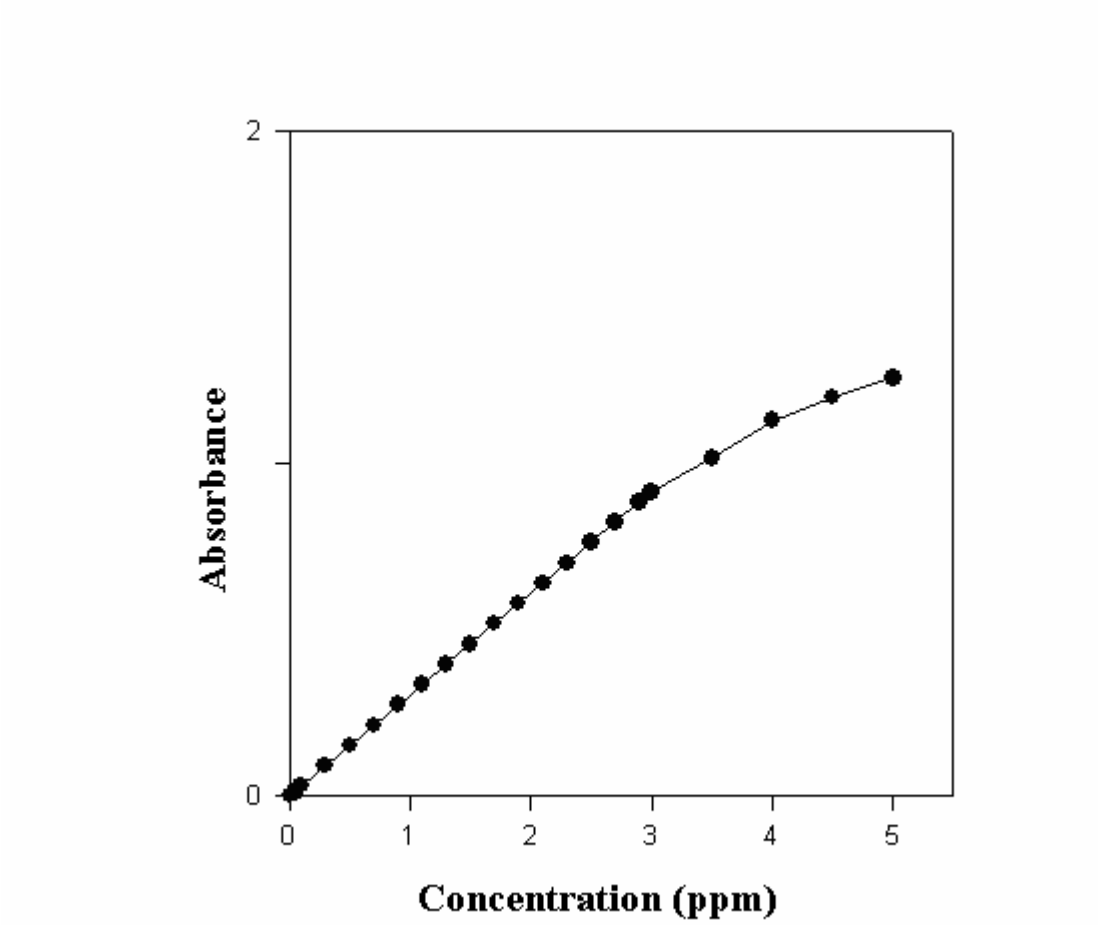

Fig.-15: Absorbances of Pb –PAN complex w.r.t. PAN with the change of concentration of Pb (0.1 to 5.0 ppm) at pH= 4.5, λ_{max} =548 nm.

From the results, it has been observed that the absorbances were increases linearly with the increase of the concentration of the Pb for 0.1-3.0 ppm of Pb at 548 nm. Below 0.1 ppm of Pb the absorbances were not linear, which indicate the lower detection limit of Pb is 0.1 ppm. Above 3.0 ppm of Pb, the absorbances were not linear, which indicate the uper detection limit of Pb is 3.0 ppm.

The results indicate that the absorbance of Pb-PAN complex increases linearly with the increase of the concentration of Pb. That is, the complex formation followed the Beer's law. The molar absorption co-efficient of Pb has been calculated 6.32×10^{4} L mol^{-1} cm^{-1} or (30×10^{-2} ppm cm^{-1}).

Optimized Condition for measurement of Pb in aqueous solution

The selected analytical parameters obtained with the optimization experiments are summarized in table-12.

Table 12: Selected Analytical Parameters Obtained with the Optimization Experiments

Parameter	Studied range	Selected Value
Wavelength/λ_{max}(nm)	300 – 800	548
pH	2.9 – 5.9	4.5
Time/h	0 – 48	0-48
Temperature/ºC	15 – 40	25 ± 5
Reagent (fold molar excess, M: R)	1 : 1 – 1: 4	1 : 2
Detection limit (ppm)	0.01-5.0	0.1 – 3.0
Reproducibility (% RSD)	0 – 2	0 – 2

3.3 Precision and accuracy:

The precision of the present method was evaluated by determining different concentrations of lead (each analyzed at least five times).

The samples were prepared and measured the concentration of Pb according to the standard procedure. The results have been presented in table-13 to calculate the standard deviation.

From the result, the relative standard deviation (n=11) has been found 1.015%, which was in between 0-2% indicates that the method is precise & reproducible.

The detection limit of Pb is 0.1-3.0 ppm. The reliability of our Pb-Chelate procedure was tested by recovery studies. The average percentage recovery obtained for addition of a lead to some environmental water and industrial waste water samples was quantitative as show in (Table-14). The results of water samples analysis by the spectrophotometric method were excellent agreement with those obtained by ASS (Table-15). Hence the precision and accuracy of the method were found to be excellent.

Table-13: Standard Deviation and Relative Standard Deviation Of Pb-PAN System.

Sam. No.	Pb(II) taken (ppm)	Pb (II) Found X_1 (ppm)	Mean $\bar{X}$ (ppm)	$X_1 - \bar{X}$	$(X_1 - \bar{X})^2$	Standard deviation ($\pm$ S)	Relative standard deviation (S_r)%
1	100.0	99.5	100.27	0.68	0.46	$\pm$1.018	1.015
2	100.0	98.5		1.68	2.83		
3	100.0	101		0.82	0.67		
4	100.0	100.5		0.32	0.10		
5	100.0	99.8		0.38	0.15		
6	100.0	101.5		1.32	1.74		
7	100.0	101		0.82	0.67		
8	100.0	99.5		0.68	0.46		
9	100.0	99.2		1.07	1.15		
10	100.0	101.5		1.32	1.74		
11	100.0	101		0.82	0.67		
N =11		$\sum X_1$ = 1103		$\sum X_1 - \bar{X}$ = 9.73	$\Sigma (X_1 - \bar{X})^2$ = 10.36		

Mean $\bar{X}$ =100.27

Standard deviation, S = $\sqrt{\frac{\sum (X_1 - X)^2}{N-1}}$ = $\pm$ 1.018

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

= (1.018/100.27)x 100

= 1.015%

3.4 Probable Structure of the Pb-PAN complex:

Job's method [86] of continuous variation and the molar-ratio [87] method were applied to ascertain the stoichiometric composition of the complex. A Pb-PAN (1: 2) complex was indicated by both methods. The assumed Structure is like fig-16.

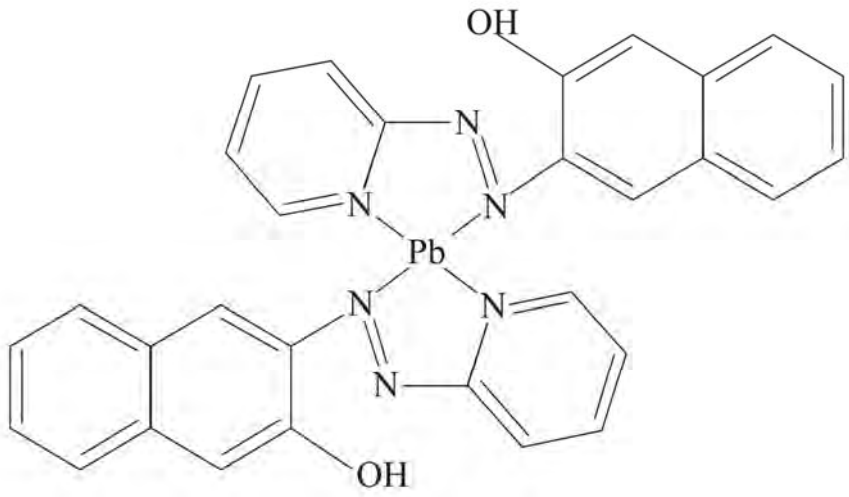

Fig: 16 Probable Structure of the Pb-PAN complex.

This is an assumed Structure of Pb-PAN complex in fig.15. We observed that Pb formed the complex that is 5 member ring a stable complex. More over the study of molar ratio also supported the stoichiometric composition of this structure.

3.5 Applications

The present method was successfully applied to the determination of lead (II) in various industrial waste water samples of various compositions (Table-14). The method was also extended to the determination of lead in a number of environmental samples. In view of the unknown composition of environmental water samples, the same equivalent portions of each such sample was analyzed for lead content, recoveries in both the ‘spiked` (added to the samples before the mineralization or dissolution) and the ‘unspiked` samples are in good agreement (Table-14). The results of industrial waste water analysis by spectrophotometric method were found to be in excellent agreement with those obtained by AAS (Table-15). The precision and accuracy of the method were excellent.

3.5.1 Determination of lead in environmental and industrial water:

Each filtered (with whatman No.-40) environmental water sample (1000-mL) was evaporated nearly to dryness with a mixture of 5mL of concentrated H_2SO_4 and 10-mL of concentrated HNO_3 in a fume cupboard following a method recommended by Greenberg et al [88], and was then cooled to room temperature. The residue was then heated with 10-mL of de-ionized water in order 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 up to the mark with de-ionized water.

Most spectrophotometric method for the determination of metal in natural water requires preconcentration of lmetal· [89]. An aliquot (1 – 2 mL) of this pre concentrated water sample was pipette into a 10-mL Calibrated flask and the lead content was determined as described under procedure using KSCN as a masking agent [90]. The analyses of environmental water samples from various sources for lead are shown in (Table-14).

The analyses of environmental water samples from various sources for Pb determination are presented in table-14.

Table-14: Determination of lead in some environmental water and industrial waste water samples. (Compare with spiked method)

Sample	Lead/ ppm		Recovery ±S (%)	S_r^b (%)
	Added	Found[a]		
Waste Water of Berger Paints, Dhaka.	0	2.3		
	100	102.08	100.2±0.4	0.33
Waste Water of Asian Paints, Dhaka	0	2.6		
	100	102.3	100.4±0.6	0.51
Waste Water of Olympic battery, Munshigong.	0	5.1		
	100	105.0	100.2±0.3	0.22
Waste Water of Rahima Afroz, Tajgaon	0	6.0		
	100	105.8	99±0.2	0.23
Waste Water of Finish masher Coal, Tajgaon	0	7.1		
	100	106.8	99±0.5	0.41

[a] Average of five replicate determinations.

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

TABLE-15: Determination of lead in some environmental water and industrial waste water samples. (Compare with AAS method)

Serial No.	Sample source	Pb/ppm	
		AAS	Proposed method
01	Waste Water of Berger Paints, Dhaka	**2.45**	**2.30±0.07**
02	Waste Water of Asian Paints, Dhaka	**2.78**	**2.60±0.05**
03	Waste Water of Olympic battery, Munshigong.	**5.25**	**5.10±0.19**
04	Waste Water of Rahima Afroz, Tajgaon.	**6.17**	**6.05±0.16**
05	Waste Water of Finish masher Coal, Tajgaon	**7.26**	**7.10±0.12**

*Average of five replicate determinations.

4.0 Conclusion

In this Thesis a new simple, sensitive, selective and inexpensive method with Pb-PAN complex has been introduced for the determination of Pb by uv-vis spectrophotometer. This method has been developed for the determination of lead in environmental and industrial waste water samples for continuous monitoring. Although many sophisticated techniques such as pulse polarography, HPLC, AAS, ICP-AES (**Inductive Coupled Plasma- Atomic Emission spectroscopy**), and ICP-MS(**Inductive Coupled Plasma- Mass spectroscopy**), are available for the determination of lead (Pb) 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 uv-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 is very reliable for the determination of lead in real samples down to ppm levels in aqueous medium at room temperature (25± 5) $^{\circ}$C.

ACKNOWLEDGEMENT

We are grateful to the authorities of different industries for their generous help in supplying industrial waste water samples. We are especially indebted to the authorities of analytical Research Division of **BCSIR** Laboratories, Dhaka for analyzing the samples by AAS.

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