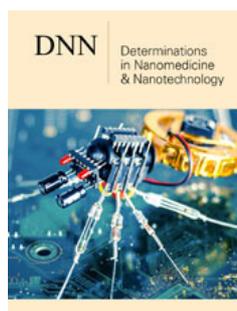


Application of Electro Analytical in Trace Metals Determinations: Environmental and Industrial Samples

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Abstract

Determination of the trace elements in both environmental and industrial sample are of great importance and attractive field for many researchers and scientists, and of high economic and environmental impact. Electro analytical methods show a remarkable sensitivity, broad scope and very low quantitation limit. A review of the modern electro analytical techniques, namely, cyclic, linear sweep, square wave and stripping voltametric techniques, in the trace metals determinations is highlighted. This review focus on the environmental and industrial applications used for each mode of electro analytical techniques.

Keywords: Electro analytical; Cyclic voltammetry; Stripping techniques; Environmental applications, Industrial applications

Abbreviations: DPCSV: Differential Pulse Cathodic-Stripping Voltammetry; PCV: Pyrocatechol Violet; CLSSV: Cathodic Linear Sweep Stripping Voltammetry; DASA: Dihydroxyanthraquinone-3-Sulphonic Acid; HMDE: Hanging Mercury Drop Electrode; LSCSV: Linear Sweep Cathodic Stripping Voltammetry; CTAB: Cetyltrimethylammonium Bromide; TB: Thymol Blue; AdCSV: Adsorptive Cathodic Stripping Voltammetry; SWAdSV: Square Wave Adsorptive Stripping Voltammetry; FI: Flow Injection; CE: Capillary Electrophoresis; HNB: Hydroxynaphthol Blue

Introduction

Trace elements determination in industrial and environmental samples are of high economic and environmental impact, and attractive area of research for many scientists. Modern electrochemical techniques are powerful and versatile analytical techniques that offer high sensitivity, accuracy, and precision as well as large linear dynamic range, with relatively low-cost instrumentation. After developing more sensitive pulse methods, the electro analytical studies are more regularly used on industrial, and environmental applications. However, electro analytical techniques can easily solve many problems of the trace metals determinations with a high degree of accuracy, precision, sensitivity, and selectivity employing this approach. Some of the most useful electro analytical techniques are based on the concept of continuously changing the applied potentials to the electrode-solution interface and the resulting measured current (Kissinger and Heineman 1996; J Wang 2006; Smyth and Vos 1992; Ozkan, Uslu and Aboul-Enein 2003; Bard and Faulkner 2001; Kellner et al. 2004; Hart 1990) [1]. Most of the chemical compounds were found to be as electrochemically active [1], During the past years, there has been extraordinary acceleration of progress in the discovery, synthesis, sensitive electrochemical analysis [2-9]. The aim of the present review is to give industrial, biological, and environmental applications used for each

mode of electro analysis techniques, namely, cyclic, linear sweep, square wave and stripping voltametric techniques. An attempt was made to choose some readily available publications describing some advances in methodology and applications.

Electroanalytical Application for the Trace Determination of Metals

Modern electroanalytical methods show a remarkable sensitivity, broad scope and very low quantitation limit. Different electroanalytical methods, especially stripping analysis, widely used for the trace metals determination in environmental, industrial and in biological samples. Various stripping techniques were used for the determination of 30 trace elements [10-75].

Environmental Samples

Square-wave voltammetric determination of eight elements viz. Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II), Cr(VI), and Mo(VI) in soil and indoor-airborne particulate matter has been examined and optimized [2]. It was found that the square-wave anodic stripping voltammetry is the conventional technique for the determination of Zn(II), Cd(II), Pb(II), and Cu(II), but square wave adsorptive cathodic stripping voltammetric method is used for the determination of Co(II), Ni(II), Mo(VI) and Cr(VI). The detection limits of these metal ions were 0.03, 0.4, 0.04, 0.1, 0.15, 0.05, 0.2, and 3.2 $\mu\text{g}/\text{kg}$ for Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II), Cr(VI), and Mo(VI), respectively. A method was described for the determination of selenium in soils and plants by Differential Pulse Cathodic-Stripping Voltammetry (DPCSV) at a hanging mercury-drop electrode [21]. An ultrasensitive adsorptive catalytic stripping (voltammetric and potentiometric) procedure for determining trace levels of chromium in the presence of cup Ferron is described [22]. A preconcentration time of 1min results in a detection limit of 1.0 ngL^{-1} . The stripping potentiometric scheme allows convenient measurements of chromium in the presence of dissolved oxygen. The identical stripping response for Cr(III) and Cr(VI) solutions makes the method applicable to the measurement of the total chromium content. The simultaneous determination of chromium and uranium is illustrated. The merits of the proposed procedure are demonstrated by the analysis of soil and groundwater samples. A differential pulse stripping voltammetry method for the trace determination of Mo(VI) in water and soil has been developed [23]. The suggested procedure can be used for determining Mo(VI) in the range 5×10^{-10} to $7 \times 10^{-9}\text{M}$, with a detection limit of $1 \times 10^{-10}\text{M}$ (4min accumulation). Direct and simultaneous voltammetric analysis of heavy metals in tap water samples at Assiut city was developed [24]. Tap water samples are analyzed to determine the total content of Cd(II), Cu(II), Pb(II) and Zn(II) by Differential Pulse Anodic Stripping Voltammetry (DPASV) while Ni(II) and Co(II) are determined by a new simple Differential Pulse Adsorptive Stripping Voltammetry (DPAdSV), using Dimethylglyoxime (DMG) as the complexing agent. This method uses sodium sulfite as the supporting electrolyte, which facilitates the removal of oxygen interference without the traditional necessity of purging with inert gas. Graphite Electrodes Modified by 8-hydroxyquinolines

exhibited an affinity to chelating Cu(II) forming a Cu(II) complex, which was employed for Cu(II) trace analysis [25]. A differential pulse voltammetry, combined with a preconcentrating-stripping process and a standard addition method was used for the analysis. A detection limit for trace copper determination in water, such as $5.1 \times 10^{-9}\text{molL}^{-1}$, was obtained. Catalytic adsorptive stripping voltammetry determination of ultra-trace amount of Mo(VI) is proposed [26]. The method is based on adsorptive accumulation of the Mo(VI)-Pyrocatechol Violet (PCV) complex on to a hanging mercury drop electrode, followed by reduction of the adsorbed species by voltammetric scan using differential pulse modulation Mo(VI) can be determined in the range 1×10^{-3} -100.0 ngmL^{-1} with a limit of detection of 0.2 pgmL^{-1} . The procedure was applied to the determination of Mo(VI) in mineral water and some analytical grade substances with satisfactory results. Differential pulse adsorptive cathodic stripping voltammetric method has been developed for trace determination of Mo(VI) in presence of alizarin red S as complexing agent [27]. The peak current is proportional to the concentration of Mo(VI) over the concentration range of 1-25ppb with a detection limit of 0.25ppb. The method has been applied to the determination of Mo(VI) in water samples.

Carbon paste electrode modified with diacetyldioxime used for the simultaneous determination of Pb(II) and Cd(II) [28]. Calibration graphs were linear in the concentration ranges of 1.0×10^{-7} - $1.5 \times 10^{-5}\text{mol/L}$ (Pb(II)) and 2.5×10^{-7} - $2.5 \times 10^{-5}\text{mol/L}$ (Cd(II)), respectively. For 5min preconcentration, detection limits of $1 \times 10^{-8}\text{mol/L}$ (Pb(II)) and $4 \times 10^{-8}\text{mol/L}$ (Cd(II)) were obtained. The diacetyldioxime modified carbon paste electrode was applied to the determination of Pb(II) and Cd(II) in water samples. Electrochemical method is described for the determination of inorganic arsenic in water at the $\mu\text{g}/\text{L}$ level, applicable in the laboratory and in the field, based on differential pulse cathodic stripping voltammetry [29]. Determination of total AS is performed by reducing As(V) to As(III) using sodium meta-bisulfite/sodium thiosulfate reagent stabilized with ascorbic acid. As(V) is quantified by difference. The detection limit was 0.5 $\mu\text{g}/\text{L}$ with a linear range from 4.5 to 180 $\mu\text{g}/\text{L}$. Adsorptive stripping voltammetric determination of Pb(II) in presence of 2,2'-dipyridyl-2,4-dioxybenzoic acid molecular complex was proposed [30]. The compounds formed by Pb(II) and 2,2'-dipyridyl-2,4-Dioxybenzoic Acid Molecular Complex (DDOB) are adsorbed on the mercury electrode. Linear dependence between the current and Pb(II) concentration in the solution was observed in the range 1.2×10^{-8} - 3.5×10^{-6} diffusion. This method natural waters. -7M Pb(II), for accumulation time 60s and stationary was applied for the determination of the Pb(II) in the anodic stripping voltammetric method with a mercury thin film electrode is reported for the establishment of baseline concentrations of Cd(II), Pb(II) and Cu(II) in natural waters [31]. A voltammetric method based on chelate adsorption at the hanging mercury electrode is described for the simultaneous determination of Cu(II), Pb(II), Cd(II), Ni(II) and Co(II) by adsorptive stripping voltammetry using quercetin as complexing agent [32] The method was applied successfully for the simultaneous determination of the

five metals in tap water samples. Differential pulse anodic stripping voltammetry was used for the determination of Zn(II), Cd(II), Pb(II) and Cu(II) in the underground water [33]. The trace elements levels found are in the ranges 0.01-0.37, 1.27-49.5, 0.41-29.8 and 0.13-98.09 µg/L for Cd(II), Cu(II), Pb(II) and Zn(II), respectively. The method was applied with satisfactory results for the determination of these metals in underground water samples.

Adsorptive cathodic stripping voltammetric determination of Mo(VI) in synthetic solutions and environmental samples was proposed [34]. This method is based on controlled adsorptive preconcentration of Mo(VI) species on the Hanging Mercury Drop Electrode (HMDE) using mixtures of nitrate and phosphate as supporting electrolytes. The method used is Cathodic Linear Sweep Stripping Voltammetry (CLSSV). The detection limit found was 1×10^{-8} M using 120s. as accumulation time. This method has been applied for the determination of Mo(VI) in environmental samples; e.g., soil, natural water and indoor airborne particulate. Determination of iron in seawater using cathodic stripping voltammetry preceded by adsorptive collection with the hanging mercury drop electrode [35]. The detection limit for the determination of iron in seawater of pH 6.9 was 6×10^{-10} M in the presence of 4×10^{-4} M catechol and after a collection period of 3 minutes. The peak current increased linearly with the metal concentration up to about 5×10^{-8} M, but the linear range could be increased by using a shorter collection period. Direct determination of sub-nanomolar levels of Zn(II) in seawater by cathodic stripping voltammetry is presented [36]. The zinc complex with ammonium pyrrolidine dithiocarbamate is adsorbed on a hanging mercury drop electrode and the reduction current of zinc is measured by voltammetry. The detection limit for Zn(II) is 3×10^{-11} M, with 10-min collection time. Dissolved Al(III) in seawater and freshwater is determined by cathodic stripping voltammetry preceded by adsorptive collection of complex ions with 1,2-Dihydroxyanthraquinone-3-Sulphonic Acid (DASA) on the hanging mercury drop electrode [37]. Direct determination of dissolved Co(II) and Ni(II) in seawater by differential pulse cathodic stripping voltammetry preceded by adsorptive collection of cyclohexane-1,2-dione dioxime complexes [38]. Detection limit for Co(II) and Ni(II) depend upon reagent blanks and are 6pM and 0.45nM, respectively, for 15-min adsorption periods.

Complex ions of Mo(VI) with 8-hydroxyquinoline (oxine) are shown to adsorb onto the hanging mercury drop electrode [39]. This property forms the basis of a sensitive electrochemical technique by which dissolved Mo(VI) in seawater can be determined directly. The peak current-Mo(VI) concentration relationship is linear up to 3×10^{-7} M; the detection limit is 4nM. Procedures are presented to determine simultaneously Cu(II), Pb(II) and Cd(II) in seawater by differential pulse cathodic stripping voltammetry preceded by adsorptive collection of complexes with 8-hydroxyquinoline (oxine) onto a Hanging Mercury Drop Electrode (HMDE) [40]. The limits of detection for a 1 min stirred adsorption time are 0.12nM Cd(II), 0.3nM Pb(II) and 0.24nM Cu(II). A sensitive stripping voltammetric procedure for determining titanium is described [41]. There is a linear relationship between the preconcentration time and peak height at

low surface coverages. With a 5min preconcentration period the detection limit is 7×10^{-10} M. The merits of the described procedure are demonstrated in the analysis of sea, river and rain waters. Ti(IV) dissolved in sea water can be determined using adsorptive cathodic stripping voltammetry in the presence of mandelic acid [42]. The sensitivity of the voltammetric technique was thus improved by a factor of 20, and the limit of detection was lowered to 7pM with 60s adsorption, sufficiently low to determine Ti(IV) in water of oceanic origin. Direct electrochemical determination of dissolved vanadium in seawater by cathodic stripping voltammetry with the hanging mercury drop electrode [43]. Polarographic measurements showed that catechol complexes of V(V) adsorb onto the hanging mercury drop electrode. This property forms the basis of a sensitive electrochemical technique by which dissolved vanadium in seawater can be determined directly. The limit of detection is 0.3nM vanadium after a 2-min collection with a stirred solution, which is decreased further to 0.1nM after a 15-min collection. A procedure for the direct determination of iodide in seawater is described [11]. Using cathodic stripping square wave voltammetry, it is possible to determine low and subnanomolar levels of iodide in seawater, freshwater, and brackish water. The minimum detection limit is 0.1-0.2nM (12 parts per trillion) at a 180-s deposition time.

Industrial Samples

A highly sensitive and selective stripping voltammetric procedure for the determination of uranium (VI) based on the adsorption properties of dioxouranium (II)-phthalate complexes onto hanging mercury drop electrode was developed [12]. The reduction current of adsorbed complex ions of U(VI) was measured by both linear sweep (LSCSV) and Differential Pulse Cathodic Stripping Voltammetry (DPCSV). As low as 2×10^{-9} mol dm⁻³ (0.5 µg/L) and 2×10^{-8} mol dm⁻³ (4.8 µg/L) with accumulation time 240 and 120s using DPCSV and LSCSV, respectively, have been determined successfully. The application of this method was tested in the determination of uranium in super-phosphate fertilizer. Application of orthogonal functions to differential pulse voltammetric analysis was suggested [13].

The study was extended to Differential Pulse Cathodic Stripping Voltammetry (DPCSV) for the simultaneous determination of tin and lead. The stripping voltammetric analysis data processed by orthogonal functions and the first-derivative (1D) methods were successfully applied to the simultaneous determination of both metals in canned soft drinks. Differential Pulse Cathodic Stripping Voltammetry (DPCSV) was used to determine ultra-trace platinum in gasoline after wick bold combustion and subsequent UV digestion [14]. Cathodic stripping voltammetry combined with the Osteryoung square-wave mode at the glassy carbon electrode gave rise to both sensitivity and selectivity of the determination of manganese in some industrial samples [15]. The detection limit with 5 min accumulation is 0.022 µg/L. Simultaneous determination of manganese in presence of Cu(II), Pb(II) and Zn(II) could be easily done using anodic stripping voltammetry at pH 4. Bismuth film electrodes were prepared ex-situ by pulsed

potential electrodeposition. The analytical performances of these electrodes for adsorptive cathodic stripping voltammetry of nickel were evaluated in nondeaerated solutions using dimethylglyoxime as complexing agent [16]. Linear calibration curves were obtained for Ni^{2+} concentrations ranging from 1×10^{-8} - $1 \times 10^{-7} \text{molL}^{-1}$ and from 1×10^{-7} - $1 \times 10^{-6} \text{molL}^{-1}$ with relative standard deviations of 5% ($n=15$) at $1 \times 10^{-7} \text{molL}^{-1}$ level. The analytical methodology was successfully applied to monitor Ni^{2+} content in industrial electrolytic baths, ground water and tap water.

Differential Pulse Cathodic Stripping Voltammetry (DPCSV) and Linear Sweep Cathodic Stripping Voltammetry (LSCSV) were used for the determination of trace amounts Cr(VI) ions in neutral phosphate media [17]. Detection limit was $5 \times 10^{-9} \text{molL}^{-1}$ and $1 \times 10^{-9} \text{molL}^{-1}$ using LSCSV and DPCSV, respectively. Differential pulse cathodic and anodic stripping voltammetry were applied for the determination of trace ions Cd(II), Co(II), Cu(II), Pb(II), Mn(II), Ni(II) and Zn(II) which are found in different grades of common salt as contaminants [19]. A procedure for the determination of lead in paints by differential-pulse anodic-stripping voltammetry is presented [44]. Differential pulse anodic stripping voltammetry with a hanging mercury drop electrode has been used for the determination of trace amounts of Cu(II), Cd(II), Pb(II) and Zn(II) ions in white cane sugar [45,46]. Trace amounts of Zn(II), Cd(II) and Pb(II) were determined in refined beet sugar by Differential Pulse Anodic Stripping Voltammetry (DPASV) at a hanging mercury drop electrode [47].

The procedure was applied to the determination of toxic elements in commercial beet sugar samples and levels of metals below 35mgkg^{-1} Pb(II), 80mgkg^{-1} Zn(II) and 10mgkg^{-1} Cd(II) were found. Determination of heavy metals (Cu(II), Cd(II), Pb(II) and Zn(II)) in concentrated refined sugar and raw syrups with differential pulse polarography and anodic stripping voltammetry was described [48]. Using differential pulse polarography, trace determinations down to 10^{-7}M were measured. But using anodic stripping voltammetry at a mercury film electrode, it was found that the refined sugar of alimentary grade contained: 57 Cu(II), 34 Zn(II), 1 Cd(II), and 6 Pb(II) $\mu\text{g/kg}$ of dry sugar. Anodic stripping voltammetry with a hanging mercury drop electrode was used for the determination of trace amounts of Zn(II), Pb(II) and Cu(II) in sugar cane spirit from different sources: commercial, oak-cask matured and home-made [49]. Experiments have been carried out to assess the potential of differential pulse voltammetry and potential stripping analysis for determining Pb(II), Cu(II) and Cd(II) directly in dissolved honey samples [50]. Se(IV) is determined by differential pulse anodic stripping voltammetry using gold electrodes [51]. A wide linear response range 0.5 - 291ng mL^{-1} , was obtained using a 5.0mm diameter gold electrode.

Mo(VI) is determined by anodic stripping voltammetry using a carbon paste electrode modified in situ with Cetyltrimethylammonium Bromide (CTAB) [52]. Differential Pulse Anodic Stripping Voltammetry exploiting the reoxidation signal is used for the determination of trace levels of molybdenum(VI). Linearity between current and concentration exists for a range of

0.5 - $500 \mu\text{gL}^{-1}$. Mo(VI) with proper preconcentration times; the limit of detection is $0.04 \mu\text{gL}^{-1}$ with an accumulation period of 10min. A chemically modified carbon paste electrode was developed for the determination of silver by incorporating the strong acid ion-exchanger into a conventional graphite-Nujol oil paste using by square wave anodic stripping voltammetry [53]. For 5 minutes of accumulation, the linear range was from $1.62 \mu\text{gL}^{-1}$ to 0.8mgL^{-1} with a detection limit of $0.27 \mu\text{gL}^{-1}$. Another type of chemically modified carbon paste electrode was suggested for the determination of silver [54]. Using differential pulse stripping voltammetry, the appropriate calibration graph for Ag(I) was obtained between $5 \times 10^{-7} \text{M}$ and $1.5 \times 10^{-6} \text{M}$ and detection limit was $2 \times 10^{-7} \text{M}$. Determination of lead and antimony in firearm discharge residues on hands by anodic stripping voltammetry using a mercury-coated graphite electrode are established [55]. Anodic stripping voltammetric determination of trace amounts of titanium has been studied using glassy carbon electrode modified with Thymol Blue (TB) [56]. The method has been successfully applied to determine titanium in two standard reference material portland cement samples, then to portland cement and cement clinker.

A voltammetric method has been used for the determination of the contents of toxic heavy metals in domestic waste and in compost produced from it [57]. Cu(II), Pb(II), Zn(II) and Cd(II) were determined in wet-digested samples of domestic waste, compost produced of that waste and in compost mixed with sewage sludge by anodic stripping voltammetry. An indirect voltammetric method is described for determination of cyanide ions and hydrogen cyanide, using the effect of cyanide on cathodic adsorptive stripping peak height of Cu-adenine using mercury electrode [58]. The detection limit was obtained as $1 \times 10^{-8} \text{M}$ for 60s accumulation time. The method was applied to the determination of cyanide in various industrial waste waters such as electroplating waste water and also for determination of hydrogen cyanide in air samples. Simultaneous determination of Cu(II), Zn(II) and Pb(II) by adsorptive stripping voltammetry in the presence of morin was suggested [59].

With an accumulation time of 60s, the peak currents are proportional to the concentration of copper, lead and zinc over the 1-60, 0.3-80 and 1-70ng/mL range with detection limits of 0.06, 0.08 and 0.06ng/mL, respectively. The procedure was applied to the simultaneous determination of Cu(II), Zn(II) and Pb(II) in some real and synthetic artificial real samples. Ni(II) and Co(II) have been determined simultaneously by means of Adsorptive Cathodic Stripping Voltammetry (AdCSV) in a computerized flow injection system [60]. The selectivity of the method was demonstrated for the analysis of high purity iron. A voltammetric method is presented for the determination of trace levels of Cr(VI) in the presence of cupferron as ligand [61]. This method based on using Square Wave Adsorptive Stripping Voltammetry (SWAdSV) in conjunction with the electrochemical batch injection analysis technique at mercury thin-film electrodes. An analytical method has been developed for the determination of dissolved chromium at concentrations less than $2 \mu\text{g/L}$ in PWR coolant by differential-pulse adsorptive stripping voltammetry at a hanging mercury drop electrode [62].

Mo(VI) has been determined by differential-pulse adsorptive stripping voltammetry in a pH 2 phosphate buffer utilising the strong adsorption of 12-molybdophosphoric acid at a hanging mercury drop electrode [63]. Calibration graphs are rectilinear up to the 7×10^{-7} M Mo(VI). A clearly defined stripping peak was observed at the 5.6×10^{-9} M level with 2 min accumulation. Adsorptive stripping voltammetry at a static mercury drop electrode for the determination of Al(III) and Fe(III) in portland cement has been employed [64]. An analytical procedure for the determination of Fe(III) and total iron in wines based on adsorptive stripping voltammetry is described [19]. Fe(III) was determined by using Solochrome Violet Red as chelating agent while catechol was used for the determination of the total iron content.

A sensitive stripping voltammetric procedure for quantifying thorium is described [65]. The chelate of thorium with the azo dye mordant blue 9 is adsorbed on the hanging mercury drop electrode. The detection limit is 4×10^{-10} M (4-min accumulation), a linear current-concentration relationship is observed up to 1.3×10^{-7} M. Square Wave Adsorptive Stripping Voltammetric Method for the determination of Ti(IV) is described [66]. The method is based on Ti(IV) complexed with Hydroxynaphthol Blue (HNB) at the static mercury drop electrode. The limit of detection was found to be $0.18 \mu\text{g/L}$ and the limit of determination to be $1.09 \mu\text{g/L}$, both using 30s of preconcentration time. Simultaneous determination of tin and lead by differential pulse polarography with addition of hyamine-2389 is described [67]. Calibration plots are linear up to 5×10^{-5} M for tin and 1.3×10^{-4} M for lead, with detection limits of 8.4×10^{-7} M and 2.4×10^{-7} M, respectively. Simple methods are proposed for the determination of tin in solders and canned fruit juices.

Traces of Fe(III) were determined by differential pulse polarography in solar-grade silicon [68]. Differential pulse polarography provides a detection limit of about $0.15 \mu\text{g g}^{-1}$ with a precision of 1-2% and linear calibration graphs up to $0.5 \mu\text{g mL}^{-1}$ Fe(III).

Differential pulse polarographic determination of Cr(VI) in semiconductor gallium arsenide based on the catalytic current produced by nitrate in the electrolytic reduction of the Cr(VI)-diethylenetriaminepentaacetate complex [69]. This method is suitable for determinations of Cr(VI) at levels as low as about $1 \mu\text{g g}^{-1}$ with about 50mg of sample. Mo(VI) was determined in steel by differential-pulse polarography [70]. The method is applicable to the determination of molybdenum in the 0.001-5% of Mo(VI) range and good agreement is reported for a number of certified British Chemical Standard and commercial steels. Ternary mixtures of metals can be resolved by using the ratio derivative polarography without the need for any pre-separation step [71,72]. The method is based on the simultaneous use of the first derivative of ratios of polarograms and measurements of zero-crossing potentials. The method has been successfully applied for resolving ternary mixtures of Cu(II), Cd(II) and Ni(II), which have overlapped polarograms. The concentration ranges to be determined are $0.30\text{-}1.40 \text{mg L}^{-1}$

for Cu(II), $0.90\text{-}4.50 \text{mg L}^{-1}$ for Cd(II) and $0.20\text{-}1.20 \text{mg L}^{-1}$ for Ni(II). An electrochemical method for the quantitative determination of boron in minerals and ceramic materials is described [73]. It is based on the abrasive attachment of mixtures of ZnO plus sample to modified graphite electrodes. A method for determining trace level of V(V) has been developed [74]. The reaction is the polarographic reduction of the bromate, catalyzed by this metal ion, in the presence of cupferron. A linear current-concentration relationship is observed between 2×10^{-8} and 3×10^{-7} M, with a detection limit of 6×10^{-9} M. The procedure is very selective and has been successfully applied to a certified steel sample.

Voltammetric determination of the iodide ion with a quinone copper(II) complex modified carbon paste electrode employing linear sweep and differential pulse voltammetry [75]. Using linear sweep voltammetry, a calibration curve was attained over the concentration ranges 1×10^{-4} – 2.5×10^{-6} M of the iodide ion at deposition time of 10min, with the detection limit 1×10^{-6} M. Using differential pulse voltammetry, linear response range for the iodide ion was between 10^{-6} and 10^{-8} M, and the detection limit was 1×10^{-8} M. This method was evaluated by analyzing the iodide ion content in a commercial disinfectant.

Conclusion

The previous survey shows that the number of publications dealing with the application of some selected modern electrochemical techniques (voltammetric techniques) to determine trace metals in industrial, and environmental samples. The importance of such applications increased steadily, and this due to the following advantages:

- Voltammetry coupled with different separation methods such as (HPLC, Flow Injection (FI) and Capillary Electrophoresis (CE)) enhancing the analytical properties for complex mixtures in different compounds.
- Only small volumes of samples are necessary, and short analysis time.
- Electroanalytical stripping procedures have been developed for the measuring down to sub- $\mu\text{g/L}$ level.
- These techniques have been developed for various cations, anions and organic molecules.
- Electroanalytical techniques (specially stripping analysis) are well known as excellent procedures for the determination of trace chemical species.
- The developed stripping voltammetric methods are simple, time saving, selective and more sensitive for the simultaneous determination of trace substances.
- Electroanalytical methods especially square wave voltammetry is a very sensitive and rapid analytical method due to it is high scan rate in all cases where the reacting species is accumulated by adsorption on the electrode surface.

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