Cheap and Disposable Gold and Silver Electrodes: Trends in the Application of Compact Discs and Digital Versatile Discs for Electroanalytical Chemistry

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Highlights

- Compact discs and digital versatile discs can be readily used to give cheap reproducible Au and Ag electrodes.

- Their fabrication and use in electroanalytical chemistry is reviewed.

- Applications, performance characteristics and construction details are reviewed.

Abstract

Increasingly more reports have focused on the use of digital versatile discs (DVDs) and compact discs (CDs) for the fabrication of electrodes. The majority of discs use Al to reflect the laser. However, a notable percentage utilise Au or Ag. This layer can be mechanically or chemically exposed allowing for the economic fabrication of

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otherwise expensive Ag and Au electrodes. Cleaning steps are not required due to the layer's mirror like surface. Mass production of these discs means they are available, reproducible and disposable. Modifications can be made by laser, inkjet printing, etching or xurography. Self-assembled monolayers and the attachment of functional groups can also be made. This review (98 references and 5 figures) is divided into four sections. The first describes the development of these electrodes and their fabrication and modification. The next three sections focused on applications for the determination of metal ions, biomedical and environmental analysis.

Keywords: Silver; gold; DVD; CD; voltammetry; amperometry; heavy metals; biomedical; environmental; disposable

1. Introduction

Compact discs (CDs) and digital versatile discs (DVDs) are commonly available cheap and can be obtained from recycled material. They are produced in massive volumes with high precision. Their exact composition differs from manufacture to manufacture, however, they are generally fabricated from several layers principally a base polycarbonate layer, dye layer for data storage and a 40-100 nm thick metal reflective layer [1-3] (figure 1a). The metal layer is designed to reflect the laser back to the detector during writing and reading of the disc. The surface is characterised by concentric tracks *ca.* 0.4 μm in width and 0.1 μm deep, [4-7] separated by 1.3 μm [8] designed as a guide for the laser to follow. For the majority of discs, the metal layer is generally formed from Al, but Ag or Au are also commonly used. The presence of this metal layer offers a number of attractive possibilities for electrochemical analysis. Aluminium exhibits relatively poor electroanalytical properties and is seldom used as an electrode material as it oxidises fairly rapidly resulting in poor conductivity. However, both Ag and Au are noted for their good electrochemical properties in a range of different applications. Nevertheless, their

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relative high costs and the extensive cleaning steps required for usage has detracted from their general acceptance. In their seminal work in 2000 Angus *et al* [9] showed the possibility of fabricating Au electrodes from CDs and showed this to be a simple and inexpensive alternative method for the fabrication of these electrodes [7,10]. The Ag or Au layer can be simply exposed either by mechanical delamination of the disc [1,7] or by removal of the upper polymer layers with a suitable solvent such as nitric acid [9,11]. A single disc can be used to manufacture many electrodes at little cost (<2 Pence Sterling/electrode) tailored to various different geometries and configurations [12,13]. The mirror like nature of the exposed reflective metal layer elevates the need for any excessive polishing cleaning steps. The low cost the disc means they can be, if needed, treated as disposable one shot devices. Further modifications can also be made by techniques such as laser [14] and inkjet printing [12,15,16] or by the heat transfer of toner masks [17-23] designs onto the metal surface. Other alternative methods for the economic fabrication of electrodes exist and have been widely used and reviewed, principally, screen-printed electrodes [24] and the application of metal wire based electrodes [25]. The technique of screen-printing is highly attractive for the mass production of electrodes of the same formulation and dimensions. However, it can be costly and time consuming if different designs and architectures are required and the reproducibility of electrodes constructed from metal wire can be difficult to control.

This present review is divided into five main sections. The first section is focused on the background regarding the development of these electrodes and describes methods used for their fabrication and modification. The next three sections then focused on the application of these devices for the determination of metal ions, and applications for biomedical and environmental analysis. This represents the first review in this area.

2. Fabrication Strategies

Angnes *et al* [9] were the first to show the possibility of fabricating Au electrodes from compact discs. The technique they developed has now become the most commonly reported fabrication method. In their approach, the disc was cut into slices, in a similar manner to that of a "pizza". Concentrated nitric acid was then applied to remove the upper protective polymer coatings to expose the Au layer below. The removal of the protective coatings was reported to require only a few minutes and the remaining polymer material could be readily removed with a jet of water. Once removed the exposed Au layer can be then used as the working electrode. Using a similar fabrication technique, Richter *et al* [26] in their pioneering work in 2003, showed a number of new applications that these CD electrodes could be employed for; including the quantification of chloride ions by potentiometry by flow injection analysis, cyanide by amperometry flow injection analysis and Pb by square wave stripping voltammetry.

The majority of reports detail the fabrication and development of electrodes with dimensions in the mm to cm range. An interesting possibility investigated by Angnes *et al* [9] who have shown the possibility of developing electrodes with dimensions in the nm range. A number of analytical advantages can be gained through the use of working electrodes with these dimensions [27] and their investigations have shown the possibility of utilising the edge of the thin metal film of a Au recordable CD to form a 8 mm x 80 nm working electrode [9]. Linear sweep investigation showed typical nanoelectrode behaviour for ferrocyanide concentrations up to 9 mM in 0.1 M KCl gaining a current density of 4 A/M/cm^{-2}. However, the preparation of the electrode was reported to be problematic.

Alternative methods [7] have also been reported including the mechanical delamination of the disc. Figure 1b shows the construction of this device. Sections

of 10 mm x 60 mm of the CD-R can be cut out with a suitable pair of scissors, and in this case, the upper Ag layer was then removed by slowly peeling it away from the lower polycarbonate substrate. A 10 mm x 30 mm section of this was then fixed with adhesive to a suitable section of polycarbonate substrate (base of compact disc) with the Ag layer now facing upwards. A section of dielectric (RS components) modified with a 5 mm diameter hole was placed over the exposed Ag layer to define the working electrode area. A strip of exposed Ag was left at the opposite end to be used as an electrical contact to the potentiostat.
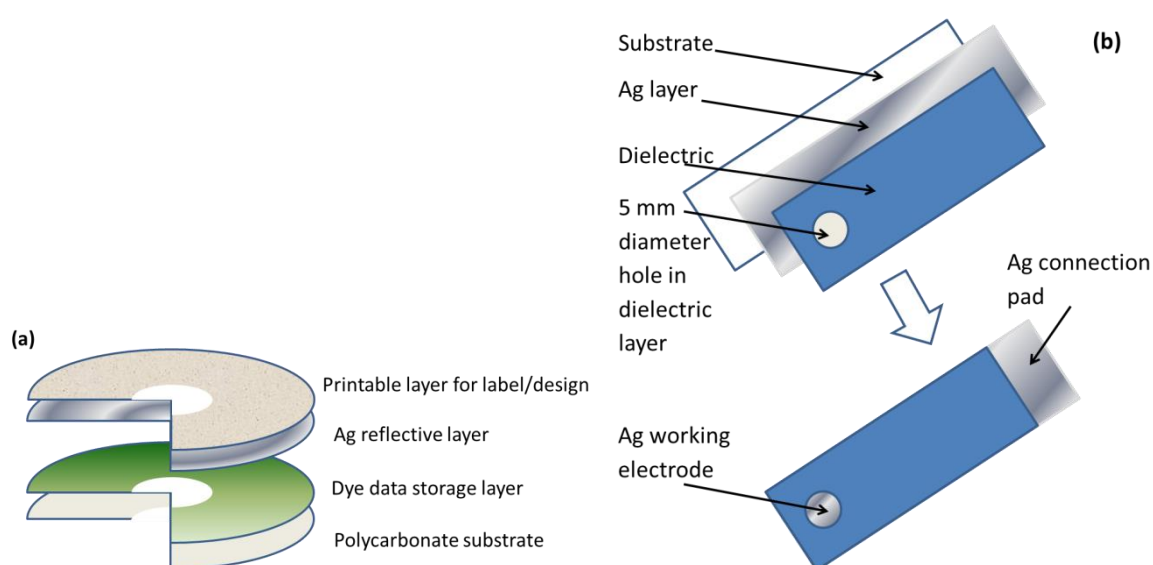

Figure 1. (a) Schematic of CD and (b) Ag CD electrode construction, after [7].

Alternatively, the metal layer can be removed by the application of sticky-backed plastic to top polymeric coatings of the disc [28]. The silver layer was then cut with scissors to an appropriate size and the surface area of the electrode was defined using a plastic hole-reinforcer (figure 2). This was then affixed to a piece of polycarbonate (base of compact disc) of the same size using electrical insulation tape. The remainder of the electrode was enclosed in electrical insulation tape, leaving an exposed pad at the opposite end for contact to be made to the potentiostat. Initial experiments utilised silver working electrodes with the area of the working electrode to be in contact with solution defined using electrical tape

(RS Components) with a disc of approximately 5 mm diameter removed using a hole-punch. This aspect of fabrication was later improved by utilising plastic hole-reinforcers of 5 mm diameter. It should be noted, that care needs to be taken whilst manipulating the very thin metal layer once liberated from its polycarbonate due its poor mechanical properties.
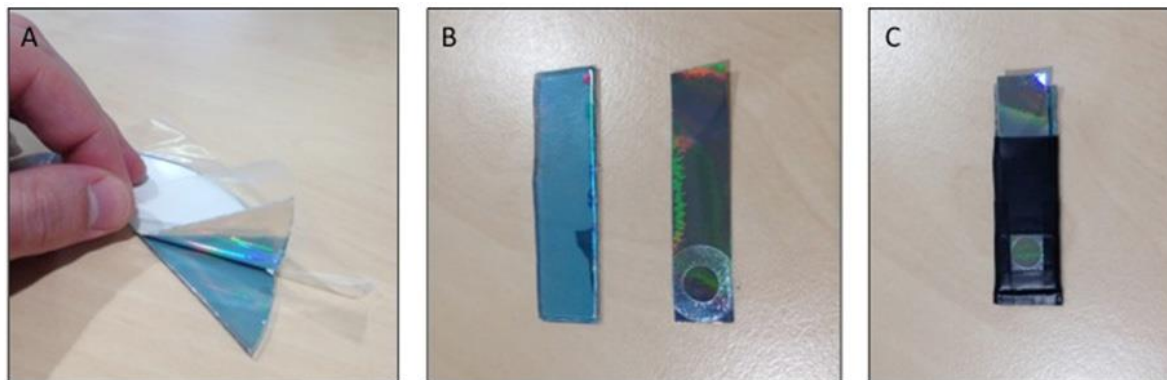

Figure 2. Ag working electrode fabrication. (A) Removal of the silver layer was facilitated by sticky-backed plastic. (B) The silver layer was then cut to an appropriate size and the surface area of the electrode defined using a plastic hole-reinforcer and affixed to a piece of polycarbonate (C) The remainder of the electrode was enclosed in electrical insulation tape and trimmed to yield the final product shown in figure 2 [28].

The Au and Ag electrodes fabricated can be further modified via a number of different techniques such as that demonstrated by Daniel *et al* [29] who have used a laser printer to transfer a design onto wax paper which can be then heat-transfer onto the Au surface of a delaminated CD-R (Figure 5). The Au layer can then etched from the unprinted regions and the toner then removed with solvent to give the required designed. The resulting Au electrodes were then used as part of a conventional batch or flow cell system for the determination of dopamine. Microfluidic flow cells (7–12 μm interlayer gap) were fabricated using a gasket spacer of the desired shape drawn and laser printed and heat transferred onto the CD. A second CD section was then heat-sealed on top of this to form the microfluidic flow cell. The overall internal volume was estimated to be 240 nL, of

which a layer of only approximately 15 nL was reported to be above each working electrode. The functionality of these electrodes as well as of the microfluidic flow cells was demonstrated by voltammetry and flow injection amperometric analysis. The repeatability of the device was investigated by recording the amperometric oxidation of dipyrone at +0.800 V for sequential injections of 10 μL of a 1.35 mM dipyrone solution in 0.1 M acetate buffer solution at a flow rate of 83 μL/min. A relative standard deviation for the amperometric response was reported as 1.16% (n = 27) with a calculated sampling frequency of *ca.* 40/h.
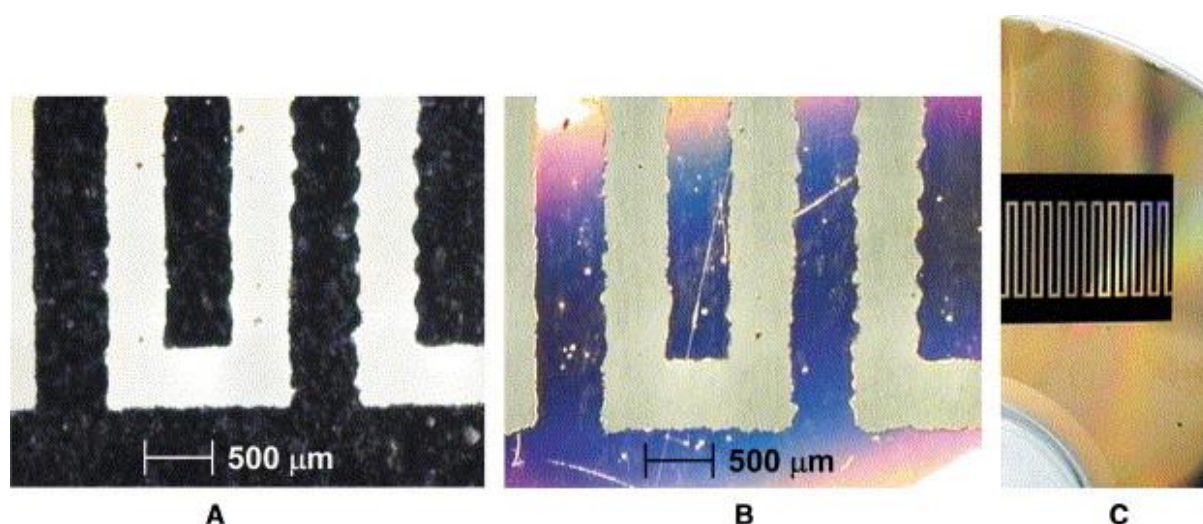

Figure 5. Construction of an interdigitated array of gold electrodes on a CD. (A) Magnification of a section after printing (by heat-transfer of toner mask), revealing the resolution of the lines defined by the toner. (B) Magnification of a section of the finished gold electrodes (after etching and toner removal). (C) Full view of the toner mask applied onto the CD. Reproduced from Daniel *et al.* [29] with permission from Elsevier B.V.

Ferreira *et al* [58] have utilised a similar approach for the determination dipyrone, along with Pb Cu, Hg, paracetamol and nitrite. Interestingly, their investigation showed the possibility to use a permanent marker pen to define the electrode design on the Au CD-R after defining by laser jet printing. Paixão *et al* [18] have developed a twin-electrode thin-layer cell which was operated in the generator – collector mode with reported collection efficiencies of 100 % for the ferri/ferrocyanide redox couple. The thin layer cell was constructed from Au CDs

to from two 500 μm diameter working electrodes. These were place facing each other, separated by a layer of toner mask (6 μm thick). The thickness of the resulting thin layer cell could be controlled by the number of layers of toner mask deposited. The thin layer cell was then heat sealed and with two holes to form the inlet and outlet channels (0.8 mm diameter). It was shown that as a result of the fast transfer speeds of solutions within the thin-layer cell, electrochemical processes involving EC mechanisms could be investigated. This was demonstrated with ascorbic acid as an irreversible model system. Digital simulation was used to relate current at both electrodes (generator and collector) to the gap, flow rate and rate constant for a typical EC mechanism.

Ferreira *et al* [30] have used the same device to determine the diffusion coefficients of $Fe(CN)_6^{3-}$, $Ru(NH_3)_6^{2+}$, and quinone were determined in water and, for $Fe(CN)_6^{4-}$, in binary mixtures with glycerol. Measurements of the diffusion coefficients of ferrocene in micellar solutions of the cationic surfactant CTABr were also performed.

3. Chemical Modifications

The surface of the Au CD electrode offers a number of possibilities for further chemical modifications. In one such investigation, Walcarius *et al* [31] have shown that by applying a suitable cathodic potential at a Au CD electrode in a surfactant-hydrolysed sol solution it is possible to generate hydroxyl ions to catalyse the poly-condensation of a self-assembled layer of hexagonally packed one-dimensional channels. These were shown to grow perpendicularly to the electrode surface and they could be controlled to deposition at heterogeneous supports. It was concluded that this process could be used for the design of complex patterns on the CD metal surface. Yu [11,32] has investigated the possibility of forming self-assembled monolayers of long-chain alkane thiols such as $n-C_{18}H_{37}SH$ adsorbed on Au CDs [32]. The results showed that there were no distinct differences in the quality and

structure monolayers and self-assembled monolayers (SAMs) formed at the CDs than those formed on standard Au substrates.

Matemadombo *et al* [33] have shown that amine substituted cobalt phthalocyanine (CoTAPc) can be deposited on Au CD surfaces by using an interconnecting layer of a SAM of mercaptopropionic acid or Lomant's reagent (dithiobis(N-succinimidyl propionate). Electrochemical investigations showed near 100 % surface coverage. SAM-CoTAPc layers were reported to show electro-catalytic activity for oxygen reduction through the Co(I) central metal ion. The modified electrode were reported to show good long term stability and promise as possible sensors.

Sibottier *et al* [34] have reported the development of an amine or thiol functionalised electro-generated sol-gel-derived silica film at a Au CD based electrode. The electrochemical deposition of this film as reported to be achieved by the formation of a so-called "nanoglue" on the electrode surface. Cathodic electrolysis was undertaken to form hydroxyl ions that catalysed the formation of organo-silica films. The electrodeposition process was reported to occur via two growth phases: an initial first slow stage resulting in rough homogeneous films with a thickness in the sub-μm range; followed by a faster gel forming step giving thicker films (>1 μm) and rougher macro-porous deposits.

The possibility of modifying Au CD electrodes with poly(4-aminophenol) has been explored by Ferreira *et al* [35] with the aim of forming polymers capable of immobilizing purine bases and oligonucleotides. Enhanced electrochemical signals in the order of three and six fold for the electrochemical response of adenine and guanine were reported at the modified electrodes. Impedance studies indicated higher charge transfer impedance at the modified electrodes containing adenosine monophosphate. Investigations by atomic force microscopy indicated that the nitrogenated bases had a strong influence on the morphology of the modified electrode surface. Au electrodes were modified by first cleaning with piranha

solution (concentrated H_2SO_4 (98 %) and H_2O_2 (30 %), 3:1 v/v) and washed with deionised water. The electrode was submitted to potential cycling in 0.10 M H_2SO_4 between -0.20 V and +1.50 V at a scan rate of 100 mV/s. The Au electrode was then modified with poly(4-aminophenol) by continuous voltammetric cycling of between 0.00 V and +1.50 V at 50mV/s using a 25 mM solution of 4-aminophenol in 0.50 M H_2SO_4. After this treatment, adenine, guanine, guanosine monophosphate (GMP) and adenosine monophosphate, and oligonucleotide were immobilized on the surface of the electrode by adsorption at room temperature.

Recently, Foguel *et al* [36] have explored the construction of Au electrodes using three kinds of Au CD-Rs (Inkjet MAM-A, MAM-A, and Archive MAM-A from CDMAM-A Inc. trade, Colorado, CO, USA). Following 4‑6 minutes surface pre-treatment with 0.2 M sulphuric acid, contact angles and the cyclic voltammetric behaviour of the behaviour of the ferro/ferricyanide redox couple for the bare commercial Au electrode were reported to be very similar. The Au CD electrode surface was also treated after the removal of the upper polymeric film with concentrated nitric acid by electro-polishing in 1.0 M sulphuric acid solution to reduce Au oxide present on the electrode surface. The electrochemical behaviour was found to be indicative of differences in physical parameters of the CD electrode surface. Whereas, differences in the original CD electrode surface were concluded to result in changes in the type of cyclic voltammograms obtained after cleaning with nitric acid. The authors also concluded from scanning tunnelling microscopy investigations that the Au CD surface is slightly more uniform than evaporated Au films. Further investigations by atomic force microscopy indicated that the laser-tracks presented in Au layer varied in height from the peripheral to the central part of the CD-Rs. The authors concluded from these investigations of the different CD-R that these were sufficiently similar as not to effect any subsequent modifications of the electrode. The possibility of immobilising onto the electrode surface an

oligopeptide mimic of the active site of the acetylcholinesterase enzyme was then evaluated. The electrodes were shown to be suitable for immobilizing biological molecules and could be used as disposable transducers for the construction of biosensors.

4. Applications

4.1 Metal Ion Analysis

4.1.1 Lead

Stripping voltammetry is one of the most sensitive and economic methods for the determination of metal ions [37,38]. Detection limits in the low μg/L region can be readily obtained with little sample pre-treatment or need for sophisticated laboratory equipment. Modern potentiostats are portable and can be operated on battery power alone allowing for analysis at the "point of care" or "in the field". Previously, stripping voltammetry at metal electrodes had been dominated by the use of Hg working electrodes. This lead to the method suffering from the perceived problems of toxicity and subsequent disposable issues led to a lack of market penetration. A number of different approaches have been made to overcome these issues, such as the use of less toxic metals and alloys; such as galinstan [39], Bi [40-42] and Sb [43] and alternative electrode materials such as screen-printed carbon [24]. Both Ag and Au electrodes have been used for some time in stripping voltammetry and offer a number of advantages in certain applications over other working electrode materials. However, the use of conventional Ag and Au electrodes has been hampered by the problems of expense and electrode fouling, requiring cleaning and extended preparation steps for their use. However, use of CD and DVD for the fabrication of Ag and Au electrodes overcomes many of these issues. Their cheap and ready available nature allows them to be treated as

disposable, allowing them to be used once and then discarded overcoming problems of fouling and carry over.

Table 1 provides a summary of the reported applications of both CD and DVD derived electrodes for the determination of metal ions.
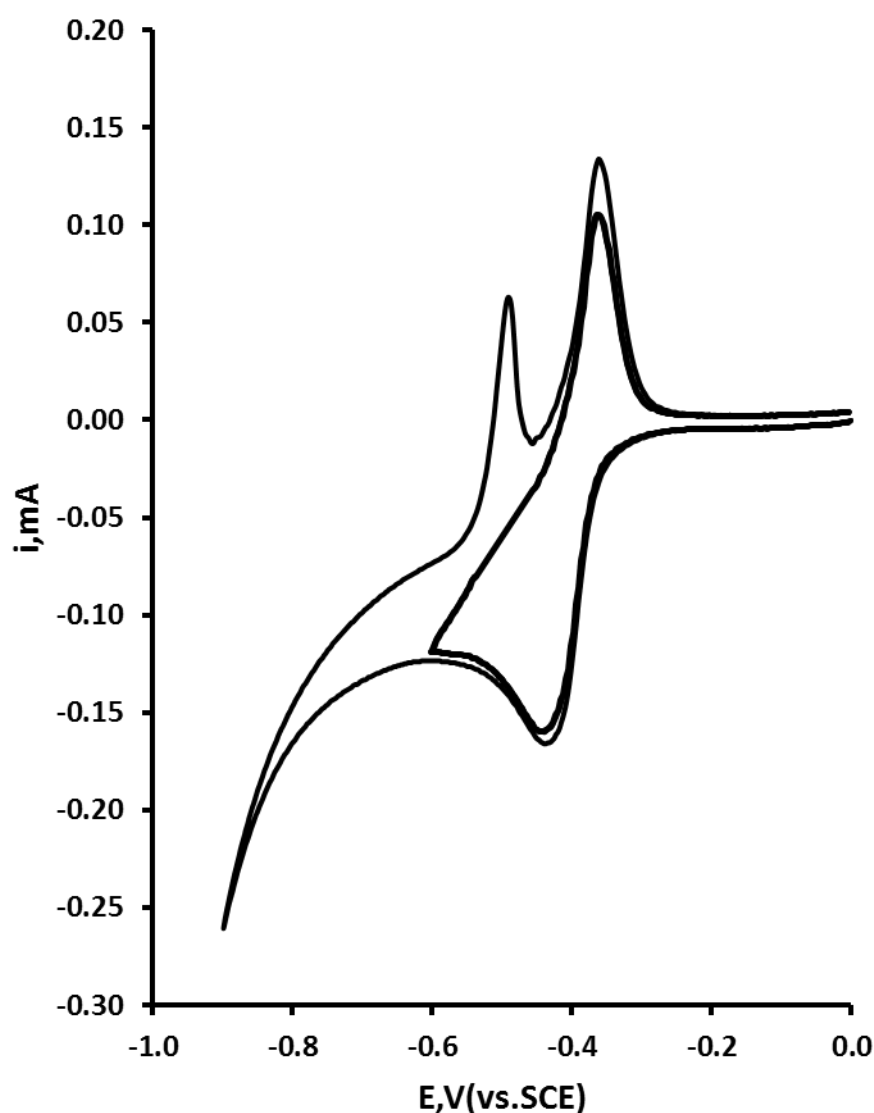

Figure 2. Typical cyclic voltammograms obtained in 0.1 M HCl containing 0.1 mM Pb at a Ag CD electrode, after [7].

Recently, the under potential deposition of Pb has been shown possible at a Ag electrode manufactured from a CD-R [7]. Cyclic voltammetric investigations in 0.1 M HCl exhibited indicative of the over and underpotential of Pb at the electrode

surface (figure 2) as previously shown by Richter *et al* [26]. Using a switching potential of -0.9 V two stripping peaks where recorded at -0.49 V and -0.37 V (*vs.* SCE) indicative of the stripping of the overpotential and underpotential multilayer and monolayers of Pb deposited on the electrode. Interestingly, this electrode showed very similar behaviour to that reported for conventional Ag electrodes [44]. Using underpotential deposition an anodic stripping voltammetry (ASV) method for the trace determination of Pb was developed. Using an accumulation time of 100 s, a linear range of 20 ng/mL to 350 ng/mL was reported with a detection limit of 6 ng/mL. The method was successful applied for the determination of Pb^{2+} in roof water runoff.

Studies have also shown the possibility of utilising square wave stripping voltammetry for the determination of Pb [26] at Ag electrodes constructed from a CD-R. Utilising a supporting electrolyte of comprising of 0.1 M $NaNO_3$ and 0.01 M HNO_3 and a more negative deposition potential of -0.7 V. Employing a deposition time of 180 s a detection limit of 0.2 ng/mL was obtained based on a signal to noise ratio of 3. The stable reproducible nature of the developed device was demonstrated with a relative standard deviation (RSD) of 2.5 % (n = 20) being reported for the measurement of a 10 ng/mL Pb solution.

The same authors [45] have employed a similar approach however, in this case, with a Au electrode fabricated from a CD-R to determine Pb in rainwater using square wave anodic stripping voltammetry (SWASV). A detection limit of 80 ng/L was reported utilising a deposition time of 300 s. The Au electrodes were prepared by removal of the polymeric layers with concentrated HNO_3. The result exposed Au layer was then cut into 3 x 40 mm slices and a *ca.* 2 or 3 mm^2 working electrode area was then defined with enamel or PVC resin. An electrical contact was made by the attachment of a wire to the opposite end of the Au strip with Teflon tape.

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The authors also reported on the development of a specially designed miniature electrochemical cell which allowed for the use of high stirring speeds and small sample volumes. Investigations undertaken by the authors showed that the stripping behaviour of Pb and other metals at the Au CD-R was best undertaken in a Cl⁻ containing supporting electrolytes. The optimum supporting electrolyte was HCl at a concentration between 50 mM and 300 mM. At higher HCl concentrations hydrogen gas evolution was reported which decrease the precision of the assay. The effect of deposition time was investigated over the range of 30 to 600 s. The peak for a 7 µg/L Pb solution was seen to increase nearly linearly with time up to 300 s, beyond which it was found to plateau. Using the optimum conditions an RSD of 2.87 % was obtained for 20 repetitive measurements of a 7 µg/L Pb solution. Four different rainwater samples were fortified with 4.8 µg/L Pb and a mean recovery of 103 % was reported. Further analysis of ten rainwater samples collected in Sao Paulo city, between January and May 2000 showed the concentrations of Pb to range from 0.25 µg/L to 2.99 µg/L. Storage of the Au electrodes was found to detrimental to the SWASV determination of Pb, presumed to result from the formation of oxidises on the electrode surface. It was found possible to overcome is issue by electrochemically cycling between 0.0 and +1.2 V in 0.05 M perchloric acid.

4.1.2 Selenium

The determination of trace Se levels at Au CD electrodes formed has been reported by Fernandes Pereira *et al* [46]. The Au electrode was prepared cutting a section of a Au recordable CD. The Au layer of the CD was exposed using concentrated HNO_3 to remove its protective film. Two areas were exposed; one to form the electrical contact and other as the working electrode.

In acidic solutions Se is present as selenous acid, H_2SeO_3 which can be electrochemically reduced through a $6e^-$, $6H^+$ process to form hydrogen selenide (eq.1) (H_2Se) or several intermetallic species with the Au working electrode of various stoichiometries (eq.2).

$$H_2SeO_3 \ + \ 6H^+ \ + \ 6e^- \ \rightarrow \ H_2Se \ + \ 3H_2O \tag{1}$$

$$H_2SeO_3 \ + \ nAu \ + \ 4H^+ \ + \ 4e^- \ \rightarrow \ Au_nSe \ + \ 3H_2O \tag{2}$$
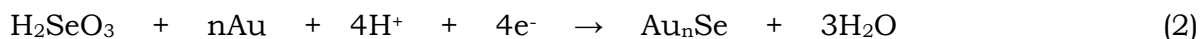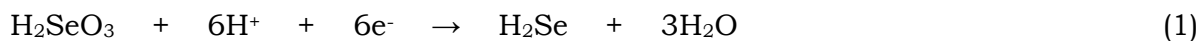
The formation of this intermetallic species can cause problems as can be difficult to fully remove between subsequent measurements. However, the disposable nature of disc based electrodes alleviates this issue as measurements can be made at fresh, clean electrode each time.

Using an accumulation potential of +0.4 V the authors used the formation of these intermetallic species to accumulate Se at the Au electrode surface. The anodic stripping of these compounds resulted in several anodic stripping peaks with the stripping peak with a peak potential (Ep) of +1.1 V being shown to give a linear response over the range 0.5 to 291 ng/mL for Se(IV). Two more anodic voltammetric peaks were also recorded, with Eps of +0.6 V and +0.8 V, but were found to be analytical inferior. Using the method of multiple standard addition an average recovery of 96.4 % was reported for a 50 ng/mL Se(IV) solution.

4.1.3 Mercury

The electrochemical determination of Hg offers a number of analytical challenges. It is known to form amalgams with a number of metals, such as Au, leading to problems with sample carry over [47] as Hg can diffuse into the working electrode making it difficult to remove. Consequently, there is a need for good quality Au

working electrodes which are cheap and potentially disposable for Hg determination to overcome such problems. To meet with these demands, a number of reports have been made utilising CD based Au electrodes [48] have determined Hg in Cod fish fillets, following acid digestion, at Au electrodes fabricated from CD-Rs by chronopotentiometric stripping analysis. The electrodes were prepared from Kodak Gold (code 1721745) CD-Rs using HNO_3 to expose the Au surface to form a working with a diameter of 0.3 cm and an area of 0.070 cm^2. The percentage recovery for a known amount of Hg introduced in the sample before digestion was reported to be 95.3 % (n=4). After each experiment the Au working electrode was cleaned electrochemically in a solution of 0.2 M H_2SO_4 by applying a potential of +1.5 V for 40 s, followed by scanning the potential five times between -0.25 and +1.5 V at a scan rate of 0.02 V/s. The electrodes were then thoroughly washed with bi-distilled water before being introduced to 10 mL of sample extract in 0.05 M HCl. The working electrode potential was set at +0.3 V for 180 s with stirring. The potential was then scanned in from +0.3 V to +0.7 V using a constant current of +0.75 µA. The resulting signal was then background subtracted using the signal obtained from a 0.05 M HCl solution. The effect of various other metal ions on the stripping response of Hg was studied and concentration ratios of 25:1 of Zn^{2+}, Pb^{2+}, Fe^{2+} and Mn^{2+} were reported to have little effect on the Hg signal. However, the addition of Cu^{2+} at concentrations above 100 µg/L resulted in a detectable shoulder, at approximately +0.45 V, on the stripping peak response obtained for 20 µg/L Hg (+0.54 V). Below this concentration ratio expectable results could still be obtained. Employing a deposition time of 600 s a detection limit of 0.30 µg/L Hg was reported with a corresponding linear range from 1 to10 µg/L. Using a shorter deposition time of 180 s, a linear range of 5 to 100 µg/L was reported. A RSD of 1.92 % (n = 6) was reported for a Hg concentration of 20 µg/L.

The possibility of determining both Hg and methyl-mercury (CH_3Hg^+) in synthetic oceanic water has been explored at a Au CD-R (Mitsui Gold Standard) based electrode by stripping chronopotentiometry [49]. A deposition potential of +0.3 V was reported to be most suitable, as the majority of other metals were reported not to be accumulated under these conditions. The use of a low stripping current was found advantageous as it was demonstrated that when the oxidation current was increased linearly, the resulting signal decreased nearly exponentially. At +0.3 V, no interference was observed for the addition of 200 μg/L of Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} and Cr^{3+} to a solution containing 10 μg/L of Hg. Copper was reported not interfere as its re-oxidation peak occurs around +0.3 V and to interfere would have to be relatively high concentrations. An RSD of 1.4 % (n = 48) was reported for a solution containing 10 μg/L of Hg with a detection limit of 8 ng/L (s/n = 3) calculated for a deposition time of 600 s. A recovery of between 93 % and 105 % was obtained for five successive runs of a NIST river water sample spiked with 20 ng/L of Hg. Methyl-mercury analysis was undertaken on an aquarium water sample containing synthetic oceanic water fortified with CH_3Hg^+.

Angnes *et al* [9] have utilised the related technique of potentiometric stripping for the determination of Cu and Hg ions. The electrode was fabricated by removing the upper protective layer with nitric acid to expose the Au substrate layer. Using an accumulation time of 60 s; deposition potential, -0.1 V with a supporting electrolyte of 0.1 M HCl linear ranges of 5 to 60 μg/L and 10 to 120 μg/L, for both Cu and Hg were reported respectively. After each run the electrode was held for 15 s at +0.7 V to ensure the complete stripping of the deposited metals. In a further study [50] the authors reported a detection limit of 30 ng/L using a 600 s deposition time with a standard deviation of 1.8 % for 20 repetitive measurements of a 25 μg/L solution of Cu in this case using a 60 s of deposition time. They showed the possibility of utilising the developed Au electrode for the analysis of Cu in sugar cane spirits and

tap water samples. The results were shown to compare well with those obtained by atomic absorption spectroscopy.

4.1.4 Cerium

Westbroek *et al* [51] have described for the chronoamperometric determination of Ce(IV) in acidic aqueous solutions to study the kinetics and mechanism of polymerization reactions which utilise Ce(IV) as initiator. A thin layer cell was designed and constructed for flow injection analysis of Ce(IV) at a Au CD electrode in 1.0 M H_2SO_4. Using an applied potential of +0.25 V a detection limit of 0.15 μM was reported.

Daniel and Gutz have shown the possibility to develop flow through cell for the determination metal complexes such as ferricyanide [52]. In further studies they have developed novel micro-reactors, based on the TiO_2-assisted photo-catalytic digestion of organic matter followed by the voltammetric determination of the liberated metal ion. In one such study [18] they showed the possibility of determining Cu^{2+} ions by cyclic voltammetry flowing liberation from its EDTA complex. For this they employed a Au CD derived electrode modified with TiO_2 by the voltammetric cycling (-0.300 to +1.100 V, 10 scans) of a $AuCl_4^-$ in a suspension of TiO_2. This resulted in the formation of a reportedly uniform brown deposit on the Au electrode surface. Electrodes modified by this procedure were reported to withstand at least one week of intense use. The electrochemical characteristics of the TiO_2 modified Au electrode was evaluated using the reversible redox couple, $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$. An enhancement of *ca.* 30 % of the voltammetric currents was recorded at the modified electrode and was attributable to the increase in the effective surface area formed by the modification process. The Cu^{2+} EDTA complex was chosen as a model system to investigate the possibility of employing the photocatalytic micro-reactor for the removal of organic matter which is a well-

known interference in the voltammetric determination of metal ions. In the absence of light no voltammetric signal for the electrochemical inactive Cu–EDTA complex was recorded at the Au-TiO$_2$ modified electrode. Similarly, UV at irradiation at 365 nm of an unmodified Au electrode resulted in no detectable signal form the Cu–EDTA complex. Whereas, irradiation at the TiO$_2$-modified Au electrode was shown to result in the typical cyclic voltammetric response of Cu, demonstrating the UV photo-catalytic destruction of the electrochemically inactive Cu-EDTA complex and the liberation of Cu^{2+} ions. The procedure was reported to be achieved in less than four minutes. In further studies the Au-TiO^2 modified electrode has been employed to determine ethylenediaminetetraacetic acid (EDTA) [53]. In this case the Au electrodes was modified by simply exposing the Au electrode to an acidic aqueous suspension of P25 TiO$_2$. A layer of TiO$_2$ less than 100 nm thick was reported to be formed on the Au surface, dominated by particles with diameters ranging from 20 nm (anatase) to 30 nm (rutile). A linear relationship between the photocurrent and the applied potential at the TiO$_2$ modified Au electrode was reported.

Analyte	Electrode Material	Sample Pre-treatment	Supporting Electrolyte	Measurement Technique	Linear Range	Detection Limit	Sample(s)	Comments	Ref.
Hg	Thin film Au electrodes (Mitsui Gold Standard CD), *ca.* 5mm^2.	Sonicated (15 min) in concentrated HCl and H_2O_2	Diluted HCl from the sample pre-treatment.	stripping chronopotentiometry	-	300 ng/L (300 s, +300 mV)	Human urine	Samples concentrations verified by CV-AAS and analysis of NIST SRM 2670.	[54]
Hg	Thin film Au electrodes (Mitsui Gold Standard CD)	Digested using a microwave oven in closed vessels in dilute HNO_3 and H_2O_2	Sample digest.	stripping chronopotentiometry	-	5 ng/g (5 minutes, +300 mV)	fish and shrimps	Validated with certified reference material.	[55]
Pb, Cu	Thin film Au electrodes (Mitsui Gold Standard CD), *ca.* 5mm^2	Sonicated (15 min) in 1:1 concentrated HCl and H_2O_2	Diluted extraction solutions.	Square-wave anodic stripping voltammetry	-	Pb and Cu; 67 and 23 ng/g respectively (-250 mV, 120 s)	lubricating oils	Method validated by comparison with GFAAS and CSA	[56]
Hg	Au, Kodak Gold Preservation CD-R	Digested in HNO_3/HCl/ H_2SO_4 by heating at 100 °C.	0.05 M HCl solution containing 0.3 M Na_2SO_4	Flow injection stripping chronopotentiometry	5 - 100 ng/mL (180 s)	0.1 ng/mL (600 s, +300 mV)	Cod fish samples	Recovery 96.2 %	[57]
Pb	Au CD-R	Dilution in electrolyte	50-300 mM HCl	SWASV	-	80 ng/L (300 s)	Rainwater	Validated with certified reference material	[45]
Pb	Ag, Verbatim	Dilution with 0.2 M HCl	0.1 M HCl	DPASV	20 – 350	6 ng/mL (100 s)	Roof runoff water	-	[7]

	CD-R					ng/mL			
Pb	Au CD-R	0.1 M $NaNO_3$ 0.01 M HNO_3	-	SWASV	-	0.2 ng/mL (180 s)	-	Coefficient of variation of 2.5 % for a 10 ng/mL Pb solution	[26]
Hg, CH₃Hg⁺	Au Mitsui Gold Standard CD-R			Stripping chronoamperometry		8 ng/L, 180 s	Synthetic ocean water	NIST river water (recovery 93 – 105 %)	[49]
Hg	Au CD-R Kodak Gold (1721745)	Acid digestion		Stripping chronoamperometry	1-10 µg/L (600 s). 5-100 µ/L (180 s)	0.3 µg/L (600 s)	Cod fish samples		[48]
Hg, Cu	Au CD		0.1 M HCl	Potentiometric stripping	5-60 ng/mL Cu, 10 – 120 ng/mL Hg				[9]
Pb, Cu, Hg	Au CD-R (Mitsui/USA)	-	0.10 M acetate buffer	SWASV	Voltam mogra m of 400 ng/mL solutio n shown	-	-	Investigations of manufacturing reference electrode from Ag epoxy.	[58]
Pb, Cu, Hg, Cd	Au CD with *in situ* formed Bi film		0.5 M KCl and 6.0 mM HCl for Cu and Hg. Cd and Pb 0.1 M acetate buffer (pH	Potentiometric stripping and SWASV.	10 – 100 µg/L	Cd^{2+} 0.38 µg/L; Pb^{2+}, 0.74 µg/L (S/N=3).	--	Microfluidic cell (internal volume 0.6 to 2.4 µL) with Ag epoxy pseudo-reference electrode. Au	[59]

			4.7) containing 2.0 mg/L of Bi.					CD working electrode. Graphite working electrode also explored.	
Cu	Au CD		0.1 M HCl	Potentiometric stripping analysis		30 ng/L (600 s accumulation time)	Sugar cane sprit and tap water	-	[50]
Cu	Au CD with amine-functionalised silica film.		Accumulation in 50:50 ethanol:water solution	Open circuit accumulation of Cu^{2+} at a 10 % amine functionalised silica surface, followed by measurement by DPASV (reduction at -1.2 V).	0.1 – 10 μM		--	Reactivation at -1.3 V for 3 minutes.	[60]
Cu	Au CD TiO_2-modified	Thin layer micro-reactor. 100 mW UV-LED (365 nm) focused on the modified electrode.	Acetate buffer solution (pH 4.7)	Cyclic voltammetry, 50 mV/s.	1.0×10^{-6} M – 5.0×10^{-3} M	5×10^{-15} M Cu	Model Cu-EDTA complex	*In situ* photocatalytic digestion Cu-EDTA complex as model complex.	[18]
Se(IV)	Au CD	-	0.1 M $HClO_4$	DPASV	0.5 – 291 ng/mL	-	Standard reference solutions		[46]
Se(IV)	Au CD	Microwave aided digestion in HNO_3 and H_2SO_4.	0.1 M $HClO_4$.	Flow injection differential pulse amperometry, -0.4 V	20 to 400 μg/L	6 μg/L, 200 s.	Fish tissue.	Flow injection analysis, 0.71 mL/min	[61]
Ce(IV)	Au CD		1.0 M H_2SO_4	Amperometry +0.25 V		0.15 μM		Flow injection analysis, 2.36 mL/min	[51]

Zn	Au CD with Hg film	Sample digested in 1:1 concentrated HCl: H_2O_2 with the aid of sonication.	0.2 M acetic acid + 0.2 M sodium acetate	Potentiometric stripping. -1.45 V (vs. Ag/AgCl)		1.35 µg/L for 45 s and 0.030 µg/L for 600 s pre-concentration	Coconut water.	Cu also determined, but below limit of detection. Good agreement with GFASS.	[62]
Cu	Au CD	Focused microwave aided digestion in HNO_3/ H_2SO_4/H_2O_2.	20 mM NaCl.	Derivative potentiometric stripping.0.8 V		92 ng/g oil for 120 s.	Lubricating oils.	Pb also determined at glassy carbon electrode. Good agreement with GFASS.	[63]
Cu, Pb, Hg, Zn	Au CD with Hg film for potentiometric stripping	Focused microwave aided digestion in HNO_3/ H_2SO_4/H_2O_2.	Square wave stripping voltammetry 20 mM NaCl. Potentiometric stripping 100 mM Na acetate.	Square wave stripping voltammetry (Cu, Pb, Hg), stripping chronopotentiometry (Cu, Pb, Zn) and potentiometric stripping (Cu, Pb, Zn).		Square wave stripping voltammetry Pb 0.04 µg/L, Cu 1.4 µg/L, Hg 1.3 µg/L. Stripping chronopotentiometry Cu 0.65 µg/L, Hg 0.69 µg/L	Crude oil and petroleum based fuels.	Good agreement with GFASS.	[64]

Table 1. Application of CD and DVD electrodes for the determination of metal ions.

Cold vapour atomic absorption spectrometry (CV-AAS), chronopotentiometric-stripping analysis (CSA), Graphite furnace atomic absorption spectrometry (GFASS), National Institute of Standards and Technology standard reference material (NIST SRM).

Table 2 summaries the wide range of different applications other than metal ion analysis that have been reported utilising CD and DVD based electrodes.

5. Biomedical and Environmental Applications

5.1 Chagas' Disease

Chagas' disease is a parasitic infection caused by the hemoflagellate *Trypanosoma cruzi* (*T. cruzi*) transmission of this disease is through the bite of contaminated hematophagous insects or through blood transfusion and blood components. Foguel *et al* [65,66] have developed an amperometric immunosensor for the determination of Chagas' disease based on a Au CD-R modified with 4-(methylmercapto)benzaldehyde (SBZA) for the immobilization of the Tc85 protein of *T. cruzi*.
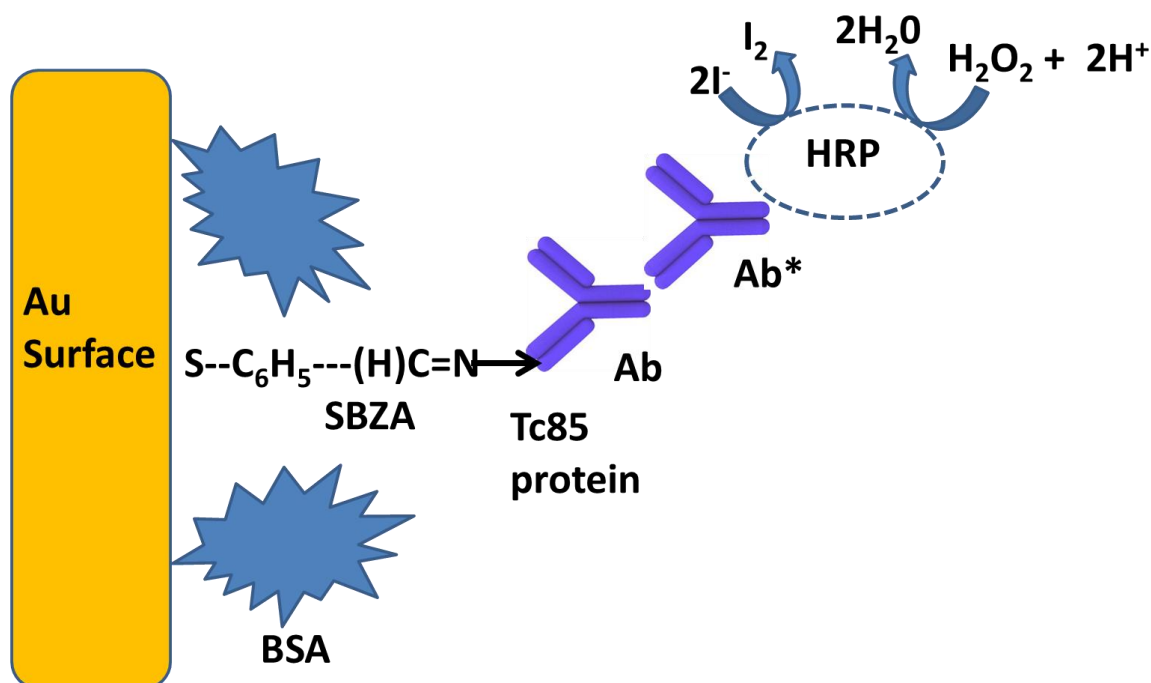

Figure 3. Chagas' immunosensor construction scheme, after Foguel *et al* [65].

The Au electrodes were cleaned by voltammetric cycling in 0.5 M sulphuric acid over the potential range 0.0 V and +1.5 V at 100 mV/s. The amperometric

immunosensor was then fabricated by modifying the surface of the Au CD electrode with a self-assembled monolayer of SBZA. The antigen Tc85 protein of *T. cruzi* was immobilised on the SBZA modified surface. After antigen immobilisation the immunoassay was performed by first blocking of the sensor surface with a saline phosphate buffer-Tween solution containing 0.5 % bovine serum albumin (Ab) (Figure 3). A 50 µL sample of serum diluted in blocking solution was then applied and following a wash step, anti-human IgG antibody conjugated to peroxidase (Ab*) was applied and incubation for 15 minutes. The resulting immunoenzymatic reaction was monitored by chronoamperometry using hydrogen peroxide as the substrate meditated by potassium iodide in pH 7.0 0.1 M phosphate buffer solution.

5.2 Thrombin

The protein thrombin regulates many processes in inflammation and tissue repair at the blood vessel wall. Frense *et al* [67] have recently reported on the application of an impedance based thrombin biosensor utilising immobilized streptavidin and a biotinylated aptamer as sensitive layer on the Au CD (Sony). The Au surface of the Au CD was exposed by removing the lacquer film by submerging the CD in 50 % nitric acid for 5 minutes. The exposed Au surface was rinsed with ethanol and then treated under UV to make the surface more hydrophilic. The Au surface was then sprayed with positive photoresist lacquer for photolithographic wet-etching of the electrode patterns (etched with 4 g KI and 1 g I_2 in 40 mL water for 5 minutes). Two different electrode patterns were fabricated; the first pattern had a fixed measurement chamber glued to the electrode surface so sample volumes of 50 µL to 400 µL can be used. The second was used as part of a flow-through channel chamber; based on an interdigitated electrode (IDE) design. Samples of 15 µL to 90 µL can be applied. The surface of the Au electrode was modified with cysteamine (20 mM for 2 h) and glutaraldehyde (300 mM for 2 h) for the protein binding.

Streptavidin, 1 µg/mL diluted in phosphate saline buffer solution, was then immobilized via the aldehyde groups. After blocking non-specific binding sites with bovine serum albumin, the biotinylated aptamer thrombin-binding aptamer (TBA) was then immobilised. Electrochemical impedance spectroscopy (EIS) was performed frequency range from 100 mHz to 200 kHz.

5.3 DNA

Ahangar and Mehrgardi [68] have fabricated a nano-porous Au electrode (NPGE) from Au CD-Rs for the electrochemical detection of single base mismatches using a ferrocene-modified DNA probe. The Au electrode was prepared from small pieces of CD-R placed in nitric acid to remove the protective layer. This was then secured to the bottom of a Teflon cell with an O-ring. The NPGE was constructed in two steps. Firstly, the Au surface of the CD-R was anodized in a phosphate buffer solution (pH 7.4) for 3 minutes, by applying a potential of +3.6 V *vs.* Ag/AgCl. Following this the anodized Au surface was reduced with 1.0 M of ascorbic acid for 5 minutes reducing the gold oxide to metallic gold. The unprotected modified DNA was drop coated onto the Au CD electrode and with $MgCl_2$ and NaH_2PO_4. An aqueous solution of 6-mercaptohexanol was then added to the modified electrode surface and the electrode washed. A 4 µM aliquot of the target DNA was then introduced to the electrode surface with 5 µL of 2 M $MgCl_2$. The electrode and sample solution were then left to incubate for 7 hours in the dark and examined electrochemically. Differential pulse voltammetry was utilised to quantify the ferrocene carboxylic acid labelled DNA present at the Au electrode. An oxidation peak with a peak potential of +0.2 V (*vs.* Ag/AgCl) was reported and levels as low as 25 pM could be detected.

5.4 Glucose

Glucose is a very important analyte; be it for monitoring blood levels by diabetics or in the food and beverage industries. A large number of enzyme based sensors have been developed and commercialised to meet these demands. Recently, Chen *et al*

[69] have reported the direct non-enzymatic determination of blood glucose levels at a Ag electrode manufactured from a CD-R. Initial voltammetric investigations on different glucose levels were recorded over the potential range from −0.7 V to 0 V. A concentration dependent voltammetric wave was record, with a peak potential (Ep) of -0.5 V. Using amperometry in a pH 6.5 phosphate buffered solution with an applied potential of -0.50 V a linear range of 0.5–13 mM (r = 0.996) was obtained. The authors postulate that this electrochemical response is due to an electro-absorbed glucose intermediate species on the surface of the Ag electrode this species can be then oxidised resulting the voltammetric wave reported. A tentative mechanism for this oxidation has been given and it is thought to occur at the carbon C1 atom of glucose [70]. The possibility of determining glucose levels in human blood sample was investigated. A 15 μL aliquot of human blood obtained from healthy fasting humans subjects was mixed with an equal volume of 0.1 M phosphate buffer. Amperometric measures showed glucose recoveries of 95.7 % to 101.3 % and the accuracy of the readings evaluated by comparison to measurements made by diabetic patients and by hospital staff using a glucose oxidase based biosensor (YSI Model 2300 Glucose Analyzer, Yellow Springs Instruments, Yellow Springs, OH). Good agreement was reported between the two devices and it was concluded that the sensor showed the possibility of a non-enzymatic method for the determination of human blood glucose levels.

5.5 Ascorbic Acid

Muñoz *et al* [71] developed an amperometric flow injection system of the determination of ascorbic acid. A Au CD modified by the electrodeposition of Pt by electrochemical deposition of Pt (K_2PtCl_4 solution 2 mM, pH 4.8 at -1.00 V for 15 min). Spectroscopic investigation showed a uniform platinum deposit, with a very rough surface. Cyclic voltammetric investigations of unmodified electrodes in a pH

4 buffer showed no response for ascorbic acid over the potential range 0.0 to +0.8 V. However, once electroplated with Pt a broad oxidation peak was recorded (Ep +0.45 V). The possibility of applying this response for the determination of ascorbic acid was explored by determining its concentration in commercial pharmaceutical tablets. The results obtained were identical than the ones obtained by the classical iodometric method. Calibration plots were linear over the range of 1–10 μM with a relative standard deviation of 1 % with a corresponding detection limit of 0.78 μM reported. The modified electrodes were stable for at least one week under reportedly intense usage. The possibility of utilising a single channel flow cell was also investigated, using an aquarium air pump to propel the moving phase. Using amperometric detection with an applied potential of +0.40 V (*vs.* Ag/AgCl), the effect of flow rate was investigated over the range 0.5 to 9.0 mL/min The signal was reported to increase with flow rate from 0.5 to 2.5 mL/min and then remained constant at flow rates above this, with a flow rate of 2.5 mL/min being reported as being optimal. The incomplete dissolution of other constituents of the tablets were reported not to affect the amperometric analysis. Eight different ascorbic acid containing pharmaceutical formulations were investigated and coefficients of variation ranging between 0.5 and 2.3 % were reported.

Latino *et al* [72] have utilised a Au CD for the determination of ascorbic acid. The CD was chemically etched in a 50 % aqueous solution of nitric acid at 80 °C to remove the upper protective layer to expose the Au metal sublayer. The layout of the electrodes was designed using computer aided design (CAD). A LPKF Protomat S103 rapid prototyping system was used to outline the design of the electrodes on the prepared Au CD substrate. The designed electrodes in the Gerber format were then processed by milling machine. Two different sensors were fabricated; the first as a "serpentine" type temperature sensor which was shown to give a linear response with temperature from room temperature (*ca.* 25 °C) up to 65 °C. The

second type was developed for the voltammetric determination of ascorbic acid. Cyclic voltammetric investigations were undertaken in 0.1 M KCl. A characteristic oxidation peak was reported at +0.8 V. Using a sample volume of 150 µL the flow system allowed for determinations of 1 µM of the analyte to be made with the possibility of making 90 determinations per hour.

5.6 Dopamine

Dopamine has been determined at electrodes fabricated from Au CD-R disks (Mitsui MAM-M Standard Gold CD-R) modified using the technique of xurography [73]. The layout of the electrodes was drawn using the CorelDraw 11.0 software package and the electrodes fabricated using a cutting plotter. Using this approach it was reported to be possible to fabricate circular structures as small as 447±12 µm (n=3) in diameter and square shaped structures (microchannels) down to 107±13 µm (n=3) in width.

The electrochemical performance of these devices was investigated by square wave voltammetry using a 40 µM solution of ferricyanide with electrodes with increasing nominal diameters from 0.50 to 3.0 mm. Well-defined peaks with an Ep values of +0.218 V was reported. The peak current showed a linear relationship with electrode area.

Dopamine is reported to promote Au surface passivation, factor that was investigated to illustrate the important advantage of using disposable electrodes in such applications. However, no linear relationship between peak current and dopamine concentration was observed when performing the same experiments using a single electrode. A gradual decrease in the current was reported while increasing the concentration of dopamine. This behaviour is commonly observed due to the formation of a polymeric film on the electrode surface. However, by using a new electrode for each determination this effect was overcome and a linear

response for dopamine over the concentration range 20 to 100 μM by square wave voltammetry.

5.8 Cysteine

At Au electrodes similar issues are seen with other strongly adsorbed species such as cysteine to that reported for dopamine. However, the disposable nature of the Au CD electrodes has been shown to avoid these problems. Lowinsohn *et al* [74] have used toner masks laser printed and heat transferred to Au CD surfaces to define the area of the working electrode area. The authors reported that the size of the disc electrodes could be easily controlled and electrodes with radii varying from 0.5 mm to 3.0 mm could be readily fabricated. The authors showed that repeated application of solutions containing cysteine to the same Au electrode resulted in a degradation of response due to adsorption of oxidation products on the electrode surface. This problem was shown to be readily overcome by using a new working electrode for each measurement. Such a situation would be an expensive solution when using conventional Au electrodes. However, Au electrodes fabricated from CD as this case could be treated as disposable and hence can be discarded after each measurement. Using such an approach no degradation of response was reported for the square wave voltammetric determination of cysteine over the concentration range 20 μg/L to 100 μg/L.

5.9 Hydrogen Peroxide

Hydrogen peroxide is an important analyte to measure in a number of different applications, as diverse as electrochemical biosensors, forensic analysis, and agriculture. Recently, several studies have utilised electrochemically roughened Ag CD based electrodes for the electro-catalytic determination of hydrogen peroxide [4,5]. By multiple cyclic voltammetric scanning of the Ag electrode dendritic

nanostructures can be generated on the electrode surface which have been shown to improve the electrochemical performance of the electrodes for the detection of hydrogen peroxide. Lain *et al* [4] have reported the optimum conditions for these roughening electrochemical oxidation–reduction voltammetric cycles to be five cycles of -0.35 V to +0.35 V in a 0.2 M KCl solution at a scan rate of 5 mV/s. Utilising amperometry in stirred solution a linear range of 10.0 µM to 22.5 mM (R = 0.999; n = 19) with an associated detection limit of 6 µM, (s/n = 3) was reported. No interferences in the determination of hydrogen peroxide in the presence of 10 fold ascorbic or uric acid were reported. However, the presence of a fivefold concentration of Fe^{3+} resulted in a 10 % increase in signal current.

More recently, Shafei and Honeychurch [75] have utilised an unmodified Ag electrode manufactured from a DVD-R for the determination of hydrogen peroxide in water. A Verbatim DVD-R was simply mechanically delaminated and the exposed Ag layer used as the working electrode without further modification. A 5 mm working area was defined with dielectric tape and the resulting Ag working electrode was used as part of a three electrode system. Using a cyclic voltammetric waveform, a limit of detection of 78.35 µM (based on three times the standard deviation of the noise) was recorded with a linear range from 0.087 mM to 3.41 mM (R^2 = 0.996) hydrogen peroxide. Figure 4 shows the typical cyclic voltammograms and resulting standard addition plot obtained for a potable water sample. The results indicate that a method based on multiple standard additions was both accurate and precise, obtaining a coefficient of variation of 4.69 % for a water sample fortified with 40.8 mg/L (1.2 mM); levels commonly reported in aquaculture and swimming pools applications.
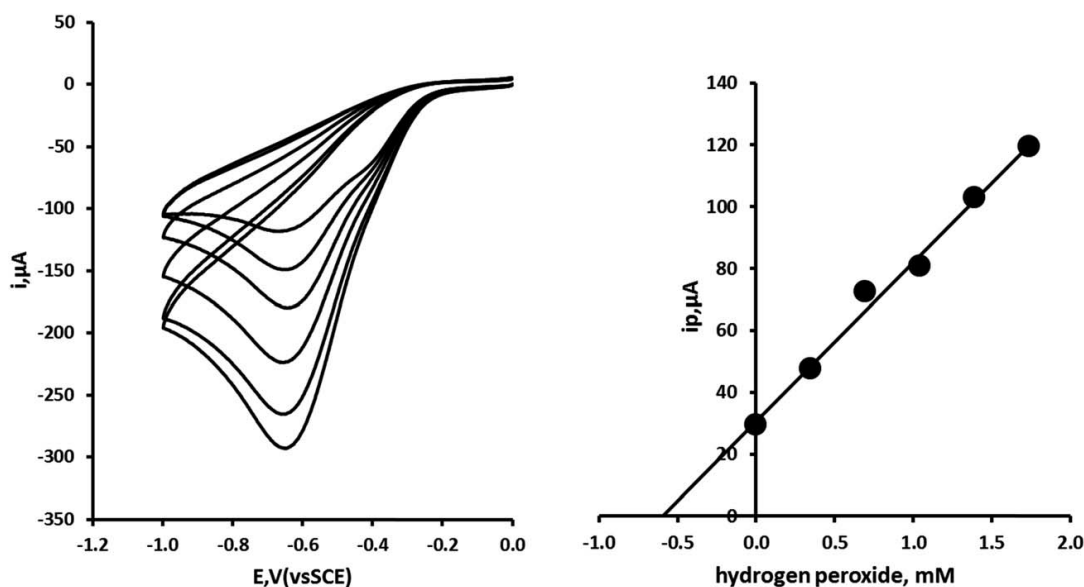
Figure 4. Multiple standard additions of hydrogen peroxide made to water sample fortified with 1.2 mM (40.8 mg/L) hydrogen peroxide. Each addition the equivalent of 348 μM (11.8 mg/L) hydrogen peroxide. Reproduced from [75] with permission from the Royal Society of Chemistry.

Paixão and Bertotti [76] have reported the development of a disposable voltammetric electronic tongue based on an electrode array for the determination of hydrogen peroxide in milk available in the Brazilian market. The addition of hydrogen peroxide to milk is prohibited leading to a demand for an efficient method for monitoring its possible presence in milk samples. The voltammetric tongue array was constructed from Au CD-R and Cu sheet as substrates with sensing elements of Au, Cu and a Au electrodes modified with a layer of Prussian Blue (PB). The individual Au and Cu working electrodes were formed by first printing toner masks to protect the metallic surface. The layout of the electrodes was defined using graphic software (Open Office.org 2.4, Sun Microsystems Inc.). The gold layer of the CD-R was first exposed with HNO_3 solution before the heat-transfer of the toner mask which was laser-printed onto waxed paper. The exposed metal layers (not covered with toner) were removed with iodine/iodide (25 g/L iodine and 100 g/L sodium iodide) and ferrous perchlorate (42 %, w/v) solutions. The toner mask was then removed with acetonitrile. A subset of electrodes were modified with a film of PB formed by potential cycling between -0.5 and +0.7 V (15 cycles) at

100 mV/s in a solution of 1 mM $FeCl_3$, 1 mM $K_3Fe(CN)_6$, 0.2 M HCl and 0.35 M KCl. The possibility of combining two individual working electrodes together as sensing units to identify basic taste substances (quinine for bitterness, sucrose for sweetness, HCl for sourness, and KCl for saltiness) was investigated. Cyclic voltammetric investigations of the four taste standards showed that the Au and PB modified electrodes gave good responses for HCl and KCl. Copper electrodes also showed good responses for both HCl and KCl but were also able to discriminate sucrose from quinine solutions. Further cyclic voltammetric investigations were recorded using this integrated sensor in three samples of untreated homogenized/pasteurized milk in the absence and presence of hydrogen peroxide at 0.015, 0.30 and 3.0 % (v/v). Using principle component analysis the ability of the integrated sensor system to discriminate samples containing hydrogen peroxide was shown to be possible.

5.10 Iodine

Lindino *et al* [77] have determined the concentration of iodate in table salt amperometically using an applied potential of +0.1 V *vs.* Ag/AgCl at Au CD-R based electrodes. The response time after the addition of each aliquot of the sample or standard was reported to be four seconds. The relative deviation between the measurement of iodate in a synthetic sample of salt, was of 0.93 % for a concentration of 4×10^{-5} M. The results showed that the proposed method could be used for determining the iodate in samples of table salt.

Cho *et al* [12] have shown the possibility of utilising an unmodified office desktop ink jet printer to modify both CD-Rs to form a number of different electrode designs. Using such an approach they showed that phospholipid films can be patterned with a lateral resolution of 50 μm. The authors projected that the approach could be effectively used for the commercial production of low-cost

biosensors and electroanalytical devices. To demonstrate the possible applications of using an office inkjet printer for patterning the authors fabricated an iodine sensor by patterning a Au CD electrode array followed by printing phospholipid films across the electrodes. Initial results were not satisfactory because of the low conductivity of phospholipid films, but by using free software (GIMP, http://www.gimp.org) they were able to design a new pattern, covering the entire surface of a gold CD-R with 84 sets of interdigital gold microelectrodes configured in parallel. Each set consisted of four pairs of 200 μm wide Au finger electrodes insulated from the connect pads at both ends; the whole sensor was produced by inkjet printing of an alkanethiolate monolayer with subsequent chemical etching. Current–voltage responses to different concentrations of iodine vapour were generally linear in the voltage range -2.0 to +2.0 V, indicating ohmic conduction behaviour in the phospholipid films. Measurement of the slopes of the current–voltage curves showed a correlation between the conductance of the device and the iodine vapour concentration. The authors explained the change in conductivity in phospholipid films to be due the accumulation of I_2 or I_3^- in the head–head group region of the lipid bilayer.

Richter *et al* [13] have described a method of defining the electrode geometries via the laser printing of designs on wax paper and heat-transferring the toner onto the Au surface of the disc and etching of the Au layer away from the unprinted regions. The toner was then removed with a solvent. The unused electrode areas were then masked with varnish. Repetitive injections (n = 10) of a mixture containing iodide, ascorbic acid, dipyrone, and acetaminophen (20, 200, 500, and 100 μM), were found to give relative standard deviations of 2.9, 4.5, 6.1, and 4.0 %, respectively. Detection limits (S/N = 3) were 0.1, 0.5, 3.1, and 1.1 mM, respectively.

Analyte	Electrode Material	Sample Pre-treatment	Supporting Electrolyte	Measurement Technique	Linear Range	Detection Limit	Sample(s)	Comments	Ref.
H_2O_2	Ag	--	0.2 M pH 7.0 phosphate buffer saline	Amperometry	10.0 μM to 22.5 mM	6 μM	--	Electrochemical roughening of electrode surface by oxidation–reduction voltammetric cycles	[4,5]
H_2O_2	Ag, Verbatim DVD-R	Addition of supporting electrolyte	0.1 M pH 7.2 phosphate buffer	Cyclic voltammetry	0.087 - 3.41 mM	78.35 μM	Potable water	--	[75]
H_2O_2	Au and Au CD modified with Prussian Blue	Milk sample diluted with water	Diluted milk sample	Cyclic voltammetry	--	--	Milk	Voltammetric electronic tongue array. HCl, KCl, quinine and sucrose also investigated	[76]
H_2O_2	Au CD modified with Prussian blue film		0.1 M pH 5.3 phosphate buffer	Amperometry	1.0 μM to 1.2 mM	0.4 μM	--	Prussian blue film formed photochemically from an acidic ferricyanide solution	[78]
Iodine	Au modified with an alkanethiolate self-assembled monolayer	--	--	Conductivity	10 % to 100 % saturated solutions	--	--	Electrodes modified with office inkjet printer	[12]
Iodine,	Au	--	Running	Capillary		0.1, 0.5,	--	Wall jet	[13]

ascorbic, uric acid dipyrone and acetaminophen			buffer of 20 mM boric acid and 12 mM sodium hydroxide (pH 9.2). Cetyltrimethylammonium hydroxide (CTAH; 0.2 mM)	electrophoresis amperometric detection, single electrode (+0.75 V) and dual electrode (E1 +1.0 V, E2 +0.7 V)		3.1, and 1.1 mM for iodide, ascorbic acid, dipyrone, and acetaminophen, respectively		configuration	
Iodine	Au CD			Amperometry, +0.1 V	2×10^{-5} – 1.0×10^{-4} M		Table salt		[77]
Iodine	Au CD	Electrochemically generated iodine	0.5 M KCl or a 1.0 M Na acetate/1.0 M acetic acid buffer solutions	Amperometry. Dual band electrode cell operated in generator – collector model. W1 = 0.5 V, W2 = 0 V. flow rate = 0.7 mL/min		1 µM thiosulphate	--	Dual-in series band electrodes thin layer electrochemical cell. Detection of electrochemically generated iodine by thiosulphate titration.	[79]
Iodide and Ascorbic Acid	Au CD	--	Sodium borate with 0.02 mM cetyltrimethylammonium pH 9.2	Amperometry, +0.9 V (*vs.* Ag/AgCl). Electrophoresis separation voltage, 4.0 kV	Iodide 2–30 mM; ascorbic acid 10–50 mM	Iodine 0.5 µM and Ascorbic Acid 1.8 µM	--	Electrophoresis microchip fabricated from a laser printed double toner layer (DTL)	[18]
Glucose	Ag	15 µL of blood	0.1 M pH 6.5 phosphate	Amperometry, -0.5 V	0.5–13 mM	0.035 mM	Human blood	Direct electrochemic	[69]

		diluted with 15 μL of buffer	buffer				samples	al oxidation of glucose	
Glucose and Ascorbic Acid	Au-Cu-modified electrode prepared by electrodeposition at the gold disk electrode from 0.1 M $CuSO_4$ solution (-0.10 V for 20 min)	Dissolved in deionized water prior to analysis	1.0 M NaOH	Amperometry, flow injection analysis	Up to 1 mM for both glucose and ascorbic acid	--	Pharmaceutical products	Glucose results compared to the Benedict test.	[80]
Ascorbic Acid	Au CD modified by the electrodeposition of Pt	Tablets powdered in a mortar and dissolved in buffer	50 mM pH 4.0 acetate buffer	Amperometry (+0.40 V) flow injection system (2.5 mL/min)	1 - 10 μM	7.8×10^{-7} M	Pharmaceutical formulations		[71]
Dopamine	Au	--	0.1 M NaCl	Square wave voltammetry	20 – 100 μM			A separate new electrode used for each measurement	[73]
Cysteine	Au	--	0.5 M NaCl	Square wave voltammetry	20 – 100 μM		--	A separate new electrode used for each measurement	[74]
DNA	Au CD electrochemical anodised. Modified with ferrocene		2 M $MgCl_2$	Differential pulse voltammetry		25 pM		Detection of single base mismatches	[68]

	carboxylic acid labelled DNA								
Dipyrone	Au	--	0.1 M pH 4.7 acetate buffer	Amperometry (+0.800 V) flow injection system (flow rate of 83 µL/min)			--	Electrode arrays microfluidic flow cells fabricated by printed toner masks	[29]
Dipyrone	Au	Samples dissolved in phosphate buffer	0.05 M pH 7 phosphate buffer	Amperometry (+0.600 V vs Ag/AgCl) flow cell (flow rate 2 mL/min)	1.0 µM – 10 µM	0.1 µM	Commercial pharmaceutical tablets	Good agreement with iodometric analysis.	[81]
Dipyrone, paracetamol and nitrite	Au	Tablets crushed and dissolved in 100 mL of deionized water	0.1 M pH 4.7 acetate buffer	Linear sweep voltammetry	Paracetamol, 0.3 – 2.8 mM; nitrite 20 – 100 µM, dipyrone, up to 1.2 mM	--	Pharmaceutical tablet formulations	Ag glue deposited on the gold surface used as reference electrode	[58]
Paracetamol	Au electrode modified by drop casting a composite consisting of carbon nanotubes		0.1 M pH 9 phosphate buffer.	Differential pulse voltammetry	0.5 - 80 µM	0.01 µM	Tablet, river and waste water samples		[82]

	and copper nanoparticles								
p-Nitroph enol	Au electrode modified with nano-porous Hg/Au amalgam	--	0.05 M pH 5 phosphate buffer	Square wave voltammetry	5 μM – 250 μM	1 μM	River, tap and sea water	--	[83]
Ciclopir ox olamine	Au random microarray	Diluted in buffer.	0.10 M pH 5.0 Britton Robinson buffer.	Amperometry, +0.85 V vs. Ag/AgCl.	0.06 mM – 1.1 mM	3 μM	Pharmaceuti cal products	Good agreement with those found by potentiometri c titration and the labelled values.	[18]
Terbutal ine	Au electrode drop coated with MWCNT in DMF (1.0 mg/mL). Allowed to dry at room temperatur e		0.1 M pH 8.0 phosphate buffer (.086 M K_2HPO_4 and 0.014 M NaH_2PO_4).	Amperometry. Flow electrochemical cell with impingent jet.	3.0×10^{-6} to 5.0×10^{-4} M	5.8×10^{-7} M	Commercial pharmaceuti cal syrup samples	Good agreement obtained with high performance liquid chromatogra phy and capillary electrophores is-tandem mass spectrometry.	[84]
Chlorpr omazine	Au	Formation of a stable cationic radical by electro-	Electrochemi cal oxidation in 0.1 M H_2SO_4; monitored in	Spectroelectrochemist ry and amperometry in a flow cell	Ampero metry, 3.3×10^{-4} - $2.0 \times 10^{-}$	7.6×10^{-5} and 4.1×10^{-5} M for the electroche	In pure form or in Amplictil tablets	--	[85]

		oxidation	*situ* at λ = 524 nm.		^{3} M; Spectroelectrochemically, 1.6×10^{-4} - 2.0×10^{-3} M	mical and spectrophotometric measurements respectively			[]
Promethazine	Au	Formation of a stable cationic radical by electro-oxidation	Electrochemical oxidation in 0.1 M H_2SO_4, +0.850 V. Monitored *in situ* at λ = 524 nm.	Spectroelectrochemistry and amperometry in a flow cell, flow rate 2.0 mL/min	1.0×10^{-6} – 5.0×10^{-3} M	1.3×10^{-6} and 3.0×10^{-5} M for spectrophotometric and electrochemical measurements	pure form or in pharmaceutical formulations	The Spectroelectrochemistry approach could overcome interferences of electroactive compounds such as dipyrone	[86]
o-Tolidine	Au	--	0.125 M acetic acid and 0.250 M $HClO_4$, 0.800 V. Monitored at 438 nm.	Spectroelectrochemical dual electrode flow cell. 1.84 mL/min.	1.12×10^{-5} - 1.12×10^{-4} M	--	--	Cell can fit in standard spectrophotometric cuvette with 1.0 cm optical path	[87]
Paraquat	Au CD	Na_2SO_4 dissolved directly into the water or tea sample and degassed with N_2	0.1 M Na_2SO_4	Square wave voltammetry	2.8×10^{-5} – 27.7×10^{-5} M	Natural water, 21 µg/L	Natural water and commercial tea samples		[88]
Thrombi	Au	Au		Impedance	1.0 -		--	Biosensor	[67]

n		electrode modified with cysteamine, glutaraldehyde, streptavidin and thrombin-binding aptamer.		spectroscopy, 100 mHz to 200 kHz	100 nM				

Table 2. Application of CD and DVD electrodes for the determination of oxidising agents and organic compounds

6. Conclusions

The fabrication of electrodes manufactured from DVDs and CDs has been shown to be versatile, highly reproducible and economic. The simplicity of construction and low cost of planar Au and Ag electrodes allows their use as disposable devices. This offers a number of possible advantages over problems such as electrode fouling and carryover. A number of studies have shown the possibility of being able to modify the exposed metal layer using readily available office printers [7,10,76] or similar techniques [73] or chemically to form self-assemble monolayers [32] of for the addition for functional groups [33]. Beyond the scope of this review, reports have shown the possibility of utilising CDs and DVDs for both sample preparation as well as quantification using approaches such as surface plasma resonance [89], centrifugal microfluidics or so called 'lab-on-a-disc' devices [90-95], DNA microarrays [96]. Their application in the exploitation of solar energy [97] and the development of batteries [98] has also been reported.

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8. References

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