

## CHAPTER 1

### INTRODUCTION

The members in group V elements or nitrogen family are nitrogen, phosphorus, arsenic, antimony and bismuth. These elements have fairly high ionization potentials. The lighter members which have fairly high electronegativities on the Pauling scale have little tendencies to lose electron to form positive ions. The principal oxidation states exhibited by the elements are -3, +3 and +5 (1). Only nitrogen has the most tendency to take up electrons to form the triple charge nitride ion,  $N^{3-}$  and phosphorus has less readily formed the phosphide ion,  $P^{3-}$ . There is less tendency for the other members of this family to form such negative ions. This family is increasing metallic or decreasing nonmetallic characteristic with increasing the atomic number (1). The state -3, +3 and +5 are readily correlated with the electronic configurations of the elements in which each atom has five valence electrons, of which two are s electrons and three are p electrons. The stability of the +3 state for all members is suggested by the  $p^3$  electrons (1). Other oxidation states are also exhibited, particularly by nitrogen. Compounds of Bi (III) are largely covalent in the solid but polar covalent

in certain polar solvents. The physical properties of the free elements themselves show a graduation from nonmetallic to metallic properties in passing from nitrogen to bismuth.

Tin, one of the element in group IV has a stronger tendency to form stable compounds in the +4 state. The metallic transition is evident in the stable +2 state of tin. The higher oxidation state of tin exhibits a greater degree of acidic behavior than the lower (2).

Physical properties and certain of the thermodynamic relationships of some of group V elements and tin are listed in Table 1 (3).

Arsenic, antimony, bismuth and tin are chosen for the present study because of their toxicities and their existances in trace amounts in all our environment, such as nutrient, blood, tissue, water or air. An increasing numbers of laboratories are involved in the measurement of a wide range of substances in environmental samples, and much of the current research in analytical chemistry is directed toward improved methods of analysis. Many analytical techniques which have found the widest application in the study of inorganic pollutants are compared in Table 2 (4).

The use of anodic stripping voltammetry (ASV) has grown rapidly during the past few years. The increasing use of the technique is due to its ability to simultaneous determination

Table 1 Physical Properties of some of the Group V elements and Tin (3)

	As	Sb	Bi	Sn
Atomic number	33	51	83	50
Electronic configuration	2,8,18,5	2,8,18,18,5	2,8,18,32,18,5	2,8,18,18,4
Atomic weight	74.92	121.75	209.0	118.7
Density	Yellow 1.97 Grey 5.73	6.67	9.80	Grey 5.77 White 7.29
m.p., °C	Grey under atmospheric pressure, 817	630	271	232
b.p., °C	615	1380	1560	2260

Table 1 (continued)

	As	Sb	Bi	Sn
Ionisation potential, eV				
1st	10.5	8.5	8.0	7.3
2nd	20.1	18.0	16.6	14.5
3rd	28.0	24.7	25.4	30.5
4th	49.9	44.0	45.1	-
5th	62.5	55.5	55.7	-
Covalent atomic radius, $^{\circ}\text{A}$	1.20 (tetrahedral)	1.36 (tetrahedral)	1.46 (tetrahedral)	1.40
Ionic radius, $^{\circ}\text{A}$				
$\text{M}^{3-}$	2.22	2.45	-	-
$\text{M}^{4+}$	-	-	-	0.74
Electronegativity	2.0	1.8	-	1.96

Table 2 Comparison of Analytical Methods for Pollutants (4)

Technique	Advantages	Limitations
Microscopy	<ol style="list-style-type: none"> <li>1. Excellent for particulate matter</li> <li>2. Identification of compound and crystalline forms possible</li> <li>3. Very sensitive</li> <li>4. Rapid</li> </ol>	<ol style="list-style-type: none"> <li>1. Not suitable for pollutants in solution</li> <li>2. Not readily quantified</li> <li>3. Requires specialised skills and training</li> </ol>
Atomic absorption and fluorescence	<ol style="list-style-type: none"> <li>1. Applicable to more than 60 elements</li> <li>2. Simple spectra and instrumentation</li> <li>3. Sensitive</li> <li>4. Rapid</li> </ol>	Simultaneous multielement analysis difficult
Atomic emission	<ol style="list-style-type: none"> <li>1. Multielement analysis feasible</li> <li>2. Sensitive</li> <li>3. Rapid</li> <li>4. Plasma source eliminates most chemical interferences</li> </ol>	Flame sources have significant matrix effects

Table 2 (continued)

Technique	Advantages	Limitations
Mass spectrometry	<ol style="list-style-type: none"> <li>1. Multielement technique</li> <li>2. Excellent sensitivity</li> <li>3. Plasma source promises rapid analysis</li> </ol>	<ol style="list-style-type: none"> <li>1. Specialised sample preparation techniques for spark source</li> <li>2. Plasma source still in development phase</li> </ol>
Neutron activation analysis	<ol style="list-style-type: none"> <li>1. Freedom from contamination</li> <li>2. Excellent sensitivity for some elements</li> <li>3. Applicable to wide variety of matrices</li> </ol>	<ol style="list-style-type: none"> <li>1. Limited availability for routine analysis</li> <li>2. Total time for multielement analysis may be long</li> </ol>
X-ray fluorescence	<ol style="list-style-type: none"> <li>1. Direct examination often feasible</li> <li>2. May be nondestructive</li> <li>3. multielement technique</li> <li>4. Rapid</li> </ol>	<ol style="list-style-type: none"> <li>1. Limited sensitivity</li> <li>2. Particle size effects must be carefully controlled</li> </ol>
Anodic stripping voltammetry	<ol style="list-style-type: none"> <li>1. Simple technique and equipment</li> <li>2. Excellent sensitivity for some elements</li> </ol>	Not suitable for wide range of elements

of several elements at concentration levels ranging down to the fraction part per billion range with relatively inexpensive instrumentation. While ASV cannot be regarded as a new analytical technique, there have been several recent developments in instrumentation and methods associated with it; these have advanced the status of ASV considerably. The technique clearly offers capabilities for the solution of numerous difficult trace analysis problems. For this reason, ASV is used in this investigation for providing analytical information of As, Sb, Bi and Sn.

An ASV measurement involves two discrete steps (5): the analytical species is reduced (electrodeposited or plated) onto or into the working electrode and then oxidized (stripped or electrolyzed) back into electrolyte solution. For the deposition step, a suitable electrode is maintained at a potential cathodic of the reduction potential of the element to be determined. The metal to be deposited arrives at the electrode surface at rate determined by their respective concentration, the diffusion property of the electrolyte solution, and the area of the electrode used. The deposition results in pre-concentration of the analyte into a small volume (small surface of the electrode). To strip this material from the electrode, its potential is systematically changed back in the direction required for oxidation, i.e., it is moved in the anodic direction.

At the oxidation potential of each analytical species, the faradaic current produced by its oxidation is measured. The readout obtained is thus stripping current as a function of the electrode potential. The stripping current due to oxidation of each analyte is proportional to the concentration of that analyte on or in the electrode and, thus, in the analytical solution.

For any electrode material employed in the ASV system, the same general plating theory applies. An elementary evaluation of the theory governing the plating process affords an indication of the parameters which can be adjusted to maximize the plating efficiency, and hence the stripping current measured. 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 reasonably approximated by the Levich equation (5, 6)

$$i(t)_{\text{dep}} = 0.62 n F A D^{2/3} \omega^{1/2} \mu^{-1/6} C(t)$$

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

$n$  = number of electrons transfer

$F$  = the Faraday constant, 96,494 coulombs

$A$  = the electrode surface area,  $\text{cm}^2$

$D$  = diffusion coefficient,  $\text{cm}^2/\text{sec}$

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



$\mu$  = the kinematic viscosity of the solution,  
cm<sup>2</sup>/sec

$C(t)$  = the ion concentration of deposition time  $t$ ,  
mole/dm<sup>3</sup>

Several different potential-time waveforms may be used to strip the deposited analyte from the electrode and obtain the quantitation parameter, the stripping current ( $i_p$ ). By far the most common choice is a linear ramp of the potential. This appears to be due to the general simplicity and wide availability of equipment having the linear ramp capability.

The simplest instrumentation required for ASV includes a three electrode potentiostat and voltage ramp generator, current measuring circuitry; a cell with working, reference, and counter electrodes; and a recorder or other readout device. Instruments designed for dc, ac or pulse polarographic measurement are generally quite adequate for stripping application.

A range of materials has found application as working electrodes for ASV, i.e., Hg, Au, Ag, Pt, C and Bi. Some of the noble metals have a mutual tendency for the formation of intermetallic compounds, i.e., AuHg. To avoid this, a carbon electrode is often used. Thus a glassy carbon (vitreous carbon) is used in this research.

Vitreous carbon has special physical properties and chemical properties (7). It has lower density, permeability and

porosity than other industrial carbon products. Its electrical and thermal conductivities resemble those of baked carbons but are considerably lower than those of graphites. The cross breaking strength of vitreous carbon is much greater than that of baked carbon and graphite, a little higher than that of pyrolytic graphite and quartz, but less than ceramics. It has a hardness values of 6 to 7 on Mohs' scale; the material retains some of its elastic properties after treatment at 1800°C. Vitreous carbon as normally prepared has an ash content up to a maximum of 200 ppm. The impurities are likely to be derived from the raw materials rather than through pick-up during the course of the processing. Vitreous carbon is highly resistant to attack by chlorine and bromine but disintegrates in the presence of alkali metals. With carbide-forming elements, diffusion may occur; i.e., a layer of  $\beta$ SiC approximately 6  $\mu$ m thick was formed on the surface of a crucible used for melting silicon. With non-carbide-forming elements including germanium, silver, gallium, phosphorus, arsenic, tellurium, zinc, tin, lead etc., the rates of attack are very small.

The supporting electrolyte concentrations which are consistent from sample to sample are generally essential. Changes in the total electrolyte concentrations result in changes in the iR drop between the reference and working electrodes. Such fluctuations manifest changes in the stripping current per unit

amount of analyte and in the positions of the stripping peaks; an increase in the  $iR$  drop shifts a peak. A second problem originates from the fact that the solution resistance and the double-layer capacitance of the working electrode define an RC time constant through which changes in potential must be effected.

In the present investigation, the conditions for  $As^{3+}$ ,  $Sb^{3+}$ ,  $Bi^{3+}$  and  $Sn^{4+}$  ions to deposit at the glassy carbon electrode (GCE); i.e., type and concentration of supporting electrolyte, pH of the test solution, and deposition potential, are checked by their cathodic voltammograms. The deposition time and stripping conditions (range of potentials for ASV) for the element determined are tested by its anodic stripping voltammogram. In addition, the sensitivity of each technique is examined by the stripping current.