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VOLTAMMETRIC DETERMINATION OF TIN IN JUICY DRINK SAMPLES

Dissertation submitted in partial fulfilment for the Degree of Bachelor of Forensic Science

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CERTIFICATE

This is to certify that the dissertation entitled

"Voltammetric Determination of Tin in Juicy Drinks Samples"

is the bonafide record of research work done by

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during the period 19 January 2006 to 18 April 2006

under my supervision

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TABLE OF CONTENTS

Page

LIST OF TABLES FIGURES AND CHARTS

Page

ABSTRACT

A voltammetric method for analysis of tin in juicy drinks was developed using Anodic Stripping Voltammetry. A few parameters such as pH of the supporting electrolyte, initial potential, final potential, accumulation potential, accumulation time and scan rate were optimized. The optimum condition for the determination of tin in juicy drinks are, pH of BRB buffer is 2.32, initial potential is -0.6 V, final potential is -0.25 V, accumulation potential is 0 V, accumulation time is 90 seconds and scan rate is 10 mV/s.

Various brands of juicy drinks that are commercially available are analyzed for determination of stannous/tin (II) using the developed technique.

The voltammetric measurements were carried out using Voltammetry Analyzer with three electrodes. The electrodes are Hanging Mercury Drop Electrode (HMDE) as the working electrode, auxiliary (platinum wire) and reference electrode (Ag/AgCl/KCl). The concentration of tin is determined on each sample and then the result is compared with the standard limit set by World Health Organization (WHO).

The result shows that Sn (II) is absent in all the samples except three samples (sample B, M & N) which are from the same manufacturer. Finally, it can be concluded that the proposed method can be used for the determination on stannous in juicy drink samples.

INTRODUCTION

Toxic and persistence substances in the environment continuously accumulate and increase owing to the human activities. With reference to this, one of the major problems in the ecology is related to the path of toxic metals contained in all food chain including drinks. The main source for tin uptake by man is food and drinks, with the exception of some polluted industrial areas, where tin concentrations in water and air is high. (Locatelli and Torsi, 2004).

Tin exists mainly in the oxidation states Sn(0), Sn(II) ans Sn(IV). The toxicity of metallic tin and inorganic tin compounds on the one hand is low. Some studies even suggest that tin is an essential trace elements for human. However, organo tin compounds have been proven to be toxicological relevance. Triorganotin compounds are particularly toxic explaining their wide use as biocides in antifouling paints or pesticides. Tin is generally considered to be nontoxic in its metallic form. Cases of poisoning with tin are almost unknown, because ingested tin is poorly absorbed by organism. However, massive inhalation of tin by exposed industrial workers may lead to irritation of the respiratory tract (Rudel, 2003).

Tin is a grey-white metal. The most important inorganic tin compounds include the tin(II) and tin(IV) chlorides, tin(II) oxide, tin(II) fluoride, and thepotassium and sodium stannates. The 2+ and 4+oxidation states of tin, also known as tin(II) and tin(IV), are both fairly stable (WHO, 2005)

Tin may be released to the atmosphere from both natural and anthropogenic sources. Tin is a component of many soils and may be released in dusts from wind storms, roads, and agricultural activities. Other less significant natural sources include forest fires and volcanic missions. Gases, dusts, and fumes containing tin may be released from smelting and refining processes, industrial uses of tin, waste incineration, and burning of fossil fuels. The vapor pressure of elemental tin is negligible; tin and inorganic tin compounds are nonvolatile under environmental conditions. Tin (II) chloride is soluble in water, whereas other tin compounds tend to be only slightly soluble. Tin compounds are likely to partition to soils and sediments. Inorganic tin may undergo oxidation–reduction, ligand exchange, and precipitation reactions in the environment. The biomethylation of inorganic tin has been demonstrated in pure bacterial cultures, sediments, and decaying plant material. Inorganic tin compounds may be bioconcentrated by organisms, but data are limited. Average tin concentrations in air are generally below 0.1 $\mu g/m^3$ (ranging up to 0.8 $\mu g/m^3$), with higher concentrations near some industrial facilities. In general, tin occurs in trace amounts in natural waters. Higher inorganic tin concentrations are associated with industrial discharges and tributyltin use. In a survey of lakes and rivers, nearly 80% of samples were found to contain inorganic tin at concentrations below 1 µg/litre; higher levels of up to 37 µg/litre were reported near pollution sources. Inorganic tin concentrations ranging from 0.001 to 0.01 µg/litre have been reported for coastal waters, with levels of up to 8 µg/litre near pollution sources. Inorganic tin concentrations in sediment ranged up to 8 mg/kg dry weight in coastal areas and up to 15.5 mg/kg in rivers and lakes. Tin concentrations in the earth's crust are approximately 2–3 mg/kg. Total tin concentrations in soil can range from <1 to 200 mg/kg, but levels of 1000 mg/kg may occur in areas of high tin deposits. Certain ore deposits may contain up to 50 000 mg/kg as tin (WHO, 2005).

Pure tin exists in two allotropic crystalline modifications:grey tin (alpha form) and white tin (beta form). At low temperatures (at about 18 °C and below), the grey tin changes to white tin. The 2+ (stannous) and 4+ (stannic) oxidation states are both reasonably stable and interconverted by moderately active reagents. The Sn2+/Sn4+ potential is −0.15 V, and tin(II) can act as a mild reducing agent. Due to its amphoteric nature, tin reacts with strong acids and strong bases but remains relatively resistant to neutral solutions. A thin protective oxide film forms on tin exposed to oxygen or dry air at ordinary temperatures; heat accelerates this reaction. Tin is readily attacked by hydrogen iodide and hydrogen bromide and less readily by hydrogen chloride. Hot concentrated sulfuric acid reacts with tin to form tin(II) sulfate, whereas the diluted acid reacts only slowly with tin at room temperature. Reaction of tin with dilute nitric acid yields soluble tin nitrates; in concentrated nitric acid, tin is oxidized to insoluble hydrated tin dioxide. Organic acids such as lactic, citric, tartaric, and oxalic acid attack tin slowly in the presence of air and oxidizing substances. Molten tin reacts with phosphorus, forming a phosphide. Stannates are produced by the action of strong potassium hydroxide or sodium hydroxide on tin. (Tin(IV) chloride reacts with water to generate colloidal tin oxides (WHO, 2005).

Tin-plate is widely used in food industry as packing of canned food. Tin is a heavy metal element which can do certain harm to human health. Tin concentration in drinks must be detected and its concentration must be evaluated to ensure that the toxicity level is lower that the level that have been fixed by law. Many methods have been developed for the determination of tin such as spectrophotometry, atomic absorption spectrosmetry and polarography. However, all the methods that have been stated may not be suitable for all samples for determination of tin. The voltammetry technique (Anodic Stripping Voltammetry) may certainly be a good equipment for determining tin (II) in juicy drinks (Qiong et al, 1997).

Voltammetric technique is a technique for metal ion analysis. It can detect various type of metals with the concentration limit as low as part per billion to high part per trillion range. Its general uses are quantitative determination of organic and inorganic compounds in aqueous and nonaqueous solutions, measurements of kinetic rates and constants, determination adsorption processes on surfaces, determination electron transfer and reaction mechanisms, determination of thermodynamic properties of solvated species, fundamental studies of oxidation and reduction processes in various media and also determination of complexation and coordination values (Kounaves, 1985).

The common applications of voltammetric technique are of pharmaceutical compounds, determination of metal ion in water to sub part per billion levels, determination of redox potentials, determination of number of electron in redox reactions and also kinetic studies of reactions (Kounaves, 1985).

The common characteristic of all voltammetric techniques is that they involve the application of a potential (E) to an electrode and the monitoring of the resulting current (i) flowing through the electrochemical cell. In many cases, the applied potential is varied or the current is monitored over a period of time (t). Thus, all voltammetric techniques can be described as some function of E, I and t. They are considered active techniques because the applied potential forces a change in concentration of electroactive species at the electrode surface by electrochemically reducing or oxidizing it (Kounaves, 1985).

A typical electrochemical cell consists of the sample dissolved in a solvent, an ionic electrolyte and three electrodes. Cells (sample holder) come in variety of size, shapes and materials. The type used depends on the amount and type of sample, the technique and the analytical data to be obtained. The material of the cell (glass, Teflon, polyethelene) is selected to minimize reaction with the sample (Kounaves, 1985)

The reference electrode should provide a reversible half reaction with Nernstian behavior, be constant over time, and be easy to assemble and maintain. The most commonly used reference electrode for aqueous solutions are the calomel electrode. In auxiliary electrode, in most voltammetric techniques, the analytical reactions at the electrode surfaces occur over very short time periods. Usually the auxiliary electrode consists of a thin platinum wire, although aurum and sometimes graphite have also been used. The working electrodes are of various geometries and materials, ranging from small mercury drops to flat platinum disks. Mercury is useful because it displays a wide negative potential range (because it is difficult to reduce hydrogen ion or water at the mercury surface), its surface readily regenerated by producing a new drop or film, and many metal ions can be reversibly reduced into it. Other commonly used electrode materials are gold, platinum and glassy carbon (Kounaves, 1985).

Anodic Stripping Technique is most widely used for trace metal determination and has a practical detection limit of in the part per trillion range. This low detection limit is coupled with the ability to determine simultaneously four to six trace metals using relatively inexpensive instrumentation (http://chem.ch.huji.ac).

Metals ion in the sample solutions are concentrated into a mercury electrode during a given time period by application of a sufficient negative potential. These amalgated metals are then stripped (oxidized) out of the mercury by scanning the applied potential in the positive direction. The resulting peak current is proportional to the concentration of each metal in the sample solution, with the position of the peak potential, specific to each metal (Harvey, 2000).

Anodic stripping voltammetry has good selectivity and sensitivity. Selectivity in voltammetric analysis is due to the fact that different electroactive species undergo reduction (or oxidation) at different electrode potentials (Sabry and Wahbi, 1999).

So far, there are already many works have been done to develop the voltammetry technique. In this work, the different parameters which are include initial potential, final potential, accumulation potential, accumulation time, scan rate and also pH of the supporting electrolyte have been used. It differs from the previous works because the use of different parameters. In this work, all the parameters have been optimized for the determination of tin (II).

The Theory of Voltammetry

The electrochemical cell, where the voltammetric experiment is carried out, consists of a working (indicator) electrode, a reference electrode, and usually a counter (auxiliary) electrode. In general, an electrode provides the interface across which a charge can be transferred or its effects felt. Because the working electrode is where the reaction or transfer of interest is taking place, whenever we refer to the electrode, we always mean the working electrode. The reduction or oxidation of a substance at the surface of a working electrode, at the appropriate applied potential, results in the mass transport of new material to the electrode surface and the generation of a current. Even though the various types of voltammetric techniques may appear to be very different at first glance, their fundamental principles and applications derive from the same electrochemical theory. Here we summarize some of the electrochemical theory or laws common to all of the voltammetric techniques (Kounaves, 1985).

In voltammetry, the effects of the applied potential and the behavior of the redox current are described by several well-known laws. The applied potential controls the concentrations of the redox species at the electrode surface (C_O^0 and C_R^0) and the rate of the reaction (k^0), as described by the Nernst or Butler–Volmer equations, respectively. In the cases where diffusion plays a controlling part, the current resulting from the redox process (known as the faradaic current) is related to the material flux at the electrode–solution interface and is described by Fick's law. The interplay between these processes is responsible for the characteristic features observed in the voltammograms of the various techniques (Kounaves, 1985).

For a reversible electrochemical reaction (that is, a reaction so fast that equilibrium is always reestablished as changes are made), which can be described by **O** + ne^- Û **R**, the application of a potential E forces the respective concentrations of **O** and **R** at the surface of the electrode (that is, c_O^0 and c_R^0) to a ratio in compliance with the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{c_R^0}{c_O^0}$$

<u>Equation 1</u>

where R is the molar gas constant (8.3144 J mol$^{-1}K^{-1}$), T is the absolute temperature (K), n is the number of electrons transferred, F = Faraday constant (96,485 C/equiv), and E^0 is the standard reduction potential for the redox couple. If the potential applied to the electrode is changed, the ratio c_R^0/c_O^0 at the surface will also change so as to satisfy equation 1. If the potential is made more negative the ratio becomes larger (that is, **O** is reduced) and, conversely, if the potential is made more positive the ratio becomes smaller (that is, **R** is oxidized), (Kounaves, 1985).

For some techniques it is useful to use the relationship that links the variables for current, potential, and concentration, known as the Butler–Volmer equation:

$$\frac{i}{nFA} = k^0\{C_O \exp[-\alpha\theta] - C_R \exp[(1-\alpha)\theta]\}$$

<u>Equation 2</u>

where q = $nF(E - E^0)/RT$, k^0 is the heterogeneous rate constant, a is known as the transfer coefficient, and A is the area of the electrode. This relationship allows us to obtain the values of the two analytically important parameters, i and k^0, (Kounaves, 1985).

Finally, in most cases the current flow also depends directly on the flux of material to the electrode surface. When new **O** or **R** is created at the surface, the increased concentration provides the force for its diffusion toward the bulk of the solution. Likewise, when **O** or **R** is destroyed, the decreased concentration promotes the diffusion of new material from the bulk solution. The resulting concentration gradient and mass transport is described by Fick's law, which states that the flux of matter (F) is directly proportional to the concentration gradient:

$$\Phi = -AD_O(\partial C_O/\partial x)$$

<u>Equation 3</u>

where D_O is the diffusion coefficient of **O** and x is the distance from the electrode surface. An analogousequation can be written for **R**. The flux of **O** or **R** at the electrode surface controls the rate of reaction, and thus the faradaic current flowing in the cell. In the bulk solution, concentration gradients are generally small and ionic migration carries most of the current. The current is a quantitative measure of how fast a species is being reduced or oxidized at the electrode surface. The actual value of this current is affected by many additional factors, most importantly the concentration of the redox species, the size, shape, and material of the electrode, the solution resistance, the cell volume, and the number of electrons transferred (Kounaves, 1985).

In addition to diffusion, mass transport can also occur by migration or convection. Migration is the movement of a charged ion in the presence of an electric field. In voltammetry, the use of a supporting electrolyte at concentrations 100 times that of the species being determined eliminates the effect of migration. Convection is the movement of the electroactive species by thermal currents, by density gradients present in the solution, or by stirring the solution or rotating the electrode. Convection must be eliminated or controlled accurately to provide controlled transport of the analyte to the electrode (Kounaves, 1985).

Many voltammetric techniques have their own unique laws and theoretical relationships that describe and predict in greater detail the various aspects of the *i–E* behavior (such as curve shape, peak height, width, and position), (Kounaves, 1985).

The basic components of a modern electroanalytical system for voltammetry are a potentiostat, computer, and the electrochemical cell (Figure 1). In some cases the potentiostat and computer are bundled into one package, whereas in other systems the computer and the A/D and D/A converters and microcontroller are separate, and the potentiostat can operate independently (Kounaves, 1985).

The task of applying a known potential and monitoring the current falls to the potentiostat. The most widely used potentiostats today are assembled from discrete integrated-circuit operational amplifiers and other digital modules. In many cases, especially in the larger instruments, the potentiostat package also includes electrometer circuits, A/D and D/A converters, and dedicated microprocessors with memory (Kounaves, 1985).

A simple potentiostat circuit for a three-electrode cell with three operational amplifiers (OA) is shown in Figure 2. The output of OA-1 is connected to the counter electrode with feedback to its own inverting input through the reference electrode. This feedback decreases the difference between the inverting and noninverting inputs of OA-1 and causes the reference electrode to assume the same potential as E_{in} of OA-1. Because the potential difference between the working electrode and the reference electrode is zero the working electrode is set to the same potential as applied to the OA-1 input. With the reference electrode connected to Ein through the high impedance of OA-3, the current must flow through the counter electrode. Current flow through the reference not only is undesirable because of its higher resistance but also would eventually cause its potential to become unreliable. A three-electrode system is normally used in voltammetry for currents in the range of microamperes to miliamperes (Kounaves, 1985).

With the use of micron-sized electrodes, currents are in the pico- to nanoampere range, and thus two electrodes are often used (that is, the counter and reference are tied together). An OA acting as a current-to-voltage converter (OA-2) provides the output signal for the A/D converter. Most voltammetric techniques are dynamic (that is, they require a potential modulated according to some predefined waveform). Accurate and flexible control of the applied potential is a critical function of the potentiostat. In early analog instruments, a linear scan meant just that, a continuous linear change in potential from one preset value to another. Since the advent of digital electronics almost all potentiostats operate in a digital (incremental) fashion. Thus, the application of a linear scan is actually the application of a "staircase" modulated potential with small enough steps to be equivalent to the analog case. Not surprisingly, digital fabrication of the applied potential has opened up a whole new area of pulsed voltammetry, which gives fast experiments and increased sensitivity. In the simpler potentiostats, the excitation signal used to modulate the applied potential is usually provided by an externally adjustable waveform generator. In the computer-controlled instruments, the properties of the modulation and the waveform are under software control and can be specified by the operator. The most commonly used waveforms are linear scan, differential pulse, and triangular and square wave. The use of micro- and nanometer-size electrodes has made it necessary to build potentiostats with very low current capabilities. Microelectrodes routinely give current responses in the pico- to nanoampere range. High-speed scanning techniques such as square-wave voltammetry require very fast response times from the electronics. These diverse and exacting demands have pushed potentiostat manufacturers into providing a wide spectrum of potentiostats tailored to specific applications (Kounaves, 1985).

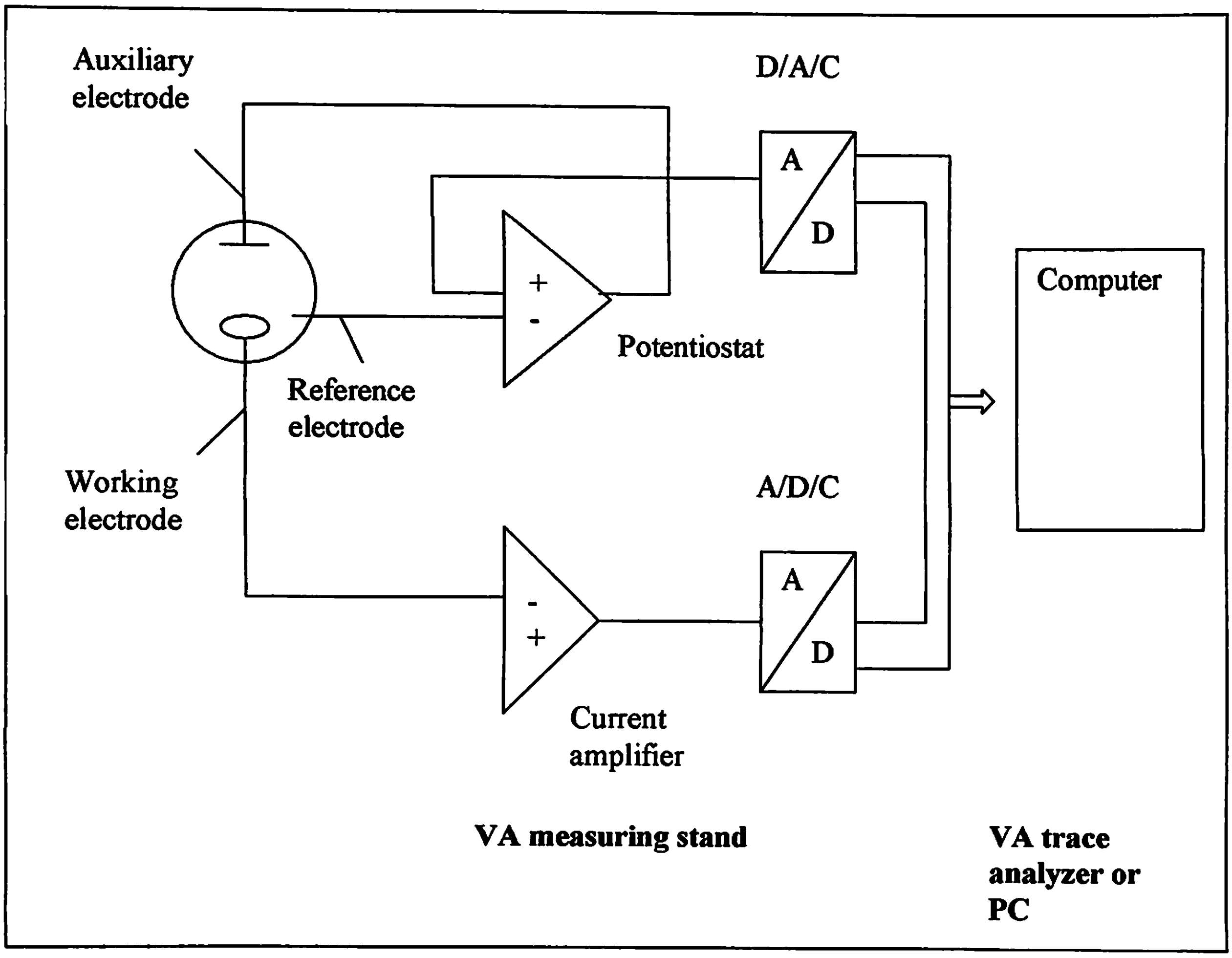

Figure 1: Block diagram of a polarograph for various voltammetric and polarographic measuring techniques.

REVIEW OF LITERATURE

A review of literature had shown the useful technique of Voltammetry in analysing metals and also organic and inorganic compounds. There are also reviews of literature on determination of tin various sample including water and drinks.

Bond (1970) reports that Anodic Stripping Voltammetry method is very sensitive and nanomolar concentrations of heavy metals can be determined after a few minutes of accumulation (Shams et al, 2003)

A case study has been done on bioavailability of tin and tin compounds. From the study, it has been concluded that the toxicity of tin in the metallic form and its inorganic compounds is low. However, organotin compounds are toxocological relevance (Rudel, 2003.

Wang (1985) and Brainina (1993) have shown that stripping methods particularly Anodic Stripping Voltammetry (ASV), are and more widely diffused as alternative to spectroscopic techniques in the determination of metals, due to capability of quantitatively evaluate concentration up to the trace level by using relatively cheap instrumenttion (Sanna et al, 2000).

Ligeai and Vittori have reported that a Cu/Nafion/Bi electrode for on-site monitoring of trace heavy metals in natural waters using anodic stripping voltammetry:

An alternative to mercury-based electrode. In their paper work, they have stated that stripping analysis has been widely recognised as a powerful tool for trace metal analysis. Its remarkable sensitivity is attributed to the combination of a preconcentration step coupled with differential measurements that generate an extremely favourable signal to noise ratio (Legeai and Vittori, 2005).

The voltammetry technique may certainly be a good alternative to spectroscopy. It does not need too expensive equipments and especially it allows to carry out a multicomponent determinations. It is certainly a valid analytical technique with good selectivity and sensitivity. Anodic Stripping Voltammetry is important in determining all the toxic heavy metals (Locatelli and Torsi, 2004).

A work has shown that stripping voltammetry can employed in direct determination of lead and copper in ethanol fuel analysis. Stripping voltammetry also can be applied for determining other metals (Munoz et al, 2004).

A comparative assessment of gastrointestinal irritant potency in man of tin (II) chloride and tin migrated from packaging has been done. The results of this work shows that in tin levels up to 267 mg/kg for beverages in canned food cause no adverse effect in healthy adults and support the tin levels of 200 mg/kg and 250 mg/kg for beverages and canned food stuffs, respectively, that are currently proposed as safe levels for adults in the general population. (Boogaard et al, 2003).

Blunden and Wallace have made a review on occurrence and effect of tin in canned food. In their paper, they discussed about background chemistry of tin, factors affecting in tin dissolutions, levels of tin food, the toxicity of tin, acute effects and chronic effects of tin to human. (Blunden and Wallace, 2003)

Voltammetry technique together with standard addition method, is certainly a valid analytical method (good selectivity and sensitivity) for simultaneously determining elements having very similar peak potentials and consequently, very strong interference problem. It is certainly suitable for metals determination since it does not need steps or particular sample treatments (Locatelli and Torsi, 2001).

A determination of trace tin food has been done using single sweep polarography. In this work, determination of tin is done to find the concentration of tin in food whether its concentration is over the limit that has been fixed by law that can cause harm to human (Qiong et al, 1997).

Stripping voltammetric method was employed for determination of tin traces in water samples. Stripping voltammetry has been recognised has a very good selectivity and sensitivity (Heppeler et al, 1995).

OBJECTIVE

1) To develop the voltammetry techniques by parameters optimization for determination of tin (II).
2) To determine stannous/tin (II) in juicy drinks
3) To study and understand the working procedure of voltammetry.