STRIPPING POTENTIOMETRY:

NOVEL METHODOLOGY AND ELECTRODE DESIGN

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by

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ABSTRACT

Wang, Yudong. **STRIPPING POTENTIOMETRY: Novel Methodology and Electrode Design**

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A novel electrode design which facilitates medium exchange in stripping potentiometry, decrease of sample volume required for each analysis, simplified analytical procedures and calibration-free performance, has been constructed. The counter and reference electrodes used in conventional three-electrode systems have been built into one unit together with a glassy carbon disk working electrode in a cylindrical arrangement.

The electrode has been used in combination with two different electrochemical cells, one of them being a disposable centrifugal tube and the other simply a drop of the sample placed on top of the invertedly positioned electrode. Typical sample volumes were 500 and 20 µl, respectively. Convection, in order to increase the diffusion controlled transport of analytes to the working electrode surface, was achieved either by rotating the centrifugal tube or by vibrating the sample drop. In the latter configuration exhaustive electrolysis was obtained after 3 to 5 minutes.

Stripping potentiometry has been used for all measurements, either with a commercial 30 kHz instrument or with a 90 kHz commercial prototype. Measurements have been made either with or without an applied constant current. Equations showing the possibility to exploit Faradays´s law subsequent to exhaustive electrolysis, and thereby eliminating the need for calibration, have been derived. This instrumental approach has been denoted coulometric stripping potentiometry.

The novel electrode design in combination with instrumental and programming developments has been used for designing new analytical procedures suitable for the determination of some environmentally hazardous heavy elements in biological and food samples. The aim of this development has been to design user-friendly analytical procedures with the ultimate aim that the user of the method should not have to be a trained chemist. Methods have been developed for the determination of lead in "unleaded" petrol, the determination of cadmium and lead in human whole blood and the determination of lead in wines. The method for the determination of lead in blood has been tested by the Centers for Disease Control, Atlanta, GA, USA as a possible instrumental candidate in the upcoming screening of US children. All methods developed have in common that the only operation needed by the operator is to mix the sample with a modifier solution and present the mixture to the instrument. The composition of the various modifiers has been optimised from a chemical point of view with respect to *e.g.* complexing ability, solvent composition, viscosity and surface tension.

KEYWORDS: Electrode design, combined electrodes, vibrating electrode, stripping potentiometry, coulometric stripping potentiometry, matrix modifying solution, internal standard, lead, cadmium, whole blood, wine, petrol.

No. of pages 35 + 6 appendices

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PART A

PART B

This thesis work is based on the following papers:

I. A Novel Batch Electrode Design for Use in Stripping Potentiometry Facilitating Medium Exchange

D. Jagner, L. Renman and Y. Wang

Electroanalysis, 4 (1992) 267.

II Stripping Potentiometry for Organolead Compounds: Application to the Determination of Total Lead in Gasoline

D. Jagner, L. Renman and Y. Wang

Anal. Chim. Acta, 267 (1992) 165.

III Simplified Stripping Potentiometry Methodology: Application to the Determination of Lead in Wine

D. Jagner, L. Renman and Y. Wang

Electroanalysis, 5 (1993) 283.

IV Determination of Lead in Microliter Amounts of Whole Blood by Stripping Potentiometry

D. Jagner, L. Renman and Y. Wang

Electroanalysis, 6 (1994) 285.

V Coloumetric Stripping Potentiometry

D. Jagner and Y. Wang

Electroanalysis, accepted for publication.

VI Determination of Cadmium in Trace Amount of Human Whole Blood with a Vibrating Electrode and Stripping Potentiometry

Y. Wang, F. Ma and D. Jagner

in manuscript

给晓莹，甜甜和爸爸妈妈

To Xiaoying, Robin, Dad and Mom

1 INTRODUCTION

In the past few decades, various stripping analysis techniques [1, 2] have proved to be powerful tools in trace analysis. Among the electrochemical analysis techniques, they are some of the few that can compete with other better known techniques, such as atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry, in trace analysis [3]. In addition to the known advantages of low cost and simplicity, these techniques also offer high sensitivity, wide linear response ranges and the possibility to achieve speciation.

In all stripping techniques, there are two steps involved. The first one is pre-concentration of the analyte on the electrode surface at a defined electrolysis potential. The second step, known as stripping, occurs when the preconcentrated analyte is released from the electrode. Different techniques differ only in how the stripping step is performed and in how the analytical signal is registered, while the pre-concentration methods are essentially identical for all.

The most wide-spread stripping analysis technique is known as anodic stripping voltammetry (ASV). Common to all voltammetric techniques is that the current through a working electrode is registered during stripping while the electrode potential is varied systematically. Though the anodic stripping voltammetry, in which the potential sweep is in the positive direction, is the most common method, there are also numerous applications of cathodic stripping voltammetry [4, 5] where the potential is varied in the negative direction during the stripping step.

Another important technique is stripping potentiometry, also known as potentiometric stripping analysis (PSA) [6, 7]. The difference between voltammetric stripping methods and stripping potentiometry is that there is no potentiostatic control of the working electrode during stripping and a potential *vs.* time curve is registered instead of a current *vs.* potential curve. The time needed for one analyte to be completely released from the electrode surface, the stripping time, is a measure of the analyte concentration.

Like the voltammetric stripping techniques, stripping potentiometry can be employed in both anodic or cathodic mode. In the anodic mode, the analyte is reduced during electrolysis and then oxidised either chemically, by oxidants present in the sample solution, or electrochemically, by a constant electric current applied through the working electrode. The latter is also known as constant-current stripping analysis (CCSA) or chrono-

potentiometric stripping analysis [8, 9]. In the cathodic mode [10], the analyte is either reduced to a soluble form or is desorbed from the electrode surface by a reducing current passed through the working electrode.

Though the stripping techniques mentioned above cover most applications of stripping analysis, there are still other alternatives. New terms such as flow-through anodic stripping coulometry appear in the literature from time to time, and these new ideas have often proved promising [11].

Stripping potentiometry, or potentiometric stripping analysis, was first suggested by Bruckenstein and Nagai [12] in 1961. The method they suggested was to monitor the stripping time after a galvanostatic electrolysis of Tl(I) and Pb(II), and use this as a measure of the analyte concentration in the sample solutions, and they named the technique chemical stripping analysis. Though the first efforts were focused mainly on the behaviour of the mercury film electrode and plating efficiency, analytical procedures for silver, lead, cadmium, bismuth and thallium were presented [12, 13, 14]. However this work did not attract much attention until first, after about ten years silence, the technique was improved by Jagner and Granéli [6, 15, 16, 17]. Since then the technique has undergone a rapid development with the introduction of CCSA [8], the development of computerised instruments [22], combination with a flow system [23] and the appearance of commercial instruments [24], and the term potentiometric stripping analysis has started to appear more frequently in the literature [1, 2, 19, 20, 21]. In addition to the great efforts given to various analytical applications of the technique, the theoretical studies [25, 26, 27] and development in the instrumentation and automation [8, 28, 29] have shown great progress in the last two decades.

As an analytical technique that involves oxidation and reduction, stripping potentiometry is used mostly for metal determinations. Though applications hitherto described do not cover all metals, they do offer one very competitive analytical technique for about 30 metals (Ag, As, Au, Ba, Bi, Cd, Co, Cs, Cu, Fe, Ga, Ge, Hg, Mn, Na, Ni, Pb, Pt, Rb, Rh, Sb, Se, Sn, Sr, Tc, Te, Ti and Zn). With the cathodic version of the technique, it is also possible to determine various nonmetals, e.g. halides, thiols and sulphides and some organic substances.

The main disadvantage of potentiometric stripping techniques, as with most other electroanalytical techniques, is that the electrode behaviour is sensitive to pre-conditioning of the working electrode surface. As pretreatment of the electrodes can have a significant

effect on the analytical signal and the reliability of the result obtained, training in correct operational procedures has often been required, since it has been difficult to develop fully automated procedures to eliminate the manual electrode operation. This is the reason that the stripping techniques and other electrochemical analytical techniques have not become very widespread in routine analysis, despite the enormous amount of research work published every year.

This thesis work is focused on applications of stripping potentiometry and is aimed mainly at developing simplified analytical methods for routine analysis in which the demands of training for operating procedure are decreased to the minimum level. Methods for the determination of lead in wine, gasoline and human blood, as well as a method for cadmium in blood, are described. The design of a novel type of combined electrode, which simplifies operating procedures, cuts down the sample amount needed for each analysis, and facilitates medium exchange is also described. The use of a new coulometric approach to stripping potentiometry, which allows calibration-free analysis to be performed is also discussed.

2 METHODOLOGY

2.1 Principles

2.1.1 Stripping potentiometry

Stripping potentiometry is comprised of two steps: the potentiostatic preconcentration and the stripping of the analyte. Usually the analytes are metal ions which are reduced to atomic form during the preconcentration electrolysis and then oxidised to ionic form during stripping. During the electrolysis the reaction can be represented by

$$M^{n+} + n\,e^- \rightarrow M(Hg) \qquad (1)$$

where M^{n+} represents analyte metal ions reduced on the electrode. Since a mercury film electrode or a mercury drop electrode is used in most cases, the metal reduced during the electrolysis forms an amalgam $M(Hg)$ film on the electrode surface. Accompanying reaction (1) there are other species, e.g. dissolved oxygen and other oxidants that are reduced during the electrolysis:

$$A_O + m\,e^- \rightarrow A_R \qquad (2)$$

where A_O and A_R are the oxidised and reduced forms of the species, respectively. When Hg(II) is used as the oxidant, the reduction of Hg(II) to Hg(0) allows *in situ* mercury plating which is convenient in practical operation.

If a hydrodynamically constant convection is applied, *e.g.* by rotating the electrode or the stirring solution, or by vibrating the electrode, a diffusion layer of a reproducible thickness is built up on the electrode surface, i.e. the reduction rate of the metal ions is constant until the concentration of the ions in the bulk of the solution has changed markedly. When a working electrode with small surface (compared with the volume of sample solution) is used, the decrease in metal ion concentration is not significant. Fick's first diffusion law states

$$-J(x,t) = D_M \frac{\partial C_M(x,t)}{\partial x} \qquad (3)$$

where J is the flux and x is the distance to the electrode surface (in the case of linear diffusion), and D_M and C_M are the diffusion coefficient and the concentration of the

metal ions respectively. From equation (3) one can get the total amount of the amalgamated metal N_M (mol) as

$$N_M = A\int_0^{t_e} -J(0,t)\,dt = A\int_0^{t_e} D_M \frac{\partial C_M(0,t)}{\partial x}\,dt = A\,D_M \int_0^{t_e} \frac{\partial C_M(0,t)}{\partial x}\,dt \quad (4)$$

where t_e is the electrolysis time and A the electrode surface area. For linear diffusion $\frac{\partial C_M(0,t)}{\partial x}$ is equal to the concentration gradient $\frac{C_M(\infty,t)-C_M(0,t)}{\delta_e}$ in which δ_e is the thickness of the diffusion layer. Then one has

$$N_M = A\,D_M \int_0^{t_e} \frac{C_M(\infty,t)-C_M(0,t)}{\delta_e}\,dt \quad (5)$$

In a diffusion controlled reaction, the surface concentration of the analyte $C_M(0,t)$ is close to zero when the overpotential is high enough. Since the bulk concentration $C_M(\infty,t)$ does not decrease much during the electrolysis one can suppose that it has the same value as its initial value C_M^0. Thus, equation (6) can be obtained:

$$N_M = A\,D_M\,C_M^0\,\delta_e^{-1}\int_0^{t_e} dt = A\,D_M\,C_M^0\,\delta_e^{-1}\,t_e \quad (6)$$

In the second step, i.e. stripping of the analyte, the potentiostatic circuit is disconnected and the potential *vs.* time curve is registered. The reaction on the electrode surface is that of the metals deposited on the electrode surface being oxidised by the oxidant Ox in the solution.

$$M(Hg) + \frac{n}{m}Ox \rightarrow M^{n+} + \frac{n}{m}Red \quad (7)$$

Supposing that reaction (7) is a diffusion controlled process and that the decrease in oxidant concentration can be neglected, one can in a way similar to that for equation (6) obtain

$$N_{Ox} = A\,D_{Ox}\,C_{Ox}^0\,\delta_s^{-1}\,\tau \quad (8)$$

where the N_{Ox} is the total amount of the oxidant transferred to the electrode surface during the stripping and τ is the transition time, i.e. the time needed for all of the reduced metals on the electrode surface to be oxidised. Here, D_{Ox} and C_{Ox}^0 are the diffusion coefficient and the bulk concentration of the oxidant, respectively, and δ_s is the thickness of the diffusion layer during the stripping.

According to reaction (7) N_{Ox} and N_M must be balanced. By combining equations (6) and (8) one obtains

$$A D_M C_M^0 \delta_e^{-1} t_e = \frac{m}{n} A D_{Ox} C_{Ox}^0 \delta_s^{-1} \tau \qquad (9)$$

and the transition time can be expressed as

$$\tau = \frac{n}{m} \frac{D_M \delta_s C_M^0}{D_{Ox} \delta_e C_{Ox}^0} t_e \qquad (10)$$

Assuming the experiment is conducted at a stable temperature so that none of the diffusion coefficients varies and that C_{Ox} is kept constant, and letting $k = \frac{n}{m} \frac{D_M}{D_{Ox} C_{Ox}^0}$ equation (10) can be written as

$$\tau = k \frac{\delta_s}{\delta_e} C_M^0 t_e \qquad (11)$$

If convection is applied constantly during both electrolysis and stripping, equation (11) can be further simplified by combining k and $\frac{\delta_s}{\delta_e}$ to k':

$$\tau = k' C_M^0 t_e \qquad (12)$$

Equation (12) describes the fundamental relationship between analyte concentration and analytical signal employed in stripping potentiometry. For equation (12) to be valid, several assumptions besides those already mentioned above must be made, one of which is that the diffusion of metal in the mercury film or mercury drop electrode is not a limiting factor, and another, that kinetic parameters do not affect the electrode reaction rates.

Equation (11) shows that the hydrodynamic conditions have a significant effect on the signal. In the past [6, 30] solution stirring was maintained during both stripping and electrolysis in order to achieve constant hydrodynamic conditions. However, in a well established modern laboratory, the external vibration can be minimised to a satisfactory level, and the introduction of computerisation in the technique makes precise time control much easier than before, so the concept of stationary stripping potentiometry has been widely accepted in recent applications [31, 32, 33]. For stripping potentiometry measurements performed in this way, δ_s is no longer constant; it increases with time after the convection is stopped, i.e. during the resting time. Since time control can be achieved in

a very precise way, a reproducible diffusion layer can still be obtained provided the resting time is kept constant.

It should be emphasised that the derivation of equation (10) is not very precise. For a more exact derivation one should start from Fick's second law of diffusion and use Laplace transformation to solve the differential equations. Several groups have reported their studies of this [25, 27, 32, 34, 35, 36]. Due to different assumptions/conditions and methods used, the results differ from each other to some degree. However, a similar or the same expression as that in equation (10) is often obtained [32, 34].

The potential during the stripping process is described by the Nernst equation

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_O}{a_R} \qquad (13)$$

where a_O and a_R are the surface activities of the oxidised and reduced forms of the metal, respectively. When the thickness of mercury film is not very large ($\leq 0.5\pi\sqrt{D_R t}$ where D_R is the diffusion coefficient of the metal in mercury film), the E *vs.* t curve can be expressed as [35]

$$E = E^0 + \frac{RT}{nF}\ln\frac{2\,d}{\sqrt{D_R\pi}} + \frac{RT}{nF}\ln\frac{\sqrt{t}}{\tau - t} = E' + \frac{RT}{nF}\ln\frac{\sqrt{t}}{\tau - t} \qquad (14)$$

where d is the thickness of the mercury film. A typical E *vs.* t stripping potentiometry curve derived from equation (14) is shown in Figure 1.

The measurement of a stepwise signal is not always an easy process, especially when a small signal is located in an area where the background is high. To determine exactly where the analyte stripping signal starts and ends can be very difficult in some circumstances. To solve this problem a differentiation of the E *vs.* t curve can be used, that is, instead of the E *vs.* t curve, a differentiated E *vs.* $\frac{dt}{dE}$ curve is registered. The introduction of the "multichannel approach" [22, 38, 39] to the data acquisition in computerised stripping potentiometry has provided this operation with enough time and potential resolution.

From equation (14) one obtains

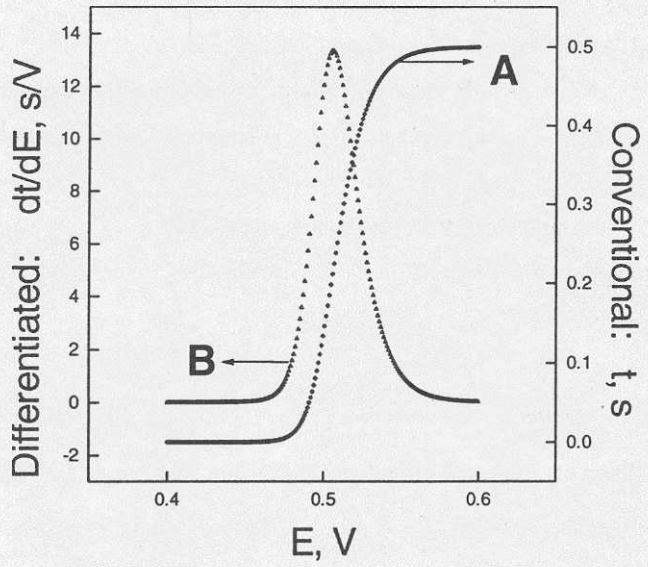


Figure 1 Calculated Stripping Potentiometry Curves

(A) Conventional; (B) Differentiated

$\tau = 0.5$ s, $E' = 0.5$ V, $n = 2$

$$t = \tau + \frac{1 - \sqrt{4\,\tau \exp\left[\frac{2nF}{RT}(E - E')\right] + 1}}{2 \exp\left[\frac{2nF}{RT}(E - E')\right]} \qquad (15)$$

and differentiation of equation (15) yields

$$\frac{dt}{dE} = \frac{nF}{RT} \frac{1 + 2\,\tau \exp\left[\frac{2nF}{RT}(E - E')\right] - \sqrt{1 + 4\,\tau \exp\left[\frac{2nF}{RT}(E - E')\right]}}{\exp\left[\frac{2nF}{RT}(E - E')\right] \sqrt{1 + 4\,\tau \exp\left[\frac{2nF}{RT}(E - E')\right]}} \qquad (16)$$

which gives a full expression of the differentiated stripping potentiometry curves. A calculated E *vs.* $\frac{dt}{dE}$ curve derived from equation (16) is shown in Figure 1, where the analyte stripping signal appears in a peak form.

By setting $d(\frac{dt}{dE}) / dE = 0$, one obtains

$$\exp\left[\frac{2nF}{RT}(E - E')\right] = \frac{1 + \sqrt{2}}{2\tau} \qquad (17)$$

which gives an expression for the peak potential, i.e. the potential at the maximum point of the E *vs.* $\frac{dt}{dE}$ curve, as

$$E_p = E' + \frac{RT}{2nF}\left(\ln\frac{1 + \sqrt{2}}{2} - \ln(t)\right) = E' + 0.0941\frac{RT}{nF} - \frac{RT}{2nF}\ln(t)$$

(18)

The maximum value of $\frac{dt}{dE}$, $(\frac{dt}{dE})_{max}$ or the peak height of the signal can now be obtained

$$(\frac{dt}{dE})_{max} = \frac{nF}{RT}\,\frac{2}{3 + 2\sqrt{2}}\,\tau = 0.343\,\frac{nF}{RT}\,\tau \qquad (19)$$

The half-width of the peak, often used for characterisation of an analytical signal, can be obtained by replacing the $\frac{dt}{dE}$ in equation (16) with $0.5\,(\frac{dt}{dE})_{max}$:

$$0.5\,\frac{nF}{RT}\,\frac{2}{3 + 2\sqrt{2}}\,\tau$$

$$= \frac{nF}{RT}\,\frac{1 + 2\tau\exp\left[\frac{2nF}{RT}(E_{1/2} - E')\right] - \sqrt{1 + 4\tau\exp\left[\frac{2nF}{RT}(E_{1/2} - E')\right]}}{\exp\left[\frac{2nF}{RT}(E_{1/2} - E')\right]\sqrt{1 + 4\tau\exp\left[\frac{2nF}{RT}(E_{1/2} - E')\right]}}$$

(20)

where the $E_{1/2}$ are the potential values when $\frac{dt}{dE} = 0.5\,(\frac{dt}{dE})_{max}$. Solving equation (20) yields

$$\exp\left[\frac{2nF}{RT}(E_{1/2} - E')\right]\tau = 11.032 \pm 10.899 \qquad (21)$$

which gives $E^{I}_{1/2} = E' + \frac{RT}{2nF} \ln(21.931) - \frac{RT}{2nF} \ln(\tau)$ and

$E^{II}_{1/2} = E' + \frac{RT}{2nF} \ln(0.133) - \frac{RT}{2nF} \ln(\tau)$, and the peak half-width is obtained as

$$E^{I}_{1/2} - E^{II}_{1/2} = 2.553 \frac{RT}{nF} = \frac{65.59}{n} \text{ mV} \qquad (22)$$

at 25 °C. Equations (18) and (19) are the same as in the literature [27, 40], while equation (22) has a difference of 0.5 mV from that reported in [27].

2.1.2 Constant current stripping potentiometry

There are two main reasons for using current in the stripping step. One is to drive the potential to the negative direction during cathodic stripping or adsorptive stripping, for which a stable reducing reagent is very difficult to find. The other is to replace, or to stabilise the chemical oxidation during anodic stripping. In the first case, the stripping time depends on the current, i_r, and other parameters as shown in equation (23):

$$\tau = \frac{D_M t_e A}{\delta_e \frac{i_r}{nF}} C_M = \frac{nF D_M t_e A}{\delta_e i_r} C_M \qquad (23)$$

Here the signal depends also on the electrode area which makes it different from anodic stripping potentiometry where only chemical oxidation occurs. In the second case, the stripping time is determined by both the current magnitude i_o and the oxidant concentration:

$$\tau = \frac{D_M t_e A C^0_M}{\frac{i_o \delta_e}{nF} + \frac{m}{n} \frac{\delta_e}{\delta_s} A D_{Ox} C^0_{Ox}} = \frac{D_M t_e C^0_M}{\frac{i_o \delta_e}{nFA} + \frac{m}{n} \frac{\delta_e}{\delta_s} D_{Ox} C^0_{Ox}} \qquad (24)$$

In this case, although the sensitivity decreases, the reproducibility can often be improved. This is especially useful in the analysis of samples of varying compositions, since the effect of variations of oxidant concentration can be diminished. In most of the papers presented in this thesis, this method is employed.

Equation (24) shows that a small negative current can increase the stripping signal, provided that high stability in the oxidant concentrations can be maintained. Xie and

Hubber [41] have shown that the sensitivity of the selected method can be increased by a factor of 15 in this way.

2.1.3 Coulometric stripping potentiometry

A new technique presented in this work is coulometric stripping potentiometry which makes it possible to obtain the analyte concentration directly from the stripping time without any calibration. The principle is based on exhaustive electrolysis in the preconcentration step, and a current-driven stripping step. Given a 100% electrolysis efficiency together with a known stripping current, one can easily calculate the initial analyte concentration by using Faraday's law.

Equation (24) shows that the stripping time τ depends on the total amount of metal ions reduced during the stripping, N_M, the stripping current and the effect of the oxidants:

$$\tau = \frac{N_M}{\frac{i_o}{nF} + \frac{m}{n}\frac{1}{\delta_s} A D_{Ox} C_{Ox}^0} \qquad (25)$$

Assuming that the sample solution volume does not change during the experiment, $N_M = V(C_M^0 - C_M^t)$ where C_M^0 is the initial bulk concentration of analyte and C_M^t is the bulk concentration of analyte at time t. Due to the consumption during electrolysis, the bulk concentration decreases with time according to [42]

$$C_M^t = C_M^0 \exp(-k t_e) \qquad (26)$$

Accordingly, $N_M = V C_M^0 [1 - \exp(-k t_e)]$, combined with equation (25) gives

$$\tau = \frac{V C_M^0 [1 - \exp(-k t_e)]}{\frac{i_o}{nF} + \frac{m}{n}\frac{1}{\delta_s} A D_{Ox} C_{Ox}^0} \qquad (27)$$

When t_e is long enough so that $[1 - \exp(-k t_e)]$ is close to 1, then equation (27) can be rewritten as

$$\tau = \frac{n F V C_M^0}{i_o + m F A D_{Ox} C_{Ox}^0 \delta_s^{-1}} \qquad (28)$$

In most cases, the concentration of oxidants and the thickness of the diffusion layer can be treated as constant, so that

$$\tau = \frac{n F V C_M^0}{i_o + i_c} \qquad (29)$$

where $i_c = m F A D_{Ox} C_{Ox}^0 \delta_s^{-1}$, denoted as chemical current below. By varying i_o and measuring τ, the value of i_c can be obtained. The oxidants added to the solution, such as Hg(II), are normally all reduced during the exhaustive electrolysis, which means the most of i_c originates from dissolved oxygen. When both i_o and i_c are known, the analyte concentration can be easily calculated by

$$C_M^0 = \frac{\tau (i_o + i_c)}{n F V} \qquad (30)$$

Besides the applications on analysis, the coulometric stripping potentiometry also offers a chance to determine the number of electrons transferred during the stripping oxidation by one single experiments. From equation (30) one can get $n = \frac{\tau (i_o + i_c)}{F V C_M^0}$. If C_M^0 and the current values are known the value of n can be calculated directly.

The key problem in coulometric stripping potentiometry is how to achieve the exhaustive electrolysis within a reasonable amount of time. By using a combined electrode with only a small volume of solution on the electrode surface, an exhaustive electrolysis within 5 min can be achieved, as is demonstrated in Paper V. Since no calibration is needed, the analytical procedure is simplified remarkably. When i_c is negligible, as e.g. in the analysis of Hg, As or Ag on gold electrodes, where the dissolved oxygen does not affect the stripping step, the procedure would be even simpler.

2.2 Cell and Electrode Design

During the years of development in electrochemical analysis, the design of electrochemical cells and electrodes has been vastly improved. The three electrode system has been completely accepted, while the old two electrode construction widely used in polarography is now seldom mentioned. The outmoded dropping mercury electrode has been replaced by the hanging mercury drop electrode and the mercury film electrode. The recent fast-growing demand for trace analysis of biological samples has made it difficult to cope with the often very small sample sizes involved. Also, the wish to minimise the use of

mercury in electrochemical analysis requires that the total volume of solution should be taken in account in the design of the electrochemical cell. Although there has been great progress in microelectrode development in the past decade, and much investment has been made in the development of small volume cells, it is still difficult to find a practical, simple and reliable design for electrochemical cells in the microliter range due to the preconception that three separated electrodes must be connected in a cell [44, 45, 46].

Another aspect which is specially important for stripping potentiometry is the facilitation of medium exchange between electrolysis and stripping to increase the sensitivity and to eliminate the effect of dissolved oxygen [15]. From equations (10) and (24) it can be seen that a lower diffusion rate of the oxidants and a thicker diffusion layer during stripping increases the signal. The lower diffusion rate can be obtained by exchanging the sample solution for a special stripping medium before the strip is initiated. This stripping medium can be a concentrated salt solution, such as 5 M $CaCl_2$, in which the solubility of oxygen is very low and the diffusion rate of oxidants is decreased dramatically due to the high viscosity. When a flow system is used, medium exchange can be easily accomplished [15, 47], while it is much more difficult in a batch mode since the electrode potential must be maintained until the strip is initiated. With three separated electrodes the medium exchange would be almost impossible.

The results presented in this thesis demonstrate the design of novel cells and combined electrodes, which allow the reduction of sample sizes and facilitate the medium exchange in batch mode.

2.2.1 The hanging drop electrode (HDE)

The original purpose of this work is to find a way to facilitate the medium exchange operation. The solution presented is to combine the conventional three electrodes into one by binding them together, which, due to the surface tension of the sample solution, allows a single sample drop to adhere to the electrode. In contrast to the hanging mercury drop electrode (HMDE), the hanging drop electrode (HDE) here denotes a drop of same solution that hangs under the electrode surface. An early design of a HDE is shown in Figure 2.

This combined electrode was manufactured by drilling a hole in the Teflon body of a normal glassy carbon disk electrode so that a piece of rubber tubing could be inserted into the hole. The tube, with one end connected to a saturated calomel electrode (SCE) while the other end contains a porous ceramic plug, is filled with hydrochloric acid and works as a salt bridge. A piece of platinum wire is inserted into the SCE and works as the counter electrode. During the medium exchange operation, a drop of solution hangs under the glassy carbon electrode and the plug, thus allowing potentiostatic control to be maintained when

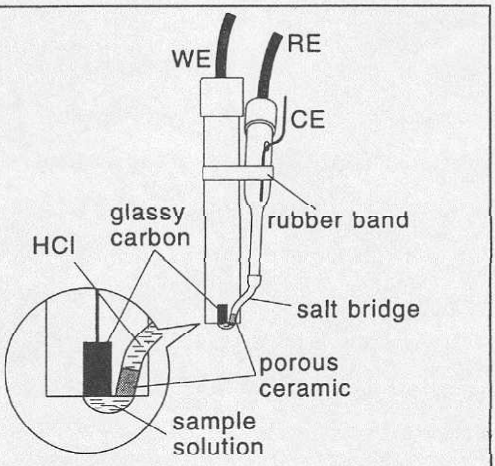


Figure 2 Hanging Drop Electrode

the electrode is withdrawn from the sample solution.

Even if this initial design may lack in refinement, it does combine the three electrodes into one body, thereby making it possible to perform medium exchange with the potentiostatic control maintained. The combined electrodes developed subsequently were a result of improving this initial prototype.

2.2.2 The combined three-in-one electrode

The initial HDE design lead to the idea of making a combined three-in-one electrode based on a novel design, in which the reference and the counter electrodes were built into a working electrode with an internal electrolyte solution. In this way, the electrolyte solution is in direct contact with the reference and counter electrodes while, via a liquid junction

beside or around the active working electrode, there is contact between the internal solution and the sample solution. Figure 3 shows the design of such an electrode.

A Teflon body holds the glassy carbon working electrode (WE) and the liquid junction together. The liquid junction can be fixed close to the working electrode in either of two ways. In the first, a porous ceramic plug is put into a hole in close proximity to the working electrode (Figure 3A), while in the other, a porous ceramic tube is plugged into a hole in the Teflon rod and the working electrode with its insulation tube is led through the ceramic tube (Figure 3B). To avoid gas formation on the counter electrode (CE) during electrolysis, a silver rod is used as the CE, and 0.5 M hydrochloric acid is normally used as the internal electrolyte. The reference electrode (RE) is also made of a piece of silver rod. A

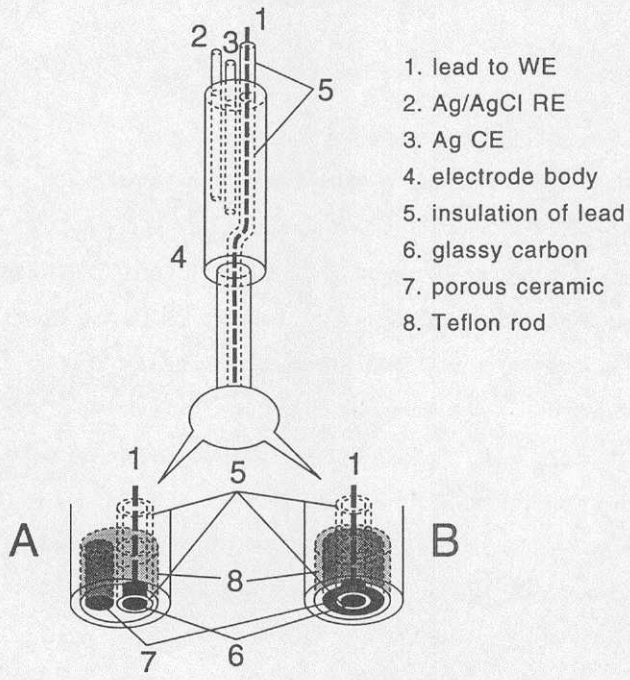


Figure 3 The Three-in-One Electrode

A: The liquid junction in a rod form. B: The liquid junction in a tube form

drop of solution hangs under the electrode tip between the working electrode and the liquid junction in the first type, or hangs under the whole porous ceramic plug in the second type.

In the first prototype three-in-one electrode, a polyethyl ethylketone (PEEK) tube was used for the insulation of the electric lead to the working electrode; and the electrode body was manufactured from Plexiglass and quartz. This electrode construction was adopted later by Radiometer, Copenhagen, and has been put into production. In their prototype of the electrode, the porous ceramic liquid junction has been replaced by conductive glass gel in a tube form; the electrode tip and whole body are also made of glass. This material extends the application area of the electrode and makes it more convenient to clean. The use of glass also makes the solution drop stay more reliably in place. The outer diameter of the electrode tip is about 7 mm and the working electrode is a glassy carbon disk with a diameter of 3 mm. Although the resistance of the liquid junction is higher than that of a porous ceramic plug, this can be offset by using a higher acid concentration of the internal solution.

The three-in-one electrode has proved to be very suitable in applications where medium exchange is employed [Paper I, 48].

2.2.3 The three-in-one electrode and a rotating sample tube

When a three-in-one electrode is being used, the electrochemical cell can be made very small, a sample tube with an inner diameter of about 8 mm is enough. The only remaining problem is the convection of the solution. Since it is difficult to rotate the combined electrode with its three connectors, and external stirring would mean that the amount of sample solution needed would increase dramatically, it is the sample solution that must be rotated. This can be accomplished as shown in Figure 4.

The electrode and a DC engine are mounted on an aluminium rail so that they can slide to the proper position and be fixed there. The whole assembly is tilted to facilitate the removal of any gas bubbles formed during the electrolysis. A smooth movement of the solution, hydrodynamically similar to when a rotating disk electrode is employed, can be obtained by fixing the electrode and the sample tube on the same axis. Though the hydrodynamic conditions are similar, it is not possible to formulate a full expression similar to the Levich equation for the rotating electrode [49] because the turbulence between the electrode and the inner wall of the tube must be taken into account.

By employing a three-in-one electrode together with a rotating tube, the amount of sample solution needed for each measurement can be decreased to 0.5 ml, while the sensitivity can be maintained at the same level as in a conventional batch mode measurement. The combined electrode with the rotating sample holder were employed in

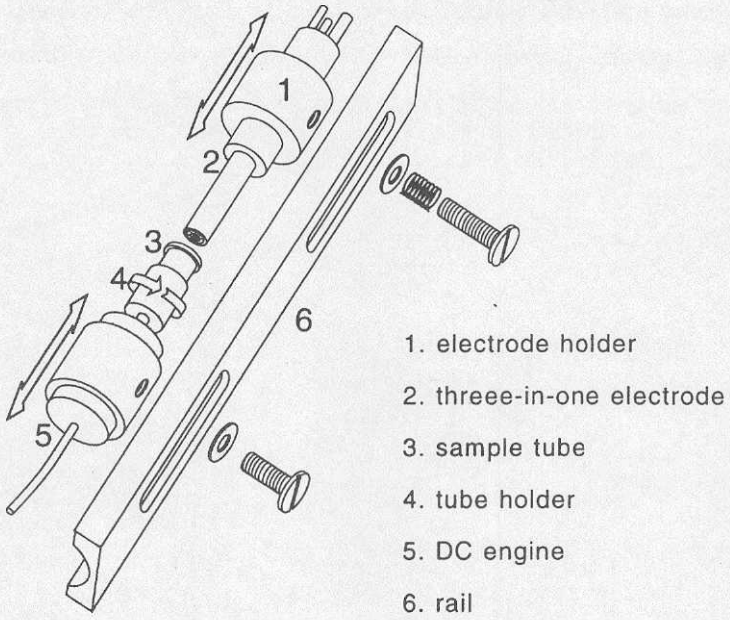


Figure 4 Three-in-One Electrode with Rotating Sample Tube

the applications described in Papers III, IV and V.

2.2.4 The three-in-one electrode and vibrated sample drops

Instead of having a hanging sample solution drop under the three-in-one electrode, it is also possible to place a single drop of a sample solution on top of the electrode when it is mounted with the glassy carbon disk facing upwards. In this way, electrolysis can be performed using only one drop of sample solution with a volume in the 10 to 20 µl range. This is a significant improvement in comparison with the rotating sample tube which requires at least 500 µl of solution for a reliable operation. For the determination of Pb in blood [cf. Paper IV], the amount of whole blood required for each measurement can be decreased from 60 µl to, in principle, 1.5 µl. In practice it is, however, difficult to handle a sample solution of this volume; the pipetting and mixing are very difficult to perform accurately, which makes them the limiting factors in decreasing the sample volume.

Although a satisfactory analysis can be made in a totally quiescent solution [31], convection of the solution during electrolysis is still desirable to obtain greater efficiency and, thereby, higher sensitivity. Since it is difficult to stir or rotate the solution directly

when the volume is so small, other alternatives had to be considered. Therefore, a vibrator was mounted onto the electrode holder; cf. Figure 5. The electrode, together with the solution drop sitting on it, is vibrated during electrolysis, which raises the electrolysing

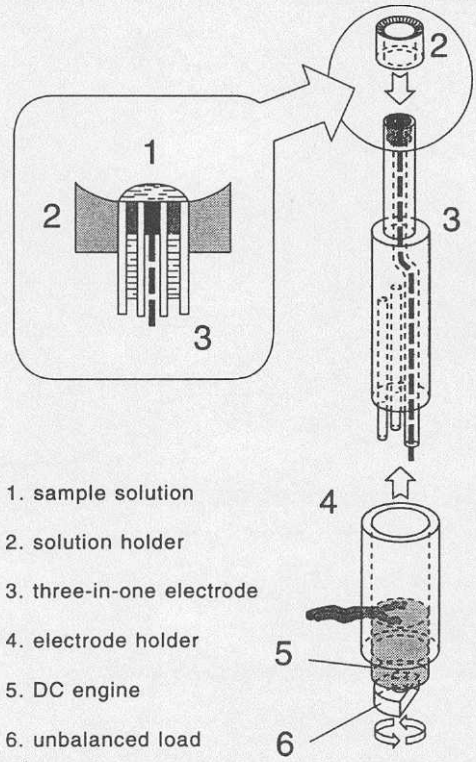


Figure 5 A Three-in-One Electrode with a Vibrated Sample Drop

efficiency by a factor of 3 to 5 in comparison with quiescent conditions. This improvement is similar to that offered by the rotating sample tube approach.

Due to the large electrode area to sample solution volume ratio (7.1 mm^2 to 15 mm^3), the analyte concentration is not constant during the electrolysis, in contrast to most other electrode/cell designs. The preconcentration of analyte on the electrode surface causes a decrease of the analyte concentration in the solution, as is shown by equation (26). The constant k is proportional to $\frac{D_M A}{\delta V}$ where A and V are the electrode area and solution volume, respectively, the D_M is diffusion coefficient for the analyte, and δ is the

thickness of the diffusion layer. From the experimental data in Paper V, the k values can be calculated at about 0.02 s^{-1} (0.022 s^{-1} for Pb(II) and 0.018 s^{-1} for Bi(III)) which means that $C_M^{t_e}$ will be lower than 1% of C_M^0 after about 4 minutes. This makes it practically possible to perform an exhaustive electrolysis and thus to employ the coulometric stripping potentiometry approach (See Section 2.1.2).

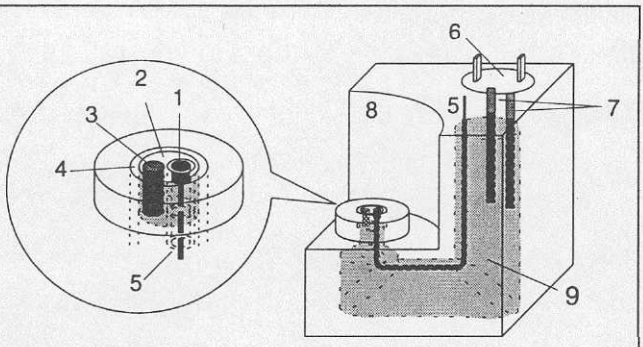
The vibrator employed in the design shown in Figure 5 is an engine with an unbalanced load. When the engine rotates at high speed, it makes the whole assembly move in an oval track. A sample holder made of Teflon is put on the electrode top, to avoid the possible splashing of the sample solution.

Possible practical drawbacks to this design are that the diffusion of sample components into the porous glass plug could lead to a high carry-over effect and also, completely filling the electrode with electrolyte solution is sometimes difficult, as air bubbles can squeeze into the electrode or be released from the solution itself by temperature changes, which can block the liquid junction.

2.2.5 The vibrating electrode

Inspired by the progress made in employing the three-in-one electrode and a vibrated solution drop, a new design in which the vibrator is built into the electrode was achieved (see Figure 6.)

The electrode tip is constructed in the same way as the combined electrode shown in Figure 4A. A glassy carbon rod and a porous ceramic plug are cast into a polystyrene body with a glass tube casing. A coated silver wire, covered by a shrinkable PVC tube as extra protection, is connected to the glassy carbon as an electric lead which is flexible and can be bent to any form without breaking. The electrode is built in a cubic form so that it can be placed on a working surface with the glassy carbon working electrode facing up. A drop of sample solution is put on the area ringed by the glass tube and the hydrophilicity of the glass will help in holding the drop in place. The total volume of the electrode assembly can be decreased since electrode is more compact and no special electrode holder or stand is needed. Together with the single drop concept, this makes the electrode convenient for field analysis with a portable instrument. The vibrator, based on the same idea as the one used with the three-in-one electrode, is not visible from the outside. The container of internal electrolyte solution is machined in a U shape with different arm lengths, with the electrode



1. glassy carbon
2. polystyrene body
3. liquid junction
4. glass tube
5. lead to WE and its insulation
6. vibrator
7. RE and CE
8. electrode body
9. internal electrolyte solution

Figure 6 The Vibrating Electrode

located in the short arm, so that the solution level in the other arm always is higher than the electrode surface. This provides an upward pressure under the liquid junction, which prevents analytes to diffuse down through the porous plug. It also prevents any gas bubbles formed on the counter electrode from moving to the electrode side and, if there is a bubble trapped under the liquid junction, it is easily moved to the other side just by turning the electrode body over.

2.3 Matrix Modifying and the Use of an Internal Standard

2.3.1 Matrix modifying

In almost all analytical techniques the digestion of samples is a time-consuming yet very critical and essential step in the whole analysis procedure. Since most techniques rely on the sample being in a liquid form, it is impossible to omit this step when solid samples are going to be analysed. However, many efforts have been made to shorten or abolish digestion in analysis of liquid sample, in order to save time and resources.

For most electrochemical analysis techniques, analysts would like to have their

analyte in a plain ionic form in a solution with a suitable pH and a stable supporting electrolyte concentration. To perform a direct analysis without digestion, a medium which can achieve all of these is required. An early attempt to achieve this for the determination of lead in whole blood was the MetExchange™ "M" reagent [50], consisting of 1.07% chromium chloride hexahydrate, 1.43% calcium acetate monohydrate and 28 ppm mercury ions. The function of the different metal ions in this reagent is to replace the lead ions in any existing complexes. The blood sample is mixed directly with the reagent 5 seconds before the analysis and an anodic stripping voltammetry measurement is then performed.

For the lead in blood and lead in wine determinations described in Papers III and IV, a matrix modifying solution which consists of 1 to 4 ppm Bi(III), 300 to 500 ppm Hg, 0.5 M to 2 M HCl, 50 mM Ca(II), 200 ppm Al(III) and Mn(II), and 10%(v/v) Triton X-100 was used. The Hg(II), Al(III), Mn(II) and Ca(II) play the same role as in the MetExchange™ "M" reagent, while the hydrochloric acid protonates potential complexing ligands in the samples, thereby releasing the lead ions and allowing chloride ions to form chlorolead(II)-chloro complexes. The high concentration of Triton X-100 helps to diminish any effects of variation in the organic compound contents and the variation of viscosity in different samples. For the same purpose, the matrix modifying solution for lead in wine analysis also contains 25% ethanol to compensate for the variation of the ethanol concentration in different samples. The mercury ions also work as the reagent for mercury plating of the working electrode.

2.3.2 The use of an internal standard

The Bi(III) ions in the matrix modifying solutions described above serve the purpose of being an internal standard. As the sensitivity of an electrode can vary with time and circumstances, a frequent calibration of the electrode, or the use of standard addition evaluations, is often required. Both of these approaches require extra work in addition to the sample analyses, which makes the whole process tedious and complicated. Employing internal standard correction can, in many cases, almost completely compensate for the variation in electrode sensitivity.

When using internal standard correction, a selected electroactive metal ion is added to the sample solution and its analytical signal is measured together with that of the analyte. Since the internal standard concentration is kept constant, the ratio between the signals of the analyte and the internal standard (called the normalised signal) will correspond to the

concentration of analyte. The internal standard correction can also deal with other factors, such as the irreproducibility in time control, convection control and other experimental parameters. Figure 7 shows the effect of internal standard correction as the stirring rate and electrolysis time vary in determination of lead in wine.

The reasons for choosing Bi(III) as an internal standard are that its signal does not

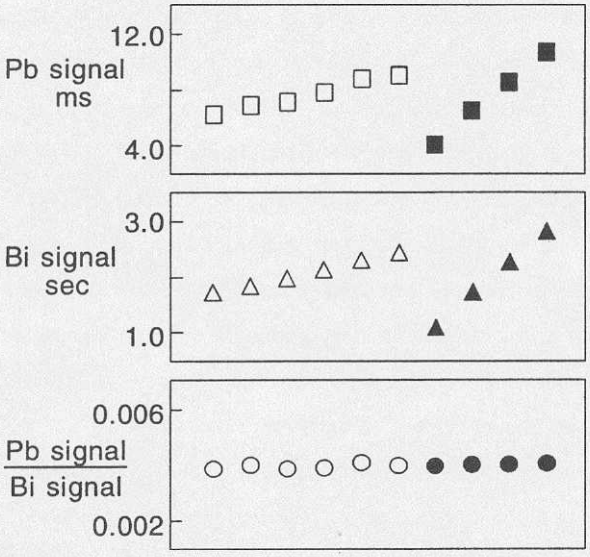


Figure 7 The Effect of Internal Standard Correction

Aqueous standard contains 150 µg/l Pb(II) after dilution 1:4 in the matrix modifying solution containing bismuth as internal standard. In the five first measurements, the rotation rate during potentiostatic deposition was varied between 750 and 2,500 rpm in six approximately equal steps at a deposition time of 160 sec. In the last four measurements, the total deposition time was varied between 60 and 210 sec at a constant rotation rate equal to 2,000 rpm.

overlap the lead signal and that its normal concentration in wine and blood samples is negligible. In addition it has a sharp stripping peak (a three-electron transfer reaction) and very high solubility in mercury. To decrease the random variations in the Bi(III) signal itself, the concentration of Bi(III) is kept at the ppm level. In a fully automatic analytical system or when otherwise necessary, the internal standard signal can also be used for self diagnosis.

2.4 Multiple Scanning

Normally, only one strip measurement is performed after each electrolysis, as this is satisfactory in most cases. However, saturation of analyte on the electrode surface or in the mercury film can occur during the electrolysis, which would limit the linear range in a given case. It is also possible that in some cases an extremely high sensitivity is needed, although the sensitivity of stripping potentiometry is seldom a problem in routine analysis applications. Another possibility is that a large oxidising current is required to minimise the influence from variations in the oxidant concentrations in the samples, so that the sensitivity has to be raised to compensate for the effect of the current. In all of these cases multiple scanning measurements can be a useful technique. Multiple scanning [51] can be performed by either of two different procedures.

The first alternative is that several short electrolyses, each one followed by a stripping measurement, are employed instead a single, long electrolysis and a single strip measurement. The stripping curves obtained are overlaid after which they can be treated as a single stripping curve to establish the stripping time. Since the surface concentration of the analyte on the electrode or the analyte concentration in the mercury film never reach a high level the risk of saturation is much smaller than during a long electrolysis. This is especially useful in adsorptive stripping potentiometry applications [51].

The second alternative is to carry out a single, long-time electrolysis and then to perform several short electrolysis and stripping cycles. In this case, the electrolysis potential is reapplied immediately after the first strip measurement, as soon as the potential reaches a predefined potential. Since the solution remains quiescent after the resting time, only diffusion removes the reoxidised metal ions from the vicinity of the electrode surface, and by rapidly reapplying the electrolysis potential most of the reoxidised metal ions can be re-reduced in a relatively short time (a few seconds). When this procedure is exploited, the signal is normally quite small (otherwise it would not be necessary to use multiple scanning) which means that if the measurement potential range is selected correctly, the total time for one strip (including the background) will be limited to 100 ms or shorter. Hence, most of the metal ions oxidised at the electrode surface will be reduced again during a short electrolysis and will contribute to the next strip measurement. With a disk electrode,

the highest efficiency that can be obtained in re-reducing the oxidised metal ions in this way is 85 to 90 %. This means that with the same total electrolysis time, 5 stripping cycles would give a signal about 4 times higher than a single electrolysis and strip measurement.

In both approaches, overlaying several stripping curves also results in higher stripping curve backgrounds, which can be compensated for either by a calculated baseline-fit correction or by experimental background subtraction [8, 43]. In the latter case, a very short electrolysis followed by a strip measurement yields a background curve which then can be digitally multiplied by a certain number, chosen for fitting best to the overlaid sample stripping curves.

The multiple scanning techniques should only be used when necessary, as they do introduce factors which can affect the precision and reproducibility of the signal, and it can be more difficult to use internal standard correction.

2.5 Instrumentation

In all of the work presented in this thesis, the Radiometer Potentiometric Stripping Unit PSU20 has been employed. Connected to an IBM compatible PC and operated under the control of the TAP2 Trace Talk Method Builder and Commander software package (Radiometer), this instrument can perform most of the stripping potentiometric measurement techniques described above. Complete analytical procedures, including the potential and time control, application of stripping current in different directions, performing multiple scanning and result evaluation such as peak localisation and integration, digital curve filtration and baseline-fit correction, sample concentration evaluation with either standard calibration or standard addition, also with internal standard correction, can all be achieved. The total weight of the stripping unit is about 7 kg and its size is 220×160×470 mm. After a simple home-made modification of the outer case the whole assembly of the combined three-in-one electrode with its rotating tube could be mounted on the instrument. Together with a portable PC this comprises a complete analytical instrument which can be carried by a single person to any place where analyses are to be performed.

3 APPLICATIONS

In recent times, lead pollution has received much attention and numerous methods have been suggested for the determination of lead in different kinds of environmental samples. In this thesis, the lead determination methods used for different samples are suggested in order to provide examples of the ways that recent progress in cell and electrode design can be used in practical analysis. Also, the objective is to present the results of efforts to simplify routine analysis procedures and to make the technique less dependent on the skill of the operator. When prepared standard solutions are available, mixing of the sample solution or standard solution with a matrix modifying solution is almost the only step that an operator needs to perform. Though the handling of the glassy carbon electrode is always tricky, complicated and requires much training before it is mastered, we have found that simply wiping the electrode with a piece of tissue before and after each measurement is satisfactory most of the time. If the electrode is stored in a proper way when not in use, polishing and other treatment are seldom necessary. This is especially true when internal standard correction is employed. The use of disposable sample tubes also contributes to simplification.

3.1 Determination of Total Lead in Gasoline (Paper II)

The problem of lead pollution has caused great concern in the past ten years [52] and one of the major sources of this pollution is the lead-containing anti-knock additives used in gasoline. Even though the introduction of "lead-free" gasoline has reduced the amount of lead released to the environment, trace amounts of organolead are still often found in "lead-free" gasoline. Such traces, probably due to rests of organolead compounds in production plants and storage containers, are almost unavoidable. Consequently, limits for maximum permissible lead content in "lead-free" gasoline has been set and various analytical methods for determination of total lead in "lead-free" gasoline have been suggested [53, 54, 55, 56]. The most commonly used method is atomic absorption spectrometry (AAS) [53, 54] in which the gasoline sample is first treated with iodine or bromine at an elevated temperature to transfer organolead to inorganic form, after which a flame AAS measurement is

performed. Electrochemical methods have been suggested as well [55, 56]; even with these, sample pre-treatment with iodine or iodine monochloride is necessary.

As demonstrated in Paper II, the common organolead additives, tetramethyllead (TML) and tetraethyllead (TEL), could be directly reduced to lead(0) and be deposited on a mercury film electrode after mixing with a matrix modifying solution at a ratio of 1 to 59. The matrix modifying solution consisted of 1500 ppm Hg(II), 0.5 M nitric acid and 1% (v/v) Triton X-100 in 90% ethanol, and the electrolysis potential was -1.2 V *vs.* SCE. Every ten seconds the potential was shifted to -1.5 V for 1 second in order to desorb any organic compounds from the gasoline that could have been adsorbed on the electrode. An oxidative stripping current of 30 μA was applied and the upper limit of stripping potential range was -0.3 V *vs.* SCE. To increase the sensitivity and to avoid saturation of the mercury film by lead, a multiple scanning procedure was employed. The linear range for the analysis was at about 0.1 to 30 ppm of total lead after a total analysis time of 5 minutes, including the time for sample preparation. At present, the maximum lead concentration allowed in "lead-free" gasoline is about 5 ppm.

The reason for using a high mercury concentration in the matrix modifying solution was to compensate for the poor mercury plating efficiency in the organic solvent. To minimise the mercury consumption, a special electrochemical cell design was employed. A glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode were bunched together; the three electrodes were then squeezed into a polyethylene tube containing the 0.6 ml of mixed sample solution, thus resulting in the sample tube hanging under the electrodes. Since there was no way to use stirring in this design, the sensitivity was limited, which was the reason why multiple scanning was applied. This problem can probably be solved by using the combined three-in-one electrode together with the rotating tube method. However at the time when this work was finished we had not yet managed to construct a combined electrode which was resistant to the organic solvent.

It was found that the TML signal was about 9% higher than the TEL and 5% higher than the aqueous lead standard in this medium. Since the organolead compounds added to gasoline is either TML or TEL, or a mixture of them, it was reasonable to use a mixed standard solution consisting of 50% of each in the calibration solution, which means that the maximum systematic error that can result is about 4.3 %.

3.2 Determination of Lead in Wine (Paper III)

For the determination of lead in wine, the method was designed in such a way that the task of the operator was minimised to mixing a wine sample with a matrix modifying solution in certain ratio before presenting the sample to the instrument. The composition of the matrix modifying solution employed was 2 M HCl and 40 mM $CaCl_2$ with 25% ethanol, 4 ppm Bi(III), 400 ppm Hg, 150 ppm Al(III), 150 ppm Mn(II) and 10% v/v Triton X-100. A stripping current of 20 μA was used and the total time was at about 3 min for each analysis. At the beginning of each measurement a cleaning potential of -2.5 V *vs.* Ag/AgCl was applied for one second, in order to desorb any organic substances adsorbed on the electrode surface. The cleaning potential was thereafter applied for 1 in every 10 seconds of electrolysis. The combined three-in-one electrode with a rotating sample tube was employed in this work.

In a sample prepared with the matrix modifying solution, the analytical sensitivity was the same for both lead in wine samples and aqueous lead standards. Therefore, all calibration could be accomplished with an aqueous lead standard. A parallel analysis with isotope dilution ICP-MS showed a good correlation between the two methods, with a correlation coefficient of 0.991 for 32 samples in the 18 to 151 μg/ml concentration range. As discussed above, bismuth was used as internal standard. The proposed method has a detection limit of 3 ppb, while typical threshold limit values for lead in wine are 100 to 200 ppb.

For the past two years this method has been used in student laboratory exercises at the University of Göteborg. The students are using Paper III as a guide line for setting up their own analysis method to determine the lead contents in different wine samples.

3.3 Determination of Lead and Cadmium in Whole Blood (Paper IV and VI)

In 1990, the USA Centres for Disease Control made a public announcement requesting a simple, reliable method for the determination of lead in whole blood, with the ultimate objective of performing a screening of the entire child population in USA [64]. The lead concentration in blood is generally considered the best measure of a persons exposure to lead. Though this is not the case for cadmium, the blood cadmium level is still

an important indicator for cadmium poisoning in the human body. To determine lead in blood, the classical technique is AAS [57 ~ 59] which has proved to be reliable in decades of routine work at different laboratories. AAS generally requires a large volume of blood sample and different kinds of sample pretreatment are often necessary. An electrochemical analysis technique which has been used is anodic stripping voltammetry which offers both high sensitivity and simple operating procedure, especially with the use of the ion exchange reagent MetExchange™ [50, 60]. The determination of lead in blood by stripping potentiometry in a flow system [61, 62] and in batch mode [63] has also been suggested. Since it was believed that dilute hydrochloric acid solution containing mercury ions was enough to transfer all of the lead in blood into an electrochemically active and stable form, no other matrix modifying solution was used in these applications. In this thesis a new method for lead determination in whole human blood is suggested. The method has been designed so that the technical skill required to perform it should be as small as possible. A matrix modifying solution with a composition of 1 M HCl, 500 ppm Hg(II), 4 ppm Bi(III), 10% (v/v) Triton X-100, 50 mM $CaCl_2$, 60 mM EDTA and 200 ppm Al(III) and Mn(II) was employed. The role of the EDTA is to diminish the possible effects of the presence of EDTA in blood standards, as it is often used as an anticoagulation reagent when blood samples are collected, and for clinical treatment of lead poisoning. Before being mixed with the matrix modifying solution, 70 µl of the blood samples or standards are first mixed with 200 µl Milli-Q water. The reason for this is to prevent coagulation when the sample is mixed with the acidic solution. With fresh blood samples this is not a problem, but with stored blood samples containing small clots problems may occur. 400 µl of the matrix modifying solution was then added. In total this resulted in a dilution of the blood samples by a factor of 10. The three-in-one electrode with the rotating tube mode was employed. Internal standard correction with Bi(III) was used for all results evaluation.

During the development of this method, four different blood standards or quality control materials from different sources were used. They included two quality control materials (bovine blood from animals on a controlled lead diet) - the IDMS pool (four different lead levels) and the BLLRS pool (nine levels) - from the Centers for Disease Control (CDC), US Department of Health and Human Services, Atlanta, USA, the Seronorm™ Trace Elements Whole Blood Standards (human whole blood spiked with lead, three lead levels) from Nycomed AS, Oslo, Norway and a blood standard from Merck (No. 131). Measurements on these samples showed a very good correlation (See Figure 8),

which indicates that the variation of blood composition does not significantly affect the analytical signal.

The stripping current and the electrolysis time can be chosen according to the desired sensitivity and stability. In the work reported in paper IV, a stripping current of 10 μA was used (for the three-in-one electrode from Radiometer, with a 3 mm glassy carbon disc as working electrode) and the total analysis time was about 3 minutes. This fulfilled the requirement set by CDC [64] and took advantage of the optimum conditions for the highest reproducibility. The electrolysis potential was -1.25 V *vs.* Ag/AgCl most of the time,

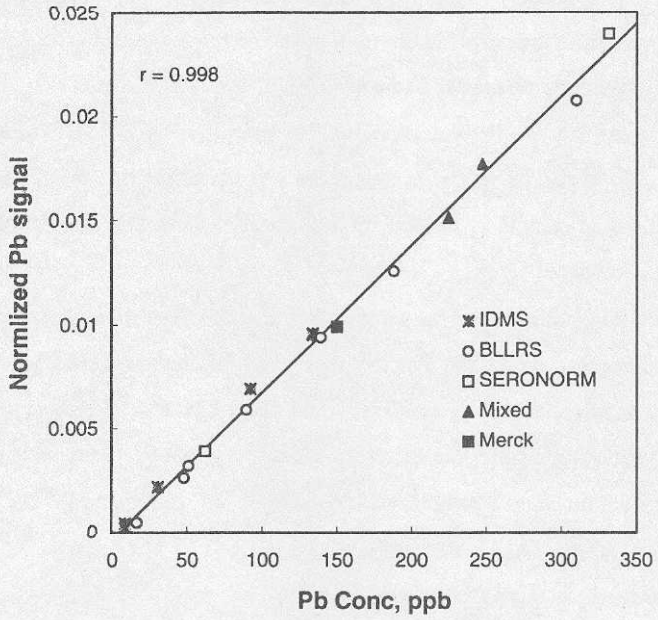


Figure 8 Lead Signals from Different Blood Standards/Reference Materials

Stripping current: 20 μA; electrolysis time: 110 sec.; home made three-in-one electrode with rotating sample tube.

although it was switched to -0.85 V *vs.* Ag/AgCl for 1 in every 10 seconds to oxidise the zinc reduced during the electrolysis. The purpose of this was to avoid any variation in the behaviour of the mercury films due to saturation by zinc.

The instrument was calibrated by a two point calibration procedure. After every 15

measurements one calibration solution was measured to check how much the sensitivity had varied. If the variation was greater than 10% a new calibration was performed. The decision for or against carrying out a new calibration was made automatically by the instrumentation.

To test the reliability of the method, an instrument assembly furnished with a complete analysis software, including self-diagnosing procedures, was lent to University Hospital, Lund, Sweden, where a screening of the blood lead levels in school children was being undertaken. After the blood samples were collected, determination of lead was performed with both graphite-furnace AAS and the stripping potentiometry method. The latter measurements were performed by laboratory staff lacking any previous experience in stripping analysis applications and who were given only a short instruction on how to operate the equipment. The results from both of the methods were in quite good agreement (slope of the correlation line at 0.90 and a correlation coefficient at 0.96 for 141 samples).

Many papers about the determination of cadmium in whole blood have been published [61, 63, 68 and 69]. Most of the methods offered have the common disadvantages that too much blood sample is needed for each analysis and that sample pretreatment is often necessary. In paper VI a new method for the determination of cadmium in blood is described. Only 20 µl of blood is needed for each analysis. The three-in-one electrode with a vibrated sample drop mode was employed. The simple matrix modifying solution used contained 400 ppm Hg(II), 1.5 ppm Bi(III) and 0.4 M HCl. The surfactant used in the matrix modifying solution for lead determination was removed because it decreased the sensitivity for cadmium too much. The blood sample was first mixed with 40 µl Milli-Q water and then 140 µl of the matrix modifying solution. 15 µl of the mixed solution was then pipetted onto the electrode surface for analysis.

Instead of using Bi(III) as the internal standard, the area of a part of the stripping background curve was used. To increase the sensitivity of the method, a nitrogen atmosphere was provided around the solution drop to prevent oxygen from being dissolved into the solution during stripping. In the determination of cadmium in whole blood, the most likely interference is lead. The described method makes it possible to measure cadmium in blood when the lead content is 40 times higher than that of cadmium.

4 FUTURE WORK

A promising direction for future development and employment of the stripping potentiometry technique is to minimise the size of the electrode and the entire instrument still further. To build a pocket-size stripping potentiometric instrument for trace metal determination is already technically possible. Stripping potentiometry and stripping voltammetry are probably the only analytical techniques for which this can be done. By combining the electrode vibration method with a screen-printed electrode [65, 66], one could make a pocket-size metal analysis kit with programs for different metals stored in a memory chip.

The low cost of a screen-printed electrode also offers the chance to collect a mass of information using a large number of identical electrodes. This would make it possible to build a calibration data base for each batch of electrodes produced, so that calibration would not be needed in the analytical laboratory.

Currently under investigation is to employ the three-in-one electrode in a wall-jet flow system for different kinds of samples in a mode similar to the batch injection analysis technique [70]. The sample solution and matrix modifying solution are sucked into a mixing tube by a pump which carries the mixed solution to the electrode surface through a needle. The electrode, is mounted at the bottom of a cell with a volume at about 20 ml and the sample solution is "injected" onto the electrode surface at a high flow-rate in order to get an efficient electrolysis.

To make stripping potentiometry more competitive, it is necessary to build fully automated analysis systems. Until now, the mixing of sample solution with matrix modifying solution, the electroanalytical procedure, result evaluation and medium exchange could all be easily automated with the instruments available on the market. The most difficult part to automate is the electrode pretreatment. In the applications described in this thesis, polishing of the electrodes is not included in routine procedures, as simply wiping off the electrode with a soft tissue is sufficient for several months continuous use. To design an apparatus for wiping the electrode surface would probably not be too complicated. If a fully automatic analytical system was realised in practice, the operators' work would be simplified to presenting the sample to the instrument and pushing the start button in order to get a full analysis report.

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