

CHAPTER II

THEORY



2.1 Anodic stripping voltammetry

2.1.1 Principle

The fundamental of an anodic stripping voltammetric measurement involves two discrete steps. The deposition step, the analytical species is firstly reduced (electrodeposited, plated) onto or into the working electrode ; and is secondly oxidized (stripped, electrolyzed) back into the electrolyte solution which is known as stripping step. For the deposition step, a suitable electrode is maintained at a potential cathodic of the reduction potentials of the elements to be determined. The metals to be deposited arrive at the electrode surface at rates determined by their respective concentrations, the diffusion property of the electrolyte solution, and the area of the electrode used. The deposition time is consequently carefully measured. The deposition results in preccncentration of the analytes into a small (surface) volume. This material is stripped from the electrode by changing the potential back in the direction required for oxidation. At the oxidation potential of each analytical species, the faradaic current is produced by its oxidation.

For a single metal ion species (M^{n+}) being reduced at

an electrode surface, it can be shown that the current flow (the deposition current at time t) is given by the Levich equation⁽³⁰⁾.

$$i(t)_{\text{dep}} = 0.62 n F A D^{2/3} W^{1/2} \nu^{-1/6} c(t) \dots (1)$$

where $i(t)_{\text{dep}}$ = the limiting current of deposition time t , ma

n = the number of electron transfer

F = the Faraday constant, 96,494 coulombs.

A = the electrode surface area, cm^2

D = the diffusion coefficient, $\text{cm}^2 \cdot \text{sec}^{-1}$

W = the rate of electrode rotation or solution stirring ($w = 2\pi N$, with $N = \text{rps}$)

ν = the kinematic viscosity of the solution, $\text{cm}^2 \text{sec}^{-1}$

$c(t)$ = the ion concentration of deposition time t , mole cm^{-3}

The stripping current due to oxidation of each analyte is proportional to the concentration of the analyte on or in the electrode and, thus, in the analytical solution. The oxidation potentials have the same qualitative meaning as their half wave potentials in polarography⁽³¹⁾. Several different current-potential curves may be used to strip the deposited analyte from the electrode

and obtained the quantitative parameter, the stripping peak current, i_p , which is given by Randles-Sevcik equation⁽³¹⁾: for reversible process

$$i_p(\text{rev}) = 602 n^{3/2} A D^{1/2} v^{1/2} c^b (X') \dots\dots\dots(2)$$

and for irreversible process

$$i_p(\text{irr}) = 602 n (\alpha n_a)^{1/2} A D^{1/2} v^{1/2} c^b (X'') \dots\dots\dots(3)$$

- where i_p = the stripping peak current, ma
- D = the diffusion coefficient, $\text{cm}^2 \text{sec}^{-1}$
- v = the rate of potential change or scan rate, volt sec^{-1}
- c^b = the concentration of oxidizable species in bulk solution, mole cm^{-3}
- α = the electron transfer coefficient
- n_a = number of electrons in the rate determining step
- X' = a current function for the reversible process
with the maximum value = 0.4463
- X'' = a current function for the irreversible process
with the maximum value = 0.4958.

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Thus, the value of i_p is directly proportional to c^b and $v^{1/2}$.

If the rate of electron transfer reaction, is very rapid compared to mass transport, the electrode reaction is called

reversible process. On the other hand, if the electron transfer rate is relatively slow, such reaction is called irreversible process⁽³²⁾.

The total current flowing through the system is⁽³³⁾

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

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

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

i_b = the 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.

The potential at which the peak occurs is related to the polarographic half-wave potential by⁽³³⁾

$$E_p = E_{1/2} - 1.1 RT/nF \dots\dots\dots (5)$$

where E_p = the peak potential, V

$E_{1/2}$ = the polarographic half-wave potential, V

R = the gas constant = 8.316 VQ/deg

T = the absolute temperature, K

It follows from Equations (2), (3), and (5) that these voltammograms can be used for analytical purposes. The peak position is independent of the analyte concentration and characterizes its nature ; and the peak height is proportional to the concentration. The sensitivity of a determination . increases with the square root of the scan rate ($i_p \propto v^{1/2}$) and with increasing the number of electron exchanged in the electrode reaction ($i_p \propto n$).

Hanging mercury drop and carbon electrodes are the most popular electrodes for ASV. Carbon electrodes, their use has become widespread in solid electrode voltammetry provide excellent substrates for mercury films. They are inert, mechanically strong and have good electrical conductivity and a high hydrogen over potential ⁽³⁰⁾. Several types of carbon electrodes such as wax-impregnated spectroscopic graphite rod, pyrolytic graphite, and glassy carbon have been used. The best appears to be glassy carbon.

The pyrolytic graphite electrode gives some limitations on its proper orientation and the impregnated carbon electrode sometimes suffers from high residual current ⁽³²⁾. Thus, a glassy carbon or vitreous carbon electrode is used in this study.

2.1.2 Standard addition

The determination of concentrations of metal ions presented in the sample is best achieved by addition of known

volumes of the standard metal ion solution to the sample. This has the advantage of eliminating matrix effects and obviating the need for calibration curves. For standard addition method the concentration of metal ion in solution is calculated by;

$$C_u = \frac{i_1 v C_s}{i_2 v + (i_2 - i_1) V} \dots\dots\dots (6)$$

where i_1 = the original peak height, μa

i_2 = the spiked peak height, μa

v = the volume of the standard solution added, cm^3

V = the original sample volume, cm^3

C_s = the concentration of the standard solution used for "spiking", $\mu g.cm^{-3}$

C_u = the original concentration, $\mu g.cm^{-3}$

2.2 Atomic absorption spectrophotometry

2.2.1 Flame atomic absorption

Atomic absorption methods rely on the absorption of light by atoms. All atoms can absorb light but only at certain wavelengths corresponding to the energy requirements of the particular atoms.

The production of atoms from a molecule of a chemical compound requires the absorption of energy, usually supplied in the form of heat. A compound such as sodium chloride, when it is

vaporized by heating in a flame, is partially or wholly dissociated into its elements in gaseous form. Some of these atoms are further excited to a state from which they can emit radiation on returning to the unexcited state. The relation between the number of atoms, N_j , in an excited state and the number of atoms N_o , in the ground state is given by⁽³⁴⁾

$$\frac{N_j}{N_o} = \frac{P_j}{P_o} \exp \frac{(-E_j)}{KT} \dots\dots\dots (7)$$

where P_j and P_o = the statistical weights of two states,

E_j = the energy difference ,

K = the Boltzmann constant,

and T = the absolute temperature.

The higher the value of E_j is (i.e. the shorter the wavelength of the spectral line corresponding to the transition between the ground state and excited state), the smaller will be the fraction of atoms in the excited state.

When a solution of a metal compound is sprayed into a flame, the amount of radiation absorbed is dependent on the concentration of the metal ion in the solution as follows Beer's law⁽³⁵⁾ .

$$A = \log \frac{P_o}{P} = abc \dots\dots\dots (8)$$

where

A = the absorbance of the sample

P_0 = the incident radiation

P = the transmitted radiation

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

Thus, the quantitative analysis of the species can be calculated directly by Beer's law or by a calibration curve plotted between the concentration of the species and the corresponding absorbance.

2.2.2 Cold vapor atomic absorption spectrophotometric technique

The conventional atomic absorption spectrophotometry has less sensitivity and high detection limit in determining trace mercury. The better method which give best result, simplicity, and economically in determining trace mercury, is cold vapor atomic absorption spectrophotometric or flameless atomic absorption spectrophotometric technique⁽³⁶⁾.

This technique is developed by Hatch and Ott⁽³⁷⁾ in 1968, for determination of mercury in the sub-microgram range. In contrast to atomic emission for which excitation of atoms is necessary, atomic absorption can be carried out at room temperature providing a supply

of ground state atoms. For mercury, free atoms are readily generated at room temperature and consequently atomic absorption measurement can be made.

For this analysis an aliquot of the sample is reduced by reducing agents such as stannous chloride or stannous sulfate. In this step, Hg(II) ion will change to volatile metallic mercury. The vapor of mercury above the solution is then flushed into the absorption cell. The 253.7 nm mercury line emitted by the mercury lamp is absorbed by the vapor in proportion to the mercury concentration, and the result is read on the meter directly in microgram of mercury.

In this thesis, trace analyses of cadmium, copper, lead, mercury, and zinc in air particulates in Bangkok Metropolis were studied. The optimum conditions for anodic stripping analyses of these metal ions were investigated and the quantitative analyses of these metal ions were performed. Quantitative analyses of these metal ions in air particulates were also performed by atomic absorption both flame and flameless techniques. In addition, the results from anodic stripping analysis and atomic absorption spectrophotometric analysis were compared.