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Razi University

**Faculty of Science
Department of Chemistry**

M.Sc. Thesis

Title of the Thesis

**Catalytic Kinetic Determination of Vanadium (V) by Linear
Sweep Voltammetry & Determination of Lead (II) by Adsorptive
Stripping Voltammetry**

Supervisor:

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By:

Mehdi Malekian

September 2007

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M. Malekian

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Dedicated to:

My Dear Parents

Abstract

Part one

A kinetic method is described for the determination of trace amounts of vanadium (V) based on its catalytic effect on the oxidation of nuclear fast red (NFR) by potassium bromate using linear sweep voltammetry at a gold electrode. The decrease in current of nuclear fast red at a fixed time of 3 min from initiation of the reaction is proportional to the concentration of V (V) for the range of 1 – 150 ng ml⁻¹. In this study experimental parameters were optimized and the effect of other cations and anions on the determination of vanadium (V) was examined. The limit of detection is 0.34 ng ml⁻¹. The relative standard deviation for eight replicate measurements of 50.0 ng ml⁻¹ of vanadium is 1.6%. The proposed methods were applied to the analysis of vanadium (V) in synthetic alloys, water, rice and human hair.

Part two

A new method is described for the determination of lead based on the cathodic adsorptive stripping of the lead - nuclear fast red (NFR) at a carbon paste electrode (CPE). The differential pulse voltammograms of the adsorbed complex of lead – NFR are recorded from -0.10 to -0.60 V. Optimal conditions were found to be an electrode containing 25% paraffin oil and 75% high purity graphite powder, 4.0×10^{-5} mol L⁻¹ NFR; buffer solution (pH of 3.0), accumulation potential and time, -0.20 V, 60 and 120 s (for high and low concentration of lead) respectively. The detection limit was found to be 0.2 ng ml⁻¹ with a 120 s accumulation time. The linear ranges are from 0.5 to 50 (t_{acc} = 120 s) and 50 to 200 ng ml⁻¹ (t_{acc} = 60 s). Application of the procedure to the determination of lead in lake water, bottled mineral water, synthetic samples and sweet fruit-flavored powder drinks samples gave good results.

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Part One

Catalytic Kinetic Determination of Vanadium (V)

by Linear Sweep Voltammetry

Chapter 1

Introduction and Literature Review

1.1. Introduction

1.1.1. Kinetic Methods of Analysis

A system under thermodynamic control is in a state of equilibrium, and its signal has a constant or steady-state value (Fig. 1.1a). When a system is under kinetic control, however, its signal changes with time (Fig. 1.1b) until equilibrium is established. Thus far, the techniques we have considered have involved measurements made when the system is at equilibrium. By changing the time at which measurements are made, an analysis can be carried out under either thermodynamic control or kinetic control [1].

There are many potential advantages to kinetic methods of analysis, perhaps the most important of which is the ability to use chemical reactions that are slow to reach equilibrium.

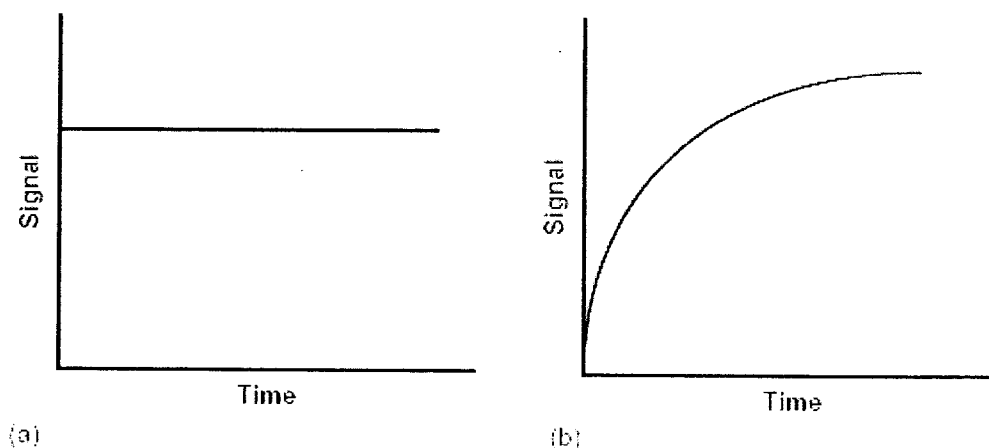


Figure 1.1. Plot of signal versus time for an analytical system that is under (a) thermodynamic control; (b) under kinetic control.

The earliest examples of analytical methods based on chemical kinetics, which date from the late nineteenth century, took advantage of the catalytic activity of enzymes. Typically, the enzyme was added to a solution containing a suitable substrate, and the reaction between the two was monitored for a fixed time. The enzyme's activity was determined by measuring the amount of substrate that had reacted. The application of catalytic reactions continued in the first half of the twentieth century, and developments included the use of nonenzymatic catalysts, noncatalytic reactions, and differences in reaction rates when analyzing samples with several analytes. Despite the variety of methods that had been developed, by 1960 kinetic methods were no longer in common use. The principal limitation to a broader acceptance of chemical kinetic methods was their greater susceptibility to errors from uncontrolled or poorly controlled variables, such as temperature and pH, and the presence of interferents that activate or inhibit catalytic reactions. Many of these limitations, however, were overcome during the 1960s, 1970s, and 1980s with the development of improved instrumentation and data analysis methods compensating for these errors [2].

1.1.2. Reaction Rate and Kinetic Equation

Every chemical reaction occurs at a finite rate and, therefore, can potentially serve as the basis for a chemical kinetic method of analysis. To be effective, however, the chemical reaction must meet three conditions. First, the rate of the chemical reaction must be fast enough that the analysis can be conducted in a reasonable time, but slow enough that the reaction does not approach its equilibrium position while the reagents are mixing. As a practical limit, reactions reaching equilibrium within 1 sec are not easily studied without the aid of specialized equipment allowing for the rapid mixing of reactants.

A second requirement is that the rate law for the chemical reaction must be known for the period in which measurements are made. In addition, the rate law should allow the kinetic parameters of interest, such as rate constants and concentrations, to be easily estimated. For example, the rate law for a reaction that is first order in the concentration of the analyte, A, is expressed as:

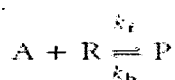
$$\text{Rate} = - \frac{d[A]}{dt} = k[A] \quad (1-1)$$

Where k is the reaction's rate constant. The integrated form of this rate law:

$$\ln [A]_t = \ln [A]_0 - kt \quad \text{or} \quad [A]_t = [A]_0 e^{-kt} \quad (1-2)$$

Provides a simple mathematical relationship between the rate constant, the reaction's elapsed time, t, the initial concentration of analyte, $[A]_0$, and the analyte's concentration at time t, $[A]_t$.

Unfortunately, most reactions of analytical interest do not follow the simple rate laws shown in equations 1.1 and 1.2. Consider, for example, the following reaction between an analyte, A, and a reagent, R, to form a product, P:



Where k_f is the rate constant for the forward reaction, and k_b is the rate constant for the reverse reaction. If the forward and reverse reactions occur in single steps, then the rate law is:

$$\text{Rate} = k_f[A][R] - k_b[P] \quad (1-3)$$

Although the rate law for the reaction is known, there is no simple integrated form. We can simplify the rate law for the reaction by restricting measurements to the beginning of the reaction when the product's concentration is negligible. Under these conditions, the second term in equation 1.3 can be ignored; thus:

$$\text{Rate} = k_f[A][R] \quad (1-4)$$

The integrated form of the rate law for equation 1.4, however, is still too complicated to be analytically useful. We can simplify the kinetics, however, by carefully adjusting the reaction conditions [3]. For example, pseudo-first-order kinetics can be achieved by using a large excess of R (i.e. $[R]_0 \gg [A]_0$), such that its concentration remains essentially constant. Under these conditions:

$$\text{Rate} = -\frac{d[A]}{dt} = k[R]_0[A] = k'[A] \quad (1-5)$$

$$\ln [A]_t = \ln [A]_0 - k't \quad \text{or} \quad [A]_t = [A]_0 e^{-k't} \quad (1-6)$$

It may even be possible to adjust conditions such that measurements are made under pseudo-zero-order conditions where:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]_0[R]_0 = k'' \quad (1-7)$$

$$[A]_t = [A]_0 - k''t \quad (1-8)$$

A final requirement for a chemical kinetic method of analysis is that it must be possible to monitor the reaction's progress by following the change in concentration for one of the reactants or products as a function of time. Which species is used is not important; thus, in a quantitative analysis the rate can be measured by monitoring the analyte, a reagent reacting with the analyte, or a product.

1.1.3. Factors Influencing Rate of Reaction

There are several factors that affect the rate of reaction:

- **Concentration:** Reaction rate increases with concentration, as described by the rate law and explained by collision theory. As reactant concentration increases, the frequency of collision increases.
- **The nature of the reaction:** Some reactions are naturally faster than others. The number of reacting species, their physical state (the particles that form solids move much more

slowly than those of gases or those in solution), the complexity of the reaction and other factors can influence greatly the rate of a reaction.

- Temperature: Usually conducting a reaction at a higher temperature delivers more energy into the system and increases the reaction rate by causing more collisions between particles, as explained by collision theory. However, the main reason why it increases the rate of reaction is that more of the colliding particles will have the necessary activation energy resulting in more successful collisions (when bonds are formed between reactants). The influence of temperature is described by the Arrhenius equation (Sec. 1.4.1.). As a rule of thumb, reaction rates for many reactions double or triple for every 10 °C increase in temperature [4], though the effect of temperature may be very much larger or smaller than this (to the extent that reaction rates can be independent of temperature or decrease with increasing temperature).
- Solvent: Many reactions take place in solution and the properties of the solvent affect the reaction rate. The ionic strength as well has an effect on reaction rate.
- Pressure: The rate of gaseous reactions increases with pressure, which is, in fact, equivalent to an increase in concentration of the gas.
- Electromagnetic Radiation: Electromagnetic radiation is a form of energy so it may speed up the rate or even make a reaction spontaneous, as it provides the particles of the reactants with more energy. This energy is in one way or another stored in the reacting particles (it may break bonds, promote molecules to electronically or vibrationally excited states...) creating intermediate species that react easily.
- A catalyst: The presence of a catalyst increases the reaction rate (in both the forward and reverse reactions) by providing an alternative pathway with a lower activation energy (Sec. 1.4.2.).

- **Isotopes:** The kinetic isotope effect consists in a different reaction rate for the same molecule if it has different isotopes, usually hydrogen isotopes, because of the mass difference between hydrogen and deuterium.
- **Surface Area:** In reactions on surfaces, which take place for example during heterogeneous catalysis, the rate of reaction increases as the surface area does. That is due to the fact that more particles of the solid are exposed and can be hit by reactant molecules.
- **Order:** The order of the reaction controls how the reactant concentration affects reaction rate.

All the factors that affect a reaction rate are taken into account in the rate equation of the reaction.

1.1.3.1. Arrhenius Equation

In short, the Arrhenius equation is an expression that shows the dependence of the rate constant k of chemical reactions on the temperature T (in Kelvin) and activation energy E_a , as shown below:

$$k = Ae^{-E_a/RT} \quad (1-9)$$

Where A is the pre-exponential factor or simply the prefactor and R is the gas constant. The units of the pre-exponential factor are identical to those of the rate constant and will vary depending on the order of the reaction. If the reaction is first order it has the units s^{-1} , and for that reason it is often called the frequency factor or attempt frequency of the reaction. When the activation energy is given in molecular units, instead of molar units, e.g. joules per molecule instead of joules per mol, the Boltzmann constant is used instead of the gas constant. It can be seen that either increasing the temperature or decreasing the

activation energy (for example through the use of catalysts) will result in an increase in rate of reaction.

Some authors define a modified Arrhenius equation that makes explicit the temperature dependence of the pre-exponential factor. If one allows arbitrary temperature dependence of the prefactor, the Arrhenius description becomes overcomplete, and the inverse problem (i.e. determining the prefactor and activation energy from experimental data) becomes singular. It has been pointed out that "it is not feasible to establish, on the basis of temperature studies of the rate constant, whether the predicted $T^{1/2}$ dependence of the pre-exponential factor is observed experimentally" [4], but if additional evidence is available, from theory and/or from experiment (such as density dependence), there is no obstacle to incisive tests of the Arrhenius law.

Taking the natural logarithm of the Arrhenius equation yields:

$$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A \quad (1-10)$$

So, when a reaction has a rate constant which obeys the Arrhenius equation, a plot of $\ln k$ versus T^{-1} gives a straight line, whose slope and intercept can be used to determine E_a and A . This procedure has become so common in experimental chemical kinetics that practitioners have taken to using it to define the activation energy for a reaction. That is the activation energy is defined to be $(-R)$ times the slope of a plot of $\ln k$ vs. $1/T$:

$$E_a \equiv -R \left(\frac{\partial(\ln k)}{\partial(1/T)} \right)_p \quad (1-11)$$

1.1.3.2. Catalysis

In chemistry and biology, catalysis is the acceleration (increase in rate) of a chemical reaction by means of a substance, called a catalyst, which is itself not consumed by the overall reaction.