

CHAPTER 1
INTRODUCTION

Nonferrous metals are materials which are not based on iron. The members of nonferrous metals according to reference 1 are beryllium, magnesium, aluminium, gallium, indium, thallium, germanium, tin, lead, antimony, bismuth, cobalt, nickel, platinum, irridium, osmium, palladium, rhodium, ruthenium, copper, silver, gold, zinc, cadmium, mercury, titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, and manganese. Compounds of tungsten, molybdenum, vanadium, and titanium are of interest in this study because of their existences in trace amounts in all our environment, such as rocks, petroleum crudes, nutrient, blood, tissue, water, and air.

Molybdenum is an essential element in plant and animal metabolism. It is a constituent of several flavoprotein enzymes such as xyanthine oxidases (from milk and animal tissue) and aldehyde oxidases (2). As a constituent of the nitrate reductase of plants and microorganisms, it is essential in plant growth. It is also involved in the function of the nitrogen fixing enzyme nitrogenase and in a hydrogenase of bacterial origin (2).

Molybdenum is a typical transition element, the second member of group VIB of the periodic system. Its oxidation states are ranging from 2- to 6+. The lowest oxidation states, 2- to 1+, occur only in organometallic compounds, others containing π -acceptor ligands, and some of the binary interstitial compounds.

Tungsten is a transition metal, the third member of group VIB of the periodic system. Its chemistry is quite similar to that of molybdenum. Its oxidation states are the same as that of molybdenum. Tungsten resembles molybdenum in the formation of iso- and hetero-poly acids, in the greater stabilities of its higher oxidation states, and in the absence of extensive coordination states; in this respect its distinction from chromium is most evident (3). The most analytically important compound of tungsten is tungstic oxide, WO_3 , which is only slightly soluble in acid solutions. Tungsten forms insoluble compounds of analytical importance with many organic reagents including benzidine, oxine, and cinchonine. There is no evidence that tungsten has a biological role, nor that tungsten compounds (except possibly in massive amounts) are poisonous (3).

Vanadium is the first member of group VB of the periodic system and a member of transition series. Vanadium exhibits oxidation states of 2+, 3+, 4+, and 5+. The chemistry of vanadium is complex because of its multivalence and because of its ability to form various ions in solution depending on the pH, such as the formation of oxo-species and a wide range of compounds with VO^{2+} groups (3). Vanadium compounds may be irritant to the conjuction and the respiratory tract. It appears to have no biological role in animals (3). There are some evidences that in traces it stimulates plant growth and that is thus resembles molybdenum. Vanadium is isomorphous with phosphorus and can be replaced in the apatite molecule. Thus, V_2O_5 has been found in human teeth. It is possible that the

presence of V_2O_5 increases the resistance of teeth to caries (3).

The last element interested is titanium, the first member of the d-block transition elements. It is classified in the group IVB of the periodic system. Titanium forms compounds in which it has the oxidation states of 2+, 3+, and 4+. Ti (IV) has a strong tendency to form anions, such as titanate ion, TiO_3^{2-} ; fluorotitanate ion, TiF_6^{2-} ; chlorotitanate ion, $TiCl_6^{2-}$; and sulfatotitanate ion, $Ti(SO_4)_3^{2-}$ (4). The soluble titanium (VI) compounds have a strong tendency to undergo hydrolytic decomposition. Incomplete hydrolysis may give rise to compounds of the type $TiOX_2$ (4). Titanium and its inorganic compounds which are strongly acidic or basic are toxic, e.g., $TiCl_4$ hydrolyses in moist air to yield hydrochloric acid. TiO_2 is inert and nontoxic, in fact it is used in the cosmetic and pharmaceutical industries (3).

Physical properties of Mo, W, V, and Ti are listed in Table 1 (5,6) and their reduction potentials involving the various states are summarized in Table 2 (6,7).

Many analytical techniques which have found the widest application in the study of trace analyses of inorganic substances are microscopy, atomic absorption and fluorescence, atomic emission, mass spectrometry, neutron activation analysis, X-ray fluorescence, and anodic stripping voltammetry. The comparison of advantages and limitations of these techniques are shown in reference 8. Among these techniques, anodic stripping voltammetry (ASV) is chosen for the investigation of Mo, W, V, and Ti compounds because of its ability to simultaneous determination of several elements at concentration

Table 1 Properties of some nonferrous metals (5,6)

	W	Mo	V	Ti
Atomic number	74	42	23	22
Atomic weight	183.92	95.95	50.95	47.90
Electronic configuration	Xe $4f^{14} 5d^4 6s^2$	Kr $4d^5 5s^1$	Ar $3d^5 4s^2$	Ar $3d^2 4s^2$
Isotopes	182, 183, 184, 186	92, 94, 95, 96, 97, 98, 100	51	46, 47, 48, 49, 50
m.p., °C	3380	2620	1920	1680
b.p., °C	5700	4600	3400	3300
Specific gravity	19.3	10.2	6.1	4.5
Atomic radius	(12 co-ordination) 1.40	(12 co-ordination) 1.41	1.35	(12 co-ordination) 1.47
Ionisation potential, ev				
I	7.98	7.18	6.74	6.83
II	14	15.2	14.65	13.57
III	24.1	27.0	29.31	27.47
IV	35.4	40.5	48.0	48.24
V	48	56	65.2	99.28
VI	-	-	128.9	-
Crystal structure	Body-centered cubic	Body-centered cubic or hexagonal close packed		Hexagonal above 880° cubic

Table 2 Standard reduction potentials of some nonferrous metals (6,7.) VS standard hydrogen electrode (SHE)

Reaction	Volts
$W_2O_5 + 2H^+ + 2e^- \rightleftharpoons 2WO_2 + H_2O$	-0.04
$WO_2 + 4H^+ + 4e^- \rightleftharpoons W + 2H_2O$	-0.12
$WO_3 + 6H^+ + 6e^- \rightleftharpoons W + 3H_2O$	-0.09
$2WO_3 + 2H^+ + 2e^- \rightleftharpoons W_2O_5 + H_2O$	-0.03
$H_2MoO_4 + 6H^+ + 6e^- \rightleftharpoons Mo + 4H_2O$	0.00
$Mo^{+3} + 3e^- \rightleftharpoons Mo$	-0.20
$MoO_2 + 4H^+ + 2e^- \rightleftharpoons Mo^{+3} + H_2O$	ca. 0.0
$MoO_3 + 6H^+ + 6e^- \rightleftharpoons Mo + 3H_2O$	+0.10
$V^{+2} + 2e^- \rightleftharpoons V$	-1.20
$V^{+3} + e^- \rightleftharpoons V^{+2}$	-0.255
$V^{+5} + e^- \rightleftharpoons V^{+4}$	-0.74; 1F NaOH
$VO^{+2} + 2H^+ + e^- \rightleftharpoons V^{+3} + H_2O$	0.337
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{+2} + H_2O$	1.00
$V(OH)_4^+ + 2H^+ + e^- \rightleftharpoons VO^{+2} + 3H_2O$	1.00
$V(OH)_4^+ + 4H^+ + 5e^- \rightleftharpoons V + 4H_2O$	-0.25
$Ti^{+2} + 2e^- \rightleftharpoons Ti$	-1.63
$Ti^{+3} + e^- \rightleftharpoons Ti^{+2}$	-2.00
$TiO_2 + 4H^+ + 4e^- \rightleftharpoons Ti + 2H_2O$	-0.86
$Ti(OH)^{+3} + H^+ + e^- \rightleftharpoons Ti^{+3} + H_2O$	0.06

levels ranging down to the fraction part per billion range with relatively inexpensive and simple equipments. In addition, anodic stripping voltammetric technique clearly offers capability for the solution of numerous difficult trace analysis problems.

An anodic stripping voltammetric technique involves two discrete steps: the deposition and stripping step. For the deposition step, a suitable electrode is maintained at a reduction potential of the element to be analyzed. The metal ions to be deposited arrive 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 preconcentration of the analyte into a small volume, small surface of the electrode. To strip this material from the electrode, its potential is changed back in the anodic direction, the direction required for oxidation. Several different current-potential curves may be used to strip the deposited analyte from the electrode and obtain the quantitation parameter, the stripping current, i_p , which is given by the Randles-Sevcik equation (9):

for reversible process

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

and irreversible process

$$i_p \text{ (irr)} = 602 n (\alpha n_a)^{\frac{1}{2}} A D^{\frac{1}{2}} v^{\frac{1}{2}} C^b(X'')$$

where

- i_p = stripping current, mA
- n = number of electrons transfer
- A = electrode surface area, cm^2

D	=	diffusion coefficient of oxidizable species, $\text{cm}^2 \text{sec}^{-1}$
V	=	rate of potential change or scan rate, volt sec^{-1}
C^b	=	concentration of oxidizable species in bulk solution, mole cm^{-3}
α	=	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

The value of i_p is seen to be directly proportional to C^b and $V^{1/2}$.

If the rate of the electron transfer reaction is very rapid compared to the mass transport, the electrode reaction is called reversible process. In the other hand, if the electron transfer rate is relatively slow, such reaction is called irreversible (9).

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.

Materials applied as working electrodes for ASV are in wide range such as Pt, Au, Ag, Bi, B_4C and C. Some of the noble metals

have a mutual tendency for the formation of intermetallic compounds, i.e., AgHg. To avoid this a carbon electrode is often used. Primary among these carbon electrodes are pyrolytic, impregnated, and glassy carbon. Pyrolytic graphite electrode, introduced for both aqueous and nonaqueous system, gives some limitations on its proper orientation. Impregnated carbon electrode, given excellent potential range, sometimes suffers from high residual current (9). These limitations should not exist for electrode made of glassy carbon. Thus, a glassy carbon or vitreous carbon of which properties were previously referred in reference 10, is used in this study.

In the present work, the condition for W (VI), Mo (VI), V (V), and Ti (IV) ions to deposit at the glassy carbon electrode are investigated. The optimum conditions involving type and concentration of the supporting electrolyte, pH of the test solution, and deposition potential can be obtained by their cathodic voltammograms. The deposition time and stripping conditions (range of potential for ASV) for the element determined are tested by its anodic stripping voltammogram. Finally, the sensitivity of each technique is examined by the stripping current.