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# ADSORPTIVE STRIPPING VOLTAMMETRY IN TRACE ANALYSIS

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# Adsorptive stripping voltammetry in trace analysis

Abstract - Adsorptive stripping voltammetry enables the determination of organic compounds and metal complexes exhibiting adsorption properties in the concentration range from $1.10^{-6}$ to $1.10^{-10}$ mol $L^{-1}$. A survey of this technique and its applications is given.

## 1. INTRODUCTION

In trace analysis, mainly of heavy metal ions, anodic stripping voltammetry (ASV) is popular because of the low limit of determination - ranging to sub ppb concentrations, its accuracy and precision, as well as the low cost of instrumentation for this analytical method. ASV is based on previous electrolytical accumulation of the compound to be determined on the working electrode, followed by voltammetric dissolution (oxidation) of the reduced substance formed. In addition, some anions or organic compounds can be accumulated on a mercury electrode to form an insoluble compound with the mercury ions obtained by dissolution of the mercury electrode at positive potentials. In this type of cathodic stripping voltammetry (CSV), the reduction process of the mercury compound on the electrode surface is studied. The most important step, leading to a substantial increase in the sensitivity in both types of methods is electrolytic accumulation of the species on the working electrode (refs. 1,2).

In addition to the electrolytic process described above, some other principles can be used for accumulation of the substance to be determined. One of these is adsorption. Many organic compounds exhibit surface-active properties that are manifested by their adsorption from solution onto the surface of a solid phase. This phenomenon forms the basis for adsorptive stripping voltammetry (AdSV), where the species to be determined are accumulated on the electrode by adsorption. The first description of this method was published many years ago in connection with the observation that the faradaic response increases after adsorptive accumulation of sulphur (ref. 3), poorly soluble inorganic compounds, alkaloids (ref. 4) and some benzophenones (ref. 5) on a mercury electrode. The adsorptive accumulation of the reduction products of methylene blue at a hanging mercury drop electrode (HMDE) leading to an increase in the height of the anodic polarographic peak in dependence on the accumulation time is described in ref. 6,7. Similar measurements performed with a graphite electrode are described in ref. 8. Further development of this method, primarily for practical applications, was closely connected with the development of other electrodes, such as various types of carbon electrodes and static mercury electrodes.

From the definition of AdSV it follows that this method is characterized by the nonelectrolytic nature of the accumulation process, where adsorption plays an important role. The adsorption of the analyte itself is, however, not the only way of accumulation in AdSV. The reaction of a metal ion to be determined with a suitable reagent may lead to the formation of a complex which is adsorbed on the surface of the electrode, or the reaction of a metal ion with the reagent adsorbed on the electrode surface, represent other two ways of adsorptive accumulation which is utilized for the determination of metals. In AdSV determinations of reducible organic compounds the deposit is stripped off during a cathodic potential scan similarly as in CSV. In CSV the accumulation process is, as mentioned above, connected with an electrolytic process: the formation of an insoluble salt on the electrode surface resulting either from the reaction between the electrochemically oxidized analyte and a reagent

(determination of Mn, Pb, Co), or from the reaction between the analyte and electrochemically oxidized material of the electrode (determination of $Cl^-$, $Br^-$, $S^{2-}$ and organic SH-compounds). In CSV, where the analyte reacts with the oxidized electrode material, the adsorption of the formed compound plays often a certain role in the accumulation process. In spite of the fact that the accumulation process is not fully of electrolytic nature (and in many cases the accumulation mechanism is not known in details) these methods are reffered in the literature as CSV methods. Another type of nonelectrolytic accumulation in stripping voltammetry is the chemical interaction of the analyte with a modified electrode surface. As the accumulation mechanism is complex in this case and differs at different CME, these methods are commonly classified as stripping voltammetry with the use of CME and here are briefly considered only such methods, where the accumulation is achieved by adsorption.

AdSV can be employed in the trace analysis of a wide variety of organic compounds exhibiting surface active properties. When the given compound contains an electrochemically reducible or oxidizable group, the peak current on the voltammetric curve recorded after completion of the accumulation period then corresponds practically only to the reduction (or oxidation) of the whole amount of the adsorbed electroactive species. Only tensammetric adsorption/ /desorption peaks are obtained for electroinactive compounds (such as detergents, crude oil components, alkaloids, etc.).

## 2. THEORETICAL BACKGROUND

The action of interfacial forces at the boundary between two phases, here an electrode in solution, leads to the formation of an interface with a thickness usually comparable to molecular dimensions. If these interfacial forces lead to an increase in the concentration of some substance at the solid phase- solution interface compared to the concentration in solution, then this substance is adsorbed on the surface of the solid phase. Adsorption equilibrium is established between the concentration in the solution and that on the surface of the electrode. At a given temperature, the amount of substance adsorbed is dependent on its concentration in solution. The velocity of formation of the adsorbed layer is affected both by the rate of the actual adsorption of the substance from the solution layer in direct contact with the electrode and also by the rate of diffusion of the substance from the bulk of the solution to the electrode surface. The slower of these two processes then becomes the rate- -controlling step in the formation of the adsorbate.

For fast, diffusion-controlled adsorption, which occurs most often in adsorption accumulation, where during the accumulation period the mass transport is assumed under the limiting current condition, the following relationship was derived for the peak current of the reduction of adryamycin (ref. 9) at a HMDE, assuming that $I_p \sim \Gamma$:

$$I_p = k\,A\,\Gamma = k\,AC\left[(D/r)t_{acc} + 2(D/\pi)^{1/2}t_{acc}^{1/2}\right] \qquad (1)$$

where k is a proportionality constant, A is the electrode surface area, is the surface concentration of adriamycin, C is the adriamycin concentration in solution, D is its diffusion coefficient, r is the HMDE radius and $t_{acc}$ is the accumulation period. At large values of C and/or $t_{acc}$, $I_p$ approaches a limiting value $I_p^{max}$, for which it is assumed that

$$I_p^{max} = k\,A\,\Gamma_m \,. \qquad (2)$$

It holds for this maximal value of the surface excess of the adsorbed substance $\Gamma_m$ for complete electrode coverage, i.e. when the coverage $\emptyset = 1$ and for unidirectional diffusion transport to the electrode that (ref.10):

$$\Gamma_m = 7.36 \times 10^{-4}\,C\,D^{1/2}\,t_m^{1/2} \qquad (3)$$

where $t_m$ is the time required for complete electrode coverage.

It has been found experimentally that $I_p$ increases linearly with $t_{acc}^{1/2}$ (refs. 11-14) (of course, assuming that $\emptyset \ll 1$ and that there is no interaction between the adsorbed molecules and also that the adsorption of the compound is controlled by its diffusion to the electrode), which is the criterion for diffusion-controlled adsorption. $I_p$ is roughly proportional to the product of C and $t_{acc}^{1/2}$ when neither of these two values is too large. The slope of the

dependence of $I_p$ on $t_{acc}^{1/2}$ is then proportional to the concentration of the studied substance.

It thus follows that the AdSV method should be employed under conditions where the peak height increases linearly with the concentration of the studied substance. When this dependence deviates from linearity (especially when $I_p$ approaches a limiting value), the experimental conditions must be modified (dilution of the solution, decrease of the accumulation time, accumulation under non-stirring conditions) or the measurement must be carried out using a calibration curve describing the curvature of the dependence of $I_p$ on C. It also follows from Eqs. (1) to (3) that $I_p$ is dependent on the rate of transport of the substance to the electrode, which can be increased by stirring the solution. In contrast to electrolytic accumulation (e.g. anodic stripping voltammetry), the $I_p$ value obtained for adsorptive accumulation is directly proportional to the scan rate.

When the amount of substance adsorbed on the electrode surface is determined by the actual adsorption rate, which is smaller than the diffusion rate, it can be assumed that the concentration of surface active substance at the surface of the electrode equals that in the bulk of the solution. This is also true for low adsorptivity of the surface active substance. These two cases are not useful in AdSV.

## 3. EXPERIMENTAL ARRANGEMENT

### Apparatus

AdSV can be carried out using commercially available polarographic instruments employing the classical polarographic method (DC polarography) as well as pulse methods, especially differential pulse polarography (DPP). The latter method exhibits lower limit of determination. In the choice of a suitable voltammetric method, DPV or DCV, for recording the curves, it should be noted that difficulties can be encountered in measuring the peak height as a result of the unsuitable shape of the curve for the base electrolyte (especially at more positive potentials) and the DCV method is in such cases preferable. Apparatus with automatic timing of the individual operations is useful for controlling the individual steps in AdSV measurements (accumulation time, solution stirring, rest period, initiation of polarization); a computarized instrument is useful for this purpose.

### Electrodes

AdSV can be carried out at practically all types of electrodes employed in voltammetry for which a completely reproducible constant surface area can be ensured over the whole measuring period or during a series of measurements.

The hanging mercury drop electrode (HMDE). The above requirement of a reproducible surface is best fulfilled by the hanging mercury drop electrode. The best results are obtained with a static mercury drop electrode in which the flow rate of mercury in the capillary and thus formation of a mercury drop with the required, precisely reproducible volume is ensured by a needle valve or other type of valve controlled by an electronic circuit.

Carbon paste electrode, platinum electrode. Carbon paste electrode, made by mixing carbon powder or graphite with a binder (various types of mineral oil, etc.) and pressing the mixture into a glass tube have been widely used. Procedures for their manufacture have been given, for example in ref. 1 or ref. 15. Similarly, a platinum disk electrode can also be employed. Both these types of electrodes are especially suitable for studying adsorbable substances that can be oxidized at the electrode, as they can be polarized to much more positive potentials (e.g. +1.0V vs. SCE) than mercury electrodes which, on the other hand, can be used in a wider negative potential range. Thus, mercury electrodes are preferable for studying reducible substances. However, it is somewhat more difficult to work with nonmercury electrodes. The electrode must be conditioned prior to use, for example, by periodic polarization from negative to positive potentials and back again for a certain period of time in the base electrolyte. After recording the curve, the electrode surface must be renewed, e.g. by removing the surface layer of the paste. The difficulties connected with producing a good-quality carbon paste electrode are reflected in

the lower precision in analytical determinations than that obtained for hanging mercury drop electrodes. The choice of binder is also important for paste electrodes: suitable selection can sometimes lead to more specific adsorption. It should be noted when using paste electrodes that the substance can also be accumulated as a result of dissolution in the binder during $t_{acc}$. This is then a combined adsorption-extraction effect or can consist purely of extraction (refs.16,17). Whether or not extraction is involved can be determined by removing the surface layer of paste after $t_{acc}$ and recording the curve.

As quinoid groups in either the reduced or oxidized state (of the quinone--hydroquinone type) may be present on the carbon particles, chemisorption of the substance in solution can play an important role in some cases. This type of electrodes can, in a certain sense, be considered to be modified by the presence of these groups.

Chemically modified electrodes. AdSV can also be carried out using electrodes modified by bonding a substance with a known structure to the electrode surface. However, electrodes with chemically modified surfaces are still not often used in analytical chemistry because of the complicated and difficult reproduction of the electrode surface. In addition, the accumulation process at these electrodes is far more complex than for reversible adsorption at a mercury electrode and they are thus difficult to employ for routine analyses. The detection limit is also usually much higher. Thus, the use of modified electrodes for AdSV will be considered only briefly.

## 4. GENERAL EXAMINATION OF THE POSSIBILITY OF AdSV DETERMINATION

It is relatively simple to decide whether a substance can be determined by using AdSV at a mercury electrode. First, the voltammetric behaviour of the compound (at a concentration of $10^{-6}$mol $L^{-1}$) is examined at a hanging mercury drop electrode (HMDE) in different supporting electrolytes using the differential pulse method (DPV). In the optimum supporting electrolyte, the initial potential is then set (zero Volt or -0.1V vs.SCE), a new mercury drop is formed and the voltage scan towards more negative potentials (at a rate of 20 mV $s^{-1}$) is immediately begun. After the voltammetric curve has been recorded, a new mercury drop is again formed and the same initial potential is applied for a period of 60 s to the working electrode in stirred solution. After this accumulation period ($t_{acc}$), stirring is stopped and the voltage scan is run as previously after a quiescent period of 10 s. If the surface activity of the compound leads to its accumulation, a substantial increase in the peak current is obtained as not only the substance transported to the electrode by diffusion but also that adsorbed on the electrode surface is reduced during the voltage scan. For oxidizable organic compounds, a solid type of working electrode is used in a similar way: the accumulation is studied at 0 V or with an "open circuit" and then the voltammetric curve is recorded towards more positive potentials. The stripping process can be evaluated by the DPV or DCV mode (in the latter case at a scan rate of 100 mV $s^{-1}$); the DCV method yields higher limit of determination but yields improved signal to background characteristics and thus peak measurement is usually easier (and more precise), compared to the DVP method (especially at positive potentials).

After these preliminary investigations, the most suitable accumulation potential $E_{acc}$ is found by examining the dependence of the peak current $I_p$ on $E_{acc}$. The optimal accumulation time $t_{acc}$ must also be found. The dependence of $I_p$ on the analyte concentration should be linear over a reasonably wide range. The method of standard additions can be used for quantitative measurements. Three additions of a standard solution are recommended to ensure that the measured $I_p$ values correspond to the linear part of the calibration curve. When the $I_p$ value does not increase linearly during standard solutions, the sample solution must be diluted or a shorter accumulation time employed; accumulation can also be carried out in unstirred solutions.

The other parameters in AdSV have similar significance as in anodic stripping voltammetry: for example, the dependence on the magnitude of the electrode surface area, the stirring rate, the rate of increase of the polarization potential, the amplitude and polarity of the polarization pulse in the DPV

method. As the AdSV peak height often increases by up to 7% on an increase in the solution temperature by one degree C (depending on the substance studied), the measurement should be carried out in vessels thermostatted with a precision of at least $\pm 0.3^{\circ}C$.

## 5. SURVEY OF SUBSTANCES DETERMINABLE BY AdSV

AdSV can be used to determine substances with marked adsorbability on the electrode surface. Especially substances that are less polar than the solvent and also substances that can interact with a metal electrode surface exhibit a tendency to be adsorbed on the electrode interface. In general, adsorptive accumulation on the electrode for the purposes of voltammetric analysis can be employed for substances characterized by low solubility in water (base electrolyte solution). These are especially higher aliphatic alcohols, aliphatic and aromatic sulphoacids, higher fatty acids, aromatic hydrocarbons, aromatic nitrocompounds, aromatic compounds with condensed rings, hydroaromatic compounds, alkaloids, antibiotics, tensides, either cationic or anionic or even nonionic, and various macromolecular compounds. If these substances contain a group subject to a faradaic process at the electrode, reduction or oxidation occurs during recording of the voltammetric curve. For electroinactive substances, a tensammetric peak is formed on the curve in the region of desorption of the accumulated substance. It has been confirmed experimentally for this type of substances that the accumulation effect can be expected when the surface-active substance yields a well developed tensammetric peak on a mercury drop electrode at concentrations of about $10^{-5}$ mol $L^{-1}$. The higher the adsorption coefficient, the higher and narrower the tensammetric peaks. The adsorption can also be affected by suitable selection of the base electrolyte, and often also by increasing its concentration if the salting-out effect can be utilized.

This description of substances is purely orientative: when it is necessary to carry out the microanalytical determination of a given organic compound, it is advisable to carry out an experiment to determine whether it is accumulated by adsorption. The present state of polarographic instrumentation is useful here, as most commercial polarographs are equiped with a static mercury drop electrode, which is most suitable for this purpose.

### Determination of electroactive organic compounds

AdSV can be used without serious complications for studying organic compounds (characterized by surface activity) in the concentration range from $1.10^{-6}$ to $1.10^{-8}$ mol $L^{-1}$. So far, the lowest detection limit has been attained for riboflavin (using a mercury electrode) (ref.18), with a value of $2.2.10^{-11}$ mol $L^{-1}$ ($t_{acc}$ = 30 min.) and for DNOK pesticide (ref.19) (2-methyl-4,6--dinitrophenol), with a value of $5.10^{-10}$ mol $L^{-1}$ ($t_{acc}$ = 3 min.) using DPV. These values for organic substances are similar to these obtained for anodic stripping voltammetry method and therefore the application of adsorbance considerable broadens the region in which voltammetry can be employed in the trace analysis of organic compounds.

AdSV can be used in a wide variety of cases to determine organic compounds. It follows from work published so far that AdSV has been used to determine a wide range of biologically active substances, such as various pharmaceuticals, growth stimulants, pesticides and industrially important substances.

The subsequent text will give a survey of work so far published on the adsorptive accumulation of substances on both mercury electrodes and on electrodes of other materials, especially carbon paste electrodes and platinum electrodes.

Only a limited number of examples of the determination of organic compounds will be given, where chemisorption participates in the accumulation process at the electorde, with formation of mercury compounds. This method is included under cathodic stripping voltammetry.

AdSV at a hanging mercury drop electrode. The hanging mercury drop electrode is used to study substances that are accumulated by adsorption on the electrode and then reduced during a scan to more negative potentials. The selection of a

TABLE 1. AdSV of some electroactive compounds using HMDE

| Compound | Electrolyte | Accumulation potential (V) | Ref. | Compound | Electrolyte | Accumulation potential (V) | Ref. |
|---|---|---|---|---|---|---|---|
| Nitrobenzene | B-R buffer pH 7 | -0,20 | 21 | Testosterone | Borate buffer | -0.80[+] | see in 4,22 |
| Azobenzene | Ammoniacal buffer pH 9.7 | -0.35 | 24 | DNOK | B-R buffer pH 6.1 | -0.20 | 19 |
| Diazepam | Acetate buffer pH 4.6 | -0.50 | 21 | Prometryn | B-R buffer pH 3.5 | -0.70 | 19 |
| | 0.2M NaOH | -0.80 | | Paraquat | Acetate buffer pH 4.6 | -0.60 | 23 |
| Nitrazepam | Acetate buffer pH 4.6 | -0.50 | 21 | Adriamycin | Acetate buffer pH 4.54 | -0.30[+] | 9 |
| | 0.2M NaOH | -0.40 | | Tetracycline | Borate buffer pH 5.5 | -0.60[+] | 13 |
| Papaverine | 0.2M KF | -1.10 | 21 | Streptomycin | 0.01M NaOH | -1.20[+] | 25 |
| Riboflavine | 0.001M NaOH | -0.20[+] | 18 | | | | |

(V vs.SCE; [+] V vs. Ag/AgCl)

base electrolyte for AdSV can often be based on data published for the polarographic determination of a given substance. These are most often various types of buffers, but hydroxide solutions can also often be used. It has sometimes been observed that the peak height increases on dilution of the base electrolyte up to a concentration of $10^{-3}$ mol $L^{-1}$ (ref.20). This can often be useful to limit interference from impurities present in the compound used in preparing the base electrolyte. Table 1 gives a survey of some substances that have been determined by AdSV, along with the working conditions, i.e. base electrolyte and $E_{acc}$ (where given in the literature). Table 4 lists substances both electroactive and electroinactive that have been determined by AdSV, in alphabetical order.

Procedures have been developed for the determination of a number of substances in various materials, e.g. in biological fluids, where the determination is apparently more difficult because of competing adsorption of proteins and other substances in the sample. Various separation methods are useful here, as mentioned in Chapter 7.

The exchange of the base electrolyte after completion of accumulation in which the actual voltammetric measurement is carried out (ref.33) permits the extraction of biomolecules (nucleic acids, some proteins, polysacharides, lipids) from a medium that is not suitable for the polarographic determination (nonaqueous media, or solution containing various interferents - such as ascorbic acid). The exchange of electrolyte also permits the study of interactions at the electrode surface of immobilized biomolecules with substances from the solution, without interactions in the solution affecting the measurement.

Adsorptive accumulation has been used in complex investigations, such as the binding of antitumor antibiotics with DNA (ref.34) or studies of the changes in native DNA produced by small $\gamma$-irradiation doses (ref.32), as well as to investigate the interaction of nucleic acids with enzymes (ref.33) or genotoxic substances (ref.35). The adsorptive accumulation of DNA on a mercury electrode is described in ref.30; the polarographic signal corresponds to the reduction of adenine and cytosine residues in the DNA molecule. The peak of double-helical DNA is much smaller than that of single-stranded DNA under the same experimental conditions, permitting the determination of single-stranded DNA in the presence of an excess of double-stranded DNA (ref.36).

A number of substances that cannot be reduced polarographically can be determined after derivatization with a suitable, easily reducible substance or introduction of a reducible group such as nitroso-, nitro-, etc. An example of derivative formation is the determination of morphine (ref.37) estrone, estradiol and estriol (ref.38) after nitrosation. Condensation with p-(N,N-dimethylamino)-benzene-p'-azobenzyl chloride has been used to determine caprolactam in waste and natural waters (ref.39). The product of this condensation was separated from excess reagent and other interferents by using TLC.

AdSV at nonmercury electrodes. Both the carbon paste and the platinum electrode are useful for studying substances that are oxidized at the electrode after adsorptive accumulation, during scaning towards positive potential values. The accumulation is carried out either as with the mercury electrode, i.e. at a set $E_{acc}$ value, or with an open circuit. In a number of cases, accumulation is carried out either by simply immersing the electrode in a stirred solution for a given $t_{acc}$. Then the electrode is rinsed, cleaned and transferred to the pure base electrolyte, in which the actual voltammetric determination is carried out. This procedure is useful because it eliminates the effects of accompanying substances in the sample on the recording of the voltammetric curve. However, the possibility of adsorption of interferents during accumulation cannot be eliminated, which can sometimes be a serious drawback in the use of AdSV. In contrast to the mercury electrode, the use of paste electrodes is more difficult as the determination often depends on the paste composition, on previous electrode treatment, cleaning, etc. In addition, adsorptive accumulation is often accompanied by dissolution of the substance in the binder. Furthermore, the sensitivity attained is less than that for a mercury electrode. Most authors work in the concentration range from $10^{-6}$ to $10^{-8}$ mol $L^{-1}$; determination of concentrations of $1.10^{-9}$ mol $L^{-1}$ are less common.Because of all these possible complications, it is recommended that the original literature be consulted in deciding on the conditions for the determination of a specific substance.

For example, this technique can be used for the determination of chloropromazine in blood and urine (ref.15). In ref.40 an AdSV procedure is described combined with FIA (flow injection analysis) that is especially suitable for series analyses. Chloropromazine, phenothiazine and similar substances can also be determined in blood serum using adsorptive or extraction accumulation on a carbon paste electrode (ref.41). The transfer of the electrode after accumulation to the pure base electrolyte permits the determination of these substances in samples containing substances that are oxidized at the same potential, without interference in the determination of the analyte. In ref.42 the determination of adriamycine type substances in urine is described. Accumulation is carried out by simply immersing the paste electrode in a sample solution for a defined period of time; the electrode is then rinsed and transferred to the base electrolyte solution (buffer, pH 4.5) and the curve is recorded. Uric acid has been determined in blood serum and urine (ref.43). Adsorptive accumulation has also been used in series analyses using the FIA method.

The determination of butylated hydroxyanisol and other tocopherols (vitamin E) in beverages and pharmaceuticals has been described (ref.15). Series analyses were carried out in a flow-through system (FIA), with curve recording at a rate of 10 $mV.s^{-1}$. The same authors (ref.16) have studied the degree to which extraction into the interior of the electrode participates in the accumulation of uric acid, chloropromazine and butylated hydroxyanisole; uric acid is only adsorbed.

The platinum electrode. In the determination of dopamine (ref.44), accumulation was carried out by immersing the electrode into an ethanol solution of dopamine. The electrode was then rinsed with ethanol and cleaned by ultrasonics in ethanol, and then transferred to the base electrolyte (0.1 M HCl) and the curve was recorded. L-DOPA and Tyramine were determined similarly. Dopamine has been determined in the presence of ascorbic acid (ref.45).

The determination of polarographically nonreducible compounds

A number of organic compounds that cannot be reduced polarographically can appear on the polarographic curve as a result of their surface activity when polarography with an alternating voltage component or the DPP method are used, with the formation of characteristic peaks (called tensammetric maxima) at the adsorption/desorption potential. These maxima can also be obtained during polarization of a hanging mercury drop electrode, by the DCV method. Measurement of the height of these peaks can be used to determine these substances in concentrations down to about $10^{-6}$ molar. A number of these substances can be adsorptively accumulated on the electrode prior to the actual recording of the tensammetric curve, increasing the sensitivity of the determination by about one order of magnitude. The name "adsorptive stripping tensammetry" (AdST) has been proposed (ref.44) for this type of analysis, as a special case of AdSV. Some examples of AdTV determinations are summarized in Table 2.

TABLE 2. AdST of some electroinactive compounds using HMDE

| Compound | Electrolyte | Accumulation potential (V) | Reference |
|---|---|---|---|
| Polyethyleneglycols | 1 M $LiClO_4$ | -1,60 | 47 |
| Na-laurylsulphonate | 1 M NaOH | -0,70 | 52 |
| Triton-X 100 | 0,55 M NaCl | -0,60 | 55 |
| Codeine | 1 M NaOH | -0,70 | 52 |
| Monensine | 0,2 M KF | -1,10 | 46 |
| Trichlorobiphenyl | B-R buffer pH 6,5 + 20% Methanol | -0,40 | 59 |
| Biphenyl | " | -0,30 | 59 |
| DDT | " | -0,30 | 59 |
| Crude oil in water | 1 M NaOH | -0,70 | 60 |

**Determination of metal ions**

The ions of a number of metals form poorly soluble compounds with various reagents, especially complexing agents; these compounds may be adsorbed on the surface of electrodes. This property can be utilized in the adsorptive accumulation of metal chelates on an electrode after which the reduction of the adsorbed compound is measured as a peak on the voltammetric curve. This analysis procedure permits determinations of metal ions at concentration levels that are hardly or not achievable by anodic stripping voltammetry. AdSV can also be used to determine a number of cations (ref.52) (such as $Cu^{2+}$ in a $NH_4CNS$ solution), where the positive potential at which adsorptive accumulation is carried out prevents the deposition of some ions (e.g. $Pb^{2+}$), that would interfere in anodic stripping voltammetry. The sensitivity in AdSV is often greater as the metal is not dissolved in the mercury in this method, but rather a monomolecular complex layer is formed on the electrode surface. The detection limit in these determinations is about 0.1 ppb.

Table 3 lists complexing agents employed in the AdSV of traces of metal ions. Most methods have been developed for the determination of metal ions in water, especially sea water. Ref.63 discusses advantages of this application. The most extensively used method in practice is the nickel determination at a mercury electrode as Ni-dimethylglyoximate. The first work on this subject was published in 1947 and describes the increase in the polarographic current at a dropping mercury electrode as a result of adsorption of Ni-dimethylglyoximate (ref.64). The AdSV of nickel can be carried out in various materials such as water, biological materials, foodstuffs, etc. (ref.65) and in lipid fractions of biomaterials (ref.66). It has been found useful in toxicological studies to determine nickel in fingernails (ref.67), where the concentration in contaminated persons is about one order of magnitude greater than in urine or blood. Nickel has also been determined as its dimethylglyoximate using glassy carbon electrodes covered with a mercury film (ref.68). This work also describes the determination of nickel in biological materials, atmospheric dust

TABLE 3. Survey of some complex forming reagents for AdSV of metals with HMDE

| Reagent | Metal | Reference | Reagent | Metal | Reference |
|---|---|---|---|---|---|
| Catechol | U | 88, 89 | 2,2'Bipyridine | Ni | 102 |
| | Cu | 88, 90, 91 | | Co | 103 |
| | V | 92 | 8-Hydroxyquinoline | Mo | 104, 177, 178 |
| | Fe | 93 | | Cu, Cd, Pb | 105 |
| | Ge | 52 | | U | 109 |
| | Sb | 123 | Thiourea | Cu | 106 |
| Dimethylglyoxime | Ni, Co | 66, 69, 94 | $CSN^-$ | Cu | 52 |
| | Pd | 121 | | Tc | 107 |
| | Cr | 122 | Diisopropylmethyl-phosphate | U, Zr | 80 |
| Solochrom violet | Al | 95 | | | |
| | Ca, Mg, Sr, Ba | 96 | | | |
| | Dy, Ho, Y, Yt | 97 | Tributyl- or tripropylphosphate | Mo, U, V, W, Zr, Pb, Ti, U | 108, 124 |
| | Ti | 98 | | | |
| DTPA | Cr | 67 | | | |
| o-Cresolphthalexon | La, Ce, Pr | 99 | Mordant blue | Th, U | 119 |
| Eriochrom black T | Mn | 100 | Tropolone | Sn | 179 |
| Nitroso-1-naphthol | Co | 101 | | | |

in various regions, air-borne ash and rain water. The detection limit was 20 ng $L^{-1}$ and the authors state that this value could be decreased by using very pure chemicals. A study of the use of this method for speciation of metal ions in water revealed that dimethylglyoxime (ref.69) binds not only free $Ni^{2+}$ and $Co^{2+}$ ions, but also most organically bonded nickel and cobalt in weak complexes. Thus speciation studies must be carried out with great care. The detection limit(ref.69)for the determination of $Ni^{2+}$ in water is given as 1 $\mu$g $L^{-1}$. AdSV has also been used to determine nickel in cooling water (ref.70) and in the analysis of ores (ref.71). Ref.72 describes applications in flow-through methods.

An interesting example of the use of AdSV is the determination of traces of silicon in water (potable, sea, boiler) as the silicomolybdate in methylethyl ketone medium (ref.73). Ref.74 describes the determination of the carcinostatic cis-platinum. Further examples of the use of organic reagents for the adsorptive accumulation of some ions on the electrode can be found in references 75 and 76 and follow from Table 3.

It should also be noted that adsorptive accumulation has been used at variously modified electrodes. For example, a method has been proposed (ref.77) for accumulation of $Cu^{2+}$ at a HMDE with a surface layer of dithizone. A glassy carbon electrode modified with tri-n-octylphosphinooxide (TOPO) (refs.78, 79) has been proposed for the determination of uranyl ions, $UO_2^{2+}$ and $ZrO_2^{2+}$ ions have been determined using a mercury electrode in the presence of diisopropylmethyl phosphate (ref.80). $Ag^{+}$ ions have been accumulated at a carbon paste electrode with an EDTA layer as a complexing agent (ref.81) and also using zeolite containing carbon paste electrode (ref.82). Crown ether modified carbon paste electrode has been proposed for the determination of mercury ions (ref.83). Further examples of the use of modified electrodes will not be discussed here as the acumulation mechanism is far more complex than that for reversible adsorption, for example, as mercury electrodes and utilization in routine analyses could be sometimes complicated. The detection limits attained have so far also been much higher.

It should be noted in connection with the AdSV of metal chelates that a number of works have been published (especially in China), describing the use of adsorptive polarographic waves obtained at dropping mercury electrodes for the determination of metals bonded in complexes, with detection limits of the order of $10^{-7}$ to $10^{-8}$ mol $L^{-1}$. This method is similar to that described in the cited work (ref.64) on the polarography of nickel dimethylglyoximate. Examples can be found in the literature of the determination of the rare earth elements (Sc, Y, La, Nd, Pr, Sm, Eu, Gd, Tb, Tm, Yb) (ref.84), of beryllium with thoron II (ref. 85), and of aluminium (ref.86) and boron (ref.87) with beryllon III. Obviously a further decrease in the detection limit could be attained by using the AdSV technique at a hanging mercury drop electrode.

## 6. AdSV IN FLOWING SYSTEMS

The combination of the effect of spontaneous adsorption of the analyte with the medium-exchange principle led to the application of AdSV in flowing systems. Here, accumulation (usually at a given potential) is carried out during the interval when the carrier solution with the injected sample flows through the detector. This interval thus defines the $t_{acc}$ value. When the sample plug leaves the detector, the stripping process is started either without interrupting the flow or after stopping the flow. The latter is usually necessary when a peristaltic pump is used, because the pulses in the carrier strem produce large current oscillations. The use of an isocratic pump, on the other hand, permits the measurement of the stripping curve without stopping the flow, as a constant flow is ensured under these conditions. The detectors used are commercial detectors with either mercury, mercury film, carbon or carbon paste electrodes, that are often employed for electrochemical detection in HPLC. Optimum sample injection is using an injection valve with a sample loop, used in LC.

The accumulation period begins when the injected sample plug comes into contact with the electrode inside the detector and terminates when it has passed completely through the detector. If the flow rate is slow (below 0.5 mL $min^{-1}$) and the sample volume is small (less than 1 mL), dispersion of the sample plug

is limited. The amount of accumulated analyte depends on the duration of the accumulation period and on the flow rate. With increasing accumulation period, the current first increases rapidly and then more slowly, as in batch experiments. When the flow rate is varied (at constant volume and amount of injected sample), the peak current decreases with increasing flow rate, because of the decreased residence time of the sample plug in the detector (refs.26, 27, 111).

Other parameters influencing the current signal include the potential scan rate. Differential pulse voltammetry is usually performed with scan rates of maximally 5 mV $s^{-1}$; to improve the sensitivity and shorten the analysis time, however, higher rates can be employed. In this case, the frequency of the applied pulses should be increased, for example, to 5 pulses per second (ref.27).

When a HMDE is employed as the working electrode, cleaning of the electrode surface after the analysis of discrete samples is readily realized by the formation of a new drop. When a mercury film electrode (MFE) or carbon electrode is used, a "cleaning" period must be inserted between the analysis of subsequent samples. During this period, the electrode is held at a potential where the adsorbed component of the previous sample is completely desorbed from the electrode surface.

A higher selectivity is achieved automatically in flowing systems as the electroactive components whose faradaic response could interfere in the signal recording are removed from the vicinity of the electrode by the carrier stream during the reduction step. It has also been found in some cases (ref.27) that the time interval between the moment when the sample plug leaves the detector and the polarization scan is started ("washing period") can be prolonged to several seconds (half the residence time of the sample) without a significant decrease in the current value. This "washing period" further decreases the interferences from other surface-active substances. Under these conditions, growth promotors such as quinoxaline-N-dioxide derivatives can be determined by direct injection of diluted blood plasma into the carrier stream.

The application of AdSV in flowing systems simplifies the analytical procedure, improves the selectivity and sensitivity of the determination and increases the sample throughput. In addition, interference from oxygen can be minimized by employing the subtractive voltammetry technique (ref.112). In this procedure, the "analytical" and "background" stripping voltammograms are recorded by passing first the injected sample and then the carrier solution through the detector. The carrier curve is the subtracted from that of the sample. This approach leads to improvement of the detection limit and minimization of interference from oxygen so that dissolved oxygen need not be removed from the measured solution (ref.112).

Recently, flow-through AdSV methods have been described for the determination of chlorpromazine in body fluids (ref.41), dexorubicine in urine (ref.26), derivatives of quinooxaline-N-dioxide in blood plasma (ref.27) and nickel and cobalt in material with complex composition (refs.72, 113). Further progress in this field can be expected in the near future.

## 7. LIMITATIONS OF THE ADSORPTIVE STRIPPING METHOD

The high sensitivity of adsorptive stripping methods is obviously their greatest advantage. On the other hand, a serious drawback is interference from other surface-active substances that may be present in the solution. In this case, competitive adsorption usually occurs and leads to a decrease in the measured current or, at very high surface-active substances (s.a.s.) concentrations, to significant suppression of the signal. Interfering effects depend on the nature of both the analyzed and interfering substances and on their concentration ratio: in the determination of trichlorobiphenyl (ref.59) (tens of $\mu g\ L^{-1}$), a thousand-fold excess of Triton X-100 produced a 90% decrease in the signal; on the other hand, when the Triton X-100 concentration was comparable to that of trichlorobiphenyl, practically no change occured in the signal. In the determination of monensine (ref.46) (0.17 ppm), a ten-fold excess of gelatine decreased the signal by 25%. Evidently, the interfering effect of s.a.s. can be minimized by employing short accumulation times; however, this approach is not suitable in the determination of trace amounts of

TABLE 4. Organic compounds determined by AdSV or AdTV

| Compound | Reference | Compound | Reference |
|---|---|---|---|
| Adenine | 31 | Heme | 157 |
| Adriamycine | 9,26,42,118 | Hexachlorcyclohexane | 28 |
| Albumin | 126,131 | Hydralazine | 158 |
| Alcohols oxyethylated | 58,180,181 | Hydroxyanisole butyl | 15,17 |
| Alkaloids | 21,52 | Imipramine | 104 |
| Alloxazine | 18 | Jatrorubine | 185 |
| Amethopterine | 182 | Laurylsulphonate | 48,52 |
| Amines | 192 | Lipids | 33 |
| Anilines N-alkylated | 183 | Maneb | 28 |
| Atropine | 52 | Marcellomycine | 186 |
| Azobenzene | 24 | Medazepam | 129 |
| Azocompounds | 127 | Methotrexalate | 187 |
| Azodyes | 128,160 | Methylenblue | 7,8 |
| Benzodiazepines | 21,129,132 | Mytomycin | 161 |
| Benzophenones | 5 | Monensin | 46 |
| Berberine | 130 | Morphine | 37 |
| Bilirubin | 14 | Nitrazepam | 21 |
| Biphenyl | 59 | Nitrobenzene | 21 |
| Biphenyl nitrated | 59 | Nitrogroup cont. | |
| bis/2-Ethylexyl succin. | 133 | pesticides | 19 |
| Bromazepam | 129,132 | Nitrosocompounds | 38 |
| Camazepam | 132 | Novobiocin | 25 |
| Caprolactam | 39 | Nucleic acids | 33,35,36,142 |
| Chlorambucil | 114 | Orotic acid | 174 |
| Chlorazepate | 129 | Oxoapomorphine | 162 |
| Chlordiazepoxide | 184 | Oxytetracycline | 13 |
| Chlorpromazin | 7,20,40,41,111, 115,134,135 | Papaverine | 21,48 |
| | | Paraquat | 23 |
| Chlortetracycline | 13 | PCB | 59 |
| Cholesterol oxidase | 11 | Penicilin | 163 |
| Cimetidine | 12 | Pentachlorphenol | 164 |
| Clozapin | 137 | Percain | 52 |
| Cocaine | 52 | Perphenazine | 41 |
| Codeine | 52 | Pesticides | 19,28 |
| Cyadox | 27 | Petroleum comp. | 60,147 |
| Cyanuric chloride | 116 | Phenanthrene-quinones | 162,165 |
| Cyclohexanole | 47 | Phenothiazine | 41 |
| Cytochrome c | 117 | Phytohemagglutinin | 188 |
| Daunorubicin | 136 | Polyethylenglycoles | 47-50,57 |
| DDT | 59 | Polysacharides | 33 |
| Desipramine | 191 | Prazepam | 129 |
| Detergents | 54 | Progesterone | 22,38 |
| Diazepam | 21 | Promethiazine | 137 |
| Dichlorodiammine-Pt | 74 | Pterines | 167 |
| Diethazine | 137 | Purines | 189 |
| Digoxin | 20 | Quinoxaline-N-oxides | 168 |
| Diltiazem | 138 | Rescinnamine | 158 |
| Dimethylaniline N,N | 17 | Reserpine | 158 |
| Dinitronaphthalenes | 21 | Riboflavin | 7,18,20,169,170 |
| DNA | 30,32,35,36, 139-145 | Rokanol | 56 |
| | | Semicarbazones | 171 |
| Dodecylalcohol | 146 | Streptomycin | 25 |
| Dodecylbenzensulphonate | 52,60,147,148 | Surfactants | 61,62 |
| Dodecylsulphate | 146 | Temazepam | 159 |
| Dopa | 44 | Testosterone | 20,22 |
| Dopamine | 44,45,149 | Tetracycline | 13 |
| Doxorubicin | 26 | Thiamin | 7 |
| Doxycycline | 13 | Thienodiazepines | 129 |
| Dyes azo | 128 | Thiosemicarbazones | 171 |
| Dyes food,cosmetics | 29 | Tranquilizers | 137 |
| Dyes triazine | 150 | Triazine pesticides | 19 |
| Erythromycin | 25 | Triazolam | 190 |
| Estradiol | 38 | Trichlorobiphenyl | 59 |
| Estriol | 38 | Trimepramine | 135,191 |
| Estrone | 38 | Triton X 100 | 53,55,57 |
| Ferrocenecarboxaldehyde | 151 | Tyramin | 44 |
| Flavine | 152 | Uric acid | 43 |
| Fluorouracil 5- | 114 | Vitamine B 12 | 172 |
| Fluphenazine | 137 | Vitamine B 13 | 174 |
| Folic acid | 153,154 | Vitamine K 1 | 173 |
| Glucosides cardiac | 155 | Zineb | 28 |
| Hematein | 156 | Ziram | 28 |

analyte. It is then necessary to employ suitable separation of interfering compounds, e.g. the application of LC or gel chromatography (ref.21), using Sephadex (Pharmacia, Uppsala), ultrafiltration (ref.110), TLC separation (ref. 39), extraction procedures (refs.132,159), etc.

The adsorption of interfering surface-active substances in the determination of various tranquilizers in plasma can be prevented by using awax-impregnated graphite electrode covered with a Spectrapor membrane (ref.137). This membrane prevents interference from various proteins in the adsorption and electroactive accumulation of the studied tranquilizer.

Similar interferences are encountered when a mixture of surface-active substances is to be analyzed, usually even under conditions where the peak potential values of the determined substances differ sufficiently. It has been found, for example, that the simultaneous determination of diazepam and nitrazepam (with peak potential values differing by 500 mV in alkaline medium) can be carried out only at comparable concentrations of these substances (ref. 21).

If the sample contains interfering compounds that are electrochemically active but are not adsorbed on the electrode surface, then classical separation procedures are not necessary - good results can be obtained when accumulation from the sample solution is followed by exchange of this solution for the pure supporting electrolyte solution. For this purpose, a special cell for medium exchange in ASV was found useful for analysis employing an HMDE as the working electrode (ref.2). If adsorptive accumulation is carried out using a carbon paste electrode, then medium exchange is very simple; the paste electrode is simply transferred from the sample solution after completion of the accumulation period into the pure supporting electrolyte solution, after brief rinsing with water.

## 8. CONCLUSIONS

Adsorptive stripping voltammetry, both of adsorbable complexes and of electroactive compounds appears to be very promising, as it broadens the range of trace analyses down to concentrations of less than 1 $\mu$g/kg, where other physico-chemical methods are often no longer useful. This method is quite universal, as a great many organic compounds exhibit surface activity. A further advantage is the relatively inexpensive instrumentation, as a classical polarographic arrangement can be employed.

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