CHAPTER 1

INTRODUCTION

Lead, Pb, atomic number 82, atomic weight 207.19, is in group IV of the periodic table and is a member of the subgroup containing germanium and tin. The four naturally occuring isotopes, listed in order of their abundance, are 208, 206, 207 and 204. It crystallizes in the face-centered cubic system and the minimum interatomic distance is 3.492 $\overset{o}{A}$ (1).

All lead compounds must be considered cumulative poison. Symptomatically, acute lead poisoning usually affects the gastro-intestinal tract and the nervous system in the mouth, severe thirst, anovexia, nausea, severe headache, and vomiting (2). Constipation is common, which may be interrupted by diarrhea due to gastroenteritis. The effect of lead intoxication may range from simply upsetting to disabling and even fatal. Although fatal cases are rare today, low grade plumbism constitutes an important industrial hazard.

There are three means by which lead can enter the body and produce toxic symptoms: inhalation of dusts, fume, vapors, and mists; ingestion through the mount on food, tobacco or on the fingers; and through broken skin or absorption through the skin, as with tetraethyl-lead and certain other organic compounds.

Minute quantities of lead that are ingested or inhaled are subsequently eliminated by normal body processes (2). The toxicity of

lead compounds depends on their solubilities in body fluids, length of time in contact with body fluids, and upon the particle size, the smaller the particle, the greater the solubility and toxicity. The presence of lead in the body is best determined by monitoring the change of lead concentration in urine. Lead intoxication can be cured, and the recovery is usually complete. One of the treatments is the intravenous injection of sodium calcium salt of ethylenediaminetetraacetic acid which results in a heavy urinary excretion of lead (2).

Lead is thought to be toxic only when it is present in the systematic circulation. It can be stored by the body and only becomes a danger when it is returned to circulation in greater amounts than the body can safety eliminate. Prevention of lead poisoning is largely a matter of good housekeeping, personal hygiene, and careful medical control.

Several methods are used in trace quantitative determination of lead, such as polarography, atomic absorption spectrophotometry, atomic fluorescence spectrophotometry, infrared spectrophotometry, and anodic stripping voltammetry. The application of infrared spectro-photometry and anodic stripping voltammetry for determination of trace lead (II) impurity are investigated in this study.

Infrared spectrophotometry is a technique that finds a wide variety of uses both in industrial analytical laboratories and in research laboratories of all types, as it furnishes information that is useful in qualitative and quantitative analyses. It is a nondestructive type of analysis and is useful for microsamples (down to the sub-

microgram range) (3). This method is rapid and easy to reproduce and can be applied to any physical state. Moreover, spectra are easy-to-handle documents. It has the particular advantage that all organic and most inorganic substances have a characteristic spectrum in the IR region.

Infrared spectrophotometry is the investigation of the interaction between infrared radiation and matter. When a substance is exposed to infrared radiation, the amount of radiation absorbed is different for components of the radiation having different wavenumber, that is to say, the absorption is selective. The IR spectrum is obtained by recording some quantity proportional to absorption as a function of the wavelength or wavenumber. The absorbance of IR is proportional to concentration of substance as follow Beer's law (4).

$$A = \log \frac{P_o}{P} = abc \quad \dots\dots\dots\dots\dots\dots (1)$$

where A = the absorbance of the sample

P_o = the incident radiation, the radiant power impinging on the sample

P = the transmitted radiation, the radiant power transmitted by the sample

a = the absorptivity of the component at a particular wavelength (a constant)

b = the path length of the sample, cm

c = the concentration of the component, g/l

Theoretically, the constant a is a unique function of the component in question at the frequency for which it is determined, and a plot of absorbance versus concentration should give a straight line. Unfortunately, the former statement is never true, and the plot is usually linear only over a short concentration range. This failure due to the nonideal behavior of the sample. The nonideality can be traced to molecular interactions, such as association of solute molecules with themselves or association of the solute and the solvent molecules.

Base line method can be used in IR quantitative analysis for the determination of absorbance which bases on the use of chart paper with ordinate calibrated nonlinearly in absorbance units or ordinate calibrated linearly in transmittance units. The calculation for absorbance of an IR peak obtained with absorbance chart paper (4) is

$$A = A_{peak} - A_{background} \quad \dotsb \quad (2)$$

and with transmittance chart paper is

$$A = \log \frac{P_o}{P} \quad \dotsb \quad (3)$$

where P_o is the transmittance of the background and P is the transmittance of the peak maximum (see Figure 1). The way which the tangent is drawn for the calibration standards (from shoulder to shoulder or from one shoulder parallel to the infinite-absorbance, or 0% T line) is the way it must be drawn for the samples.

Anodic stripping voltammetry (ASV) has proved to be powerful method for the trace analysis of certain metal ions of environmental
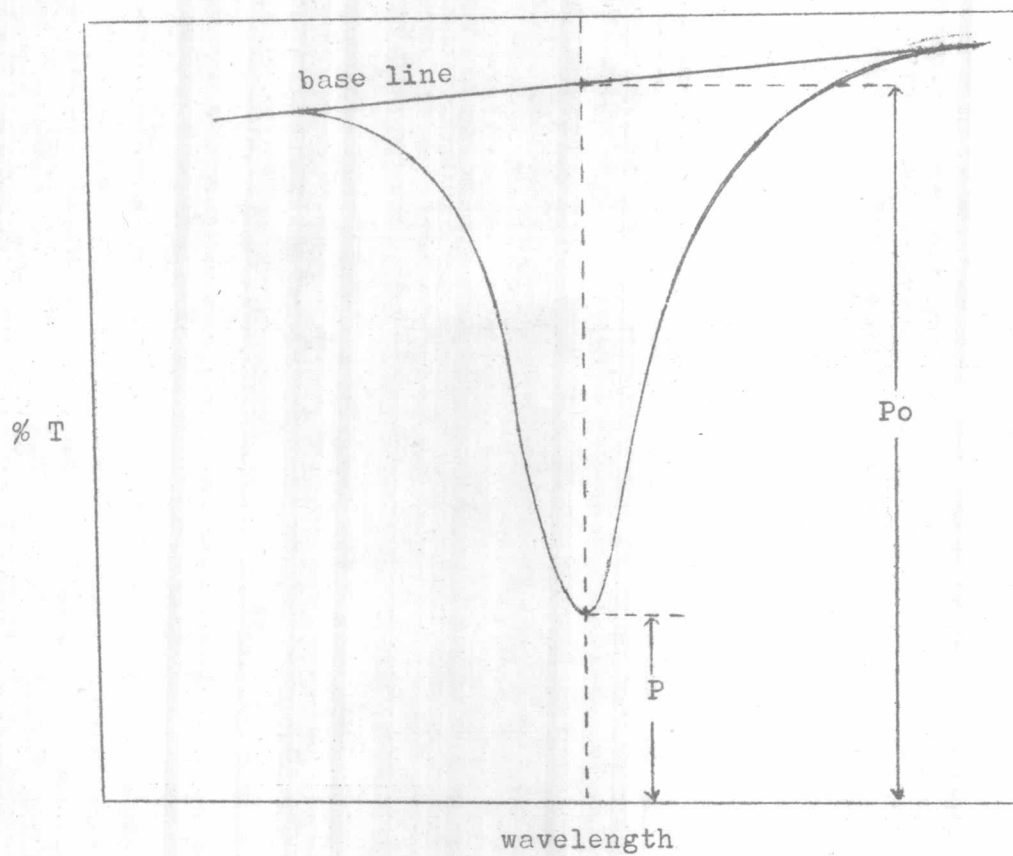
Figure 1 Use of a base line in the determination of
absorbance of an infrared peak (4)

concern (5, 6). Its sensitivity is achieved through a preconcentration process in which a metal ion in solution is reduced by a controlled potential more negative than the reduction potential of the species, and the reduced metal is deposited onto or into working electrode. The metals deposited arrive at the electrode surface at rates depend on concentrations, diffusion properties of the electrolyte solutions, and the area of the electrode used (6). The preconcentration step is of such a duration as to produce the required sensitivity, and in some instances it continued until the species is exhausted from the solution. However, practical consideration generally dictates the use of a non-exhaustive deposition. Following the preconcentration step, the potential is scanned anodically and the faradaic current produced by its oxidation is measured. A peak appears in the i-E curve with its potential, a qualitative indication of the identity of the metal ion; and the peak height, a quantitative measured of its concentration in the solution. The total current flowing through the system is (5)

$$i_t = i_f + i_c + i_b \dots\dots\dots\dots\dots \quad (4)$$

where i_f = faradaic current, due to oxidation of the species being analyzed (and is equal to i_p at the peak potential.)

i_c = charging current, due to the changing of the double layer at the electrode solution interface

i_b = background current, due to oxidation of impurities or decomposition of electrolyte.

Together, i_c and i_b make up the residual current or electrochemical noise in the system.

Quantitative analysis is made by making a measurement of the total peak current i_p, at the peak potential. The concentration is then determined by a standard addition method or the previously prepared calibration curve. For standard addition method the concentration of test species is calculated by (7).

$$\frac{i'_p}{i_p} = \frac{Co + x}{x} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where i'_p = total diffusion current of known and unknown solution

i_p = diffusion current of unknown solution

Co = known concentration

x = unknown concentration

The basic instruments required for ASV include a three-electrode potentiostat and voltage ramp generator; current measuring circuity (a cell with working, reference, and counter electrodes), and a recorder or other readout device. Instruments designed for dc, ac or pulse polarographic measurements are generally quite adequate for stripping application.

Supporting electrolyte concentration of 0.05 - 0.5 M are typical (6). Almost any indifferent electrolyte can be used, but the choice often improves the reproducibility and the resolution of the stripping peaks. If no supporting electrolyte were present in the solution, there would be another force acting on the reducible ion. This could result from the gradient of electrical potential between the two electrodes of

the cell, which causes ion to move through the solution in order to carry the current through the cell. This current is migration current. Thus, the current due to the reduction of metal ion is greater than the diffusion current.

In this thesis, trace determination of lead is studied by using infrared spectrophotometric technique and anodic stripping analysis. The method for the determination of lead in tooth paste, the decomposition of tooth paste and the investigation of lead in the decomposed sample by both techniques,are also present.