2.1 Differential Pulse Anodic Stripping Voltammetry (DPASV)

Anodic stripping voltammetry (ASV) was first used by Zbinden in 1931. Little further work was done in this area until the 1950's when the use of mercury electrodes became common. During the 1960's, the theory of ASV for mercury film electrodes (MFE) and hanging mercury drop electrodes (HMDE) was developed. At the present, a variety of techniques have been introduced which have enhanced the method's capability.

The fundamental of an anodic stripping voltammetry 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. The deposition step can be carried out in two ways. In the stoichiometric procedure, the ion of interest is removed completely from a stirred solution at a constant cathode potential. In the nonstoichiometric procedure only a fraction of the ion is deposited so it has the advantage of speed. For the deposition step, a suitable electrode is maintained at a potential cathodic of the reduction potential 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 properties of the electrolyte solution, and the area of the electrode used. The deposition time is carefully measured. The deposition results

in preconcentration 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 faradic current produced by its oxidation is measured. 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 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 [54]:

$$i(t)_{dep} = 0.62 \ nFAD^{2/3} \ W^{1/2} \ \mu^{-1/6} \ C(t) \qquad \ldots\ldots\ldots (1)$$

where $i(t)_{dep}$ = 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, $cm^2 \ sec^{-1}$

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

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

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

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) such as linear ramp stripping, ac stripping and differential pulse stripping (see Figure 1). In differential

pulse anodic stripping voltammetry (DPASV), relatively large amplitude (50-100 mV) pulses are periodically superimposed on a shallow linear potential ramp ($\sim$ 5 mV/sec) for short periods as shown in Figure 1(c). The nonfaradic current induced by the application of the pulse decays more rapidly than the faradic current. This is governed in part by the rate at which the reoxidized metal can diffuse away from the electrode surface. The current is consequently measured just prior to the pulse application and again for the same period of time at the end of the pulse life. The difference in these two measurements is amplified and read out. The choice of the measurement periods permits a high level of discrimination against the capacitative current since the current measured near the end of the pulse is predominantly due to the faradic reaction (sec Figure 2). Differential pulse stripping offers sensitivity enhancements of one to several orders of magnitude and appears to offer the highest signal - to-noise ratio of any stripping technique.

The total current flowing through the DPASV system is [55].

$$i_t = i_f + i_c + i_b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where i_f = the faradic 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
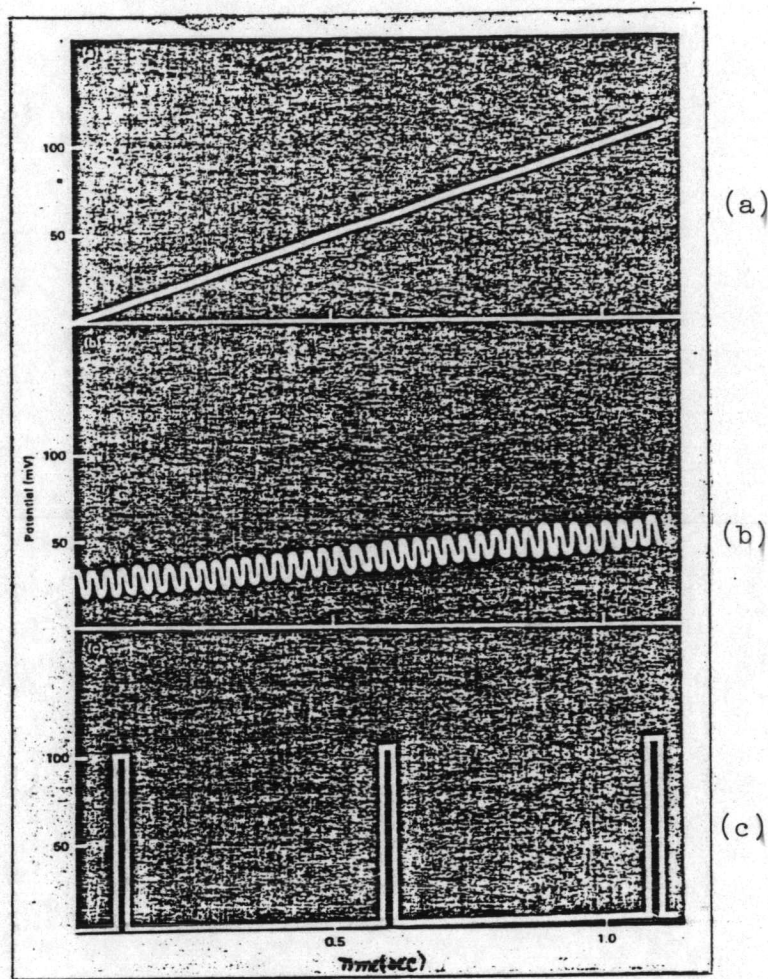
Figure 1   Potential – time waveforms used for anodic stripping

(a) Linear ramp stripping

(b) AC stripping
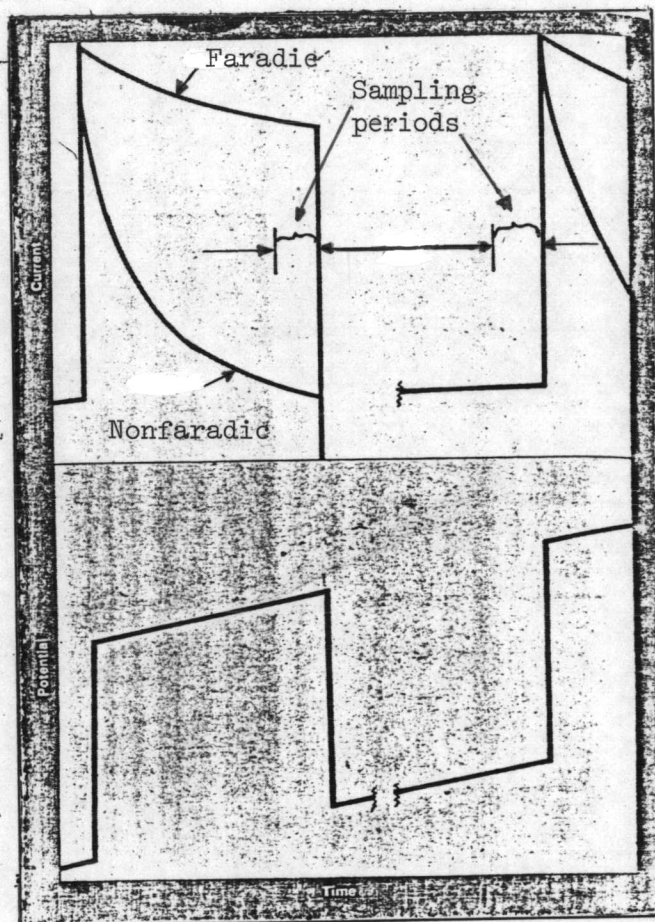
(c) Differential pulse stripping

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Figure 2   Choice of measurement periods in differential pulse

stripping to reduce contributions of nonfaradic processes

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[55]

$$E_p = E_{1/2} - 1.1\ RT/nF$$

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

The basic instrument required for DPASV includes a three electrode potentiostat and voltage ramp generator, current measuring circuit (a cell with working, reference and counter electrode), and a recorder or other readout device. Instruments designed for dc, ac or pulse polarographic measurements are generally quite adequate for stripping application.

Platinum wire or foil is widely used for the counter (auxiliary) electrode. Silver-silver chloride or calomel electrodes are popular choices for the reference. The most popular working electrodes are those involving mercury. Solid electrodes of gold, silver, platinum, carbon and bismuth have been used. For the hanging mercury electrodes (HMDE), they have two primary disadvantages. First, they typically have a low surface area - to - volume ratio. The smaller area reduces plating efficiency while the larger volume causes a broadening of the stripping peaks which limits the ability to resolve adjacent peaks. Second, only

rather minimal solution stirring procedures can be used to avoid distortion or dislodging of the drop. The stirring and area limitations impose the requirement of longer deposition times. These factors have been at least partially responsible for the development of mercury thin-film electrodes (MTFE) which offer the same potential range as the HMDE. The MTFE provides a large surface area-to-volume ratio and can be easily rotated or stirred at quite high rates.

The ideal substrate for the MTFE must meet relatively few criteria, it must have reasonable electrical conductivity, be chemically inert to the mercury and to the analysis solution, and be electrochemically inert at potentials anodic of the most easily reduced of the elements of interest. Many graphite types can be used. The results further show that the hard, nonporous (glassy or vitreous) types of carbon yield large and reproducible peaks. Such types may be readily polished to a mirror-like finish so that the surface irregularities are small in comparison to the mercury film thickness, the surface - to - volume ratio is high, and a coherent film over the entire surface is readily obtained. The use of such types of graphite or carbon strikingly simplifies the preparation of thin - film electrodes. After polishing the carbon via exacting metallographic procedures, the thin film can be quite precisely electrodeposited on the surface.

All voltammetric techniques involve analyses in a supporting electrolyte. The electrolyte is simple, such as an acid medium or it may be a buffer system particularly when pH control is essential. Supporting electrolyte concentrations of 0.05-0.5 M are typical. Almost any different electrolyte can be used, but the choice often

improves the reproducibility and resolution of the stripping peaks .

From the information mentioned above, the differential pulse anodic stripping voltammetric technique with a mercury thin film on glassy carbon electrode was selected for this study.

2.2 Standard addition

Quantitative evaluation of metals in vegetable samples can obtain by a number of methods, for example, interpretation from the calibration curve and calculation from the standard addition. In order to minimize the influence of the variation of the concentrations of the interferences presented in different vegetable samples on the accuracy of results, the vegetable samples had all been analyzed by the method of standard addition. The standard addition is best achieved by addition of known volumes of the standard metal ion solution to the sample. The method is used when the peak height is proportional to the concentration of the substance being determined. The concentration of metal ion in solution is calculated by

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

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, $\mu g\ cm^{-3}$