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POLAROGRAPHIC DETERMINATION OF ADSORBABLE MOLECULES

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Polarographic determination of adsorbable molecules

Abstract – Various electroanalytical methods that can be used to determine
surface active substances in various types of waters (natural, drinking
and waste water) are discussed.

1. INTRODUCTION

A great many organic compounds exhibit surface activity, reflected in electrochemistry by
adsorption at the solution–electrode interface. This process affects the properties of the
electrode double layer in a measureable manner, which can form the basis for determination
of the concentrations of these surface active substances in solution. A number of electro-
chemical techniques can be used for this type of measurement and many of them are derived
from polarography.

One of the very first applications of polarography was the study of surface active sub-
stances in water – termed polarographic adsorption analysis. This type of analysis is based
on the suppression of polarographic maxima by surface active substances in the solution.

Before the second world war, an instrument based on this principle, the "Coagulograf",
was used in the Prague Waterworks for evaluation of the coagulation process for purification
of potable water. (ref.1,2).

The following sections describe various electroanalytical methods that can be used to de-
termine surface active substances in variuus types of waters (natural, drinking and waste
water).

2. ELECTROANALYTICAL METHODS USED IN DETERMINATION OF SURFACE ACTIVE SUBSTANCES

Electrocapillary measurements

Measurement of elelctrocapillarity is one of the oldest methods for studying surface
activity of substances in solution. The adsorption of surface active substances on mercury
leads to a change in its surface tension, with typical consequences for the shape of the
electrocapillarity curve (refs. 1,3). Under conditions of adsorption equilibrium, the
decrease in electrocapillarity at constant potential or charge is a function of the con-
centration of the surface active substance in solution. The set of electrocapillarity curves
yields both the parameters of adsorption and information on the interfacial and electro-
analytical properties of the system. A great deal of information can be obtained directly
from curves depicting the dependence of the surface tension on potential, such as the
values of the adsorption and desorption potential, the zero charge potential, E_z, and the
potential of maximum adsorption, E_{max}. The shift in the value of E_z to negative or positive
potential on an increase in concentration indicates the presence of a surface active sub-
stance with cationic or anionic character.

Direct information on electrocapillarity has been obtained mainly by using a capillary
electrometer (refs. 1,4), measuring the drop time of the dropping mercury electrode (ref.1)
or the maximal bubble pressure (ref.5). Although this type of measurement has been vari-
ously modified in the past, simple measurement of the electrocapillarity permits studying
surface active substances up to a concentration of about 10^{-5} molar (ref.6). Methods have
been developed for studying lower concentrations of surface active substances (refs. 7,8,9),
employing a dropping mercury electrode with an extremely long drop time to measure in
stirred solutions, in which the substance is accumulated on the electrode. Under these con-
ditions, the detection limit can be shifted to a concentration of 10^{-7} to 10^{-8} mol L^{-1}.
Changes in the surface tension are a quadratic function of the concentration. Electro-
capillary measurements can quantitatively express the electrosorption activity in solution
in terms of an expression for the change in the surface tension indicating the overall
effect of the presence of the surface active substance in solution. The value of the ratio
of the relative change in the drop time (or changes in the interfacial potential) and the
corresponding change in the concentration of the adsorbing substance in the region of the
potential of maximum adsorption and at high concentrations are approximately proportional
to the magnitude of the adsorption coefficient; they are thus characteristic for the sub-
stance in the given medium (ref.10). The shape of the dependence of the relative change
in the drop time or the change in the interfacial tension on the logarithm of the concen-
tration is also characteristic.

Suppression of polarographic maxima

A further method for studying the content of surface active substances in solution is based on suppression of polarographic maxima caused by streaming of the solution around the drop of the dropping mercury electrode (DME). These polarographic maxima can be divided into maxima of the first and second kind. Maxima of the first kind appear in the rising part of the polarographic wave, are sharply defined and are especially common in polarographic measurements in solutions of low ionic strength. Maxima of the second kind are displayed in polarographic curves of more concentrated solutions and at high mercury flow rates at the DME. They appear in the limiting current region, are usually rounded and do not fall discontinuously to the limiting current value like maxima of the first kind (ref.1). Both types of maxima are sensitive to the presence of surface active substances in solution. As maxima of the second kind lie in a broader potential range than maxima of the first kind, they are better suited to observation of the adsorption of various types of surface active substances. The detection limit for maxima of the first kind corresponds to about 0.01 mg L^{-1} surface active substance, while maxima of the second kind are one order of magnitude more sensitive. Problems are encountered in the practical utilization of these maxima because of their lack of specificity and dependence on a great many parameters, such as the composition of the base electrolyte, properties of the DME, etc. A calibration curve is usually employed in quantitative measurements. Surface activity is often compared by the determination of the dilution that leads to a decrease in the height of the maximum to one half of its original value (this method is used primarily for maxima of the second kind).

Measurement of adsorption phenomena by alternating current polarography

The capacity of the electrode double layer and thus also the charging current necessary to charge the electrode to the required potential depend on the character of ions and substances present in solution. Because of their adsorption on the electrode surface, surface active substances decrease the capacity of the electrode double layer and thus also decrease the charging current. (The capacity of the electrode double layer also depends on the electrode potential – this is the differential capacity). Measurement of the differential capacity of the electrode double layer yields the greatest amount of information on the adsorption of compounds at the electrode (ref.3). The differential capacity decreases in the potential region where the given compound is adsorbed. There are sudden changes in the differential capacity at the adsorption and desorption potentials, reflected in sharp maxima on the curve of the dependence of the differential capacity on potential. In addition to impedance bridges, alternating current polarography can also be used to measure the differential capacity of the electrode double layer (refs.11,12). This method is based on superposition of a low amplitude, sinusoidally alternating current with a frequency of 10 Hz to 10 kHz on the linear voltage ramp. After refiltering off the direct current component, the signal then corresponds to the alternating current component, which is proportional to the total cell admittance. The current component for calculation of the impedance or double layer capacitance can be obtained by phase-sensitive detection of the alternating signal. The heights of these maxima can also be measured for analytical purposes.

The height of the maximum or peak at the adsorption potential on the polarographic curve is often studied by simple measurement of the dependence of the current on the potential of the polarizable electrode using alternating current polarography or differential pulse polarography (DPP), which can be carried out using commonly available polarographs. These measurements are termed tensammentry (ref.13).

The shape of the polarographic curve obtained is similar to that of the dependence of the differential capacity on potential, although the current measured is only proportional to the differential capacity.

There is a simple method for distinguishing adsorption peaks from peaks resulting from reduction or oxidation processes based on the classical D.C. polarographic curve (using an DME) of the solution: adsorption processes do not correspond to a wave at the potential at which the A.C. peak was observed; adsorption can only affect the charging current. In extreme cases, desorption can correspond to a slight increase in the charging current observed in classical polarography to a value corresponding to that in solution in the absence of the surface active substance.

The height of the adsorption/desorption peak is measured in quantitative analysis. It should, however, be recalled that the peak height depends on the concentration only over a range of about 100 in the latter, beyond which a limiting value is attained. The curve depicting the dependence of the height of this peak on the concentration usually corresponds roughly to the shape of the adsorption isotherm. The potential of this peak also corresponds to the concentration of the substance in solution. The current should be measured at a given DME surface area to yield reproducible results; in addition, the increase in the polarization voltage should be synchronized with the growth of the DME drop. Complications can follow from unsuitable selection of the instrument parameters (for example, a large time constant of the memory circuit in pulse polarography, an insufficiently fast recorder, etc.). The height and shape of the tensammetric peaks can be affected by traces of other surface active substances in solution. This competitive adsorption can cause difficulties in the analysis

of mixtures of surface active substances. The analysis of a mixture of substances rarely yields a different peak for each component; quantitative evaluation then becomes difficult or impossible. In contrast to those arising from faradaic processes, tensammetric peaks are more sensitive to the composition of the base electrolyte solution; this factor must be taken into account in practical analyses, where the concentrations of interfering substances are usually unknown. Thus it is sometimes preferable to employ the method of standard additions rather than using a calibration curve. It is then necessary that the peak heights for the sample both before and that after the standard addition lie in the region of linear dependence of the peak height on concentration.

In conclusion, it should be noted that many electroactive organic compounds that are reduced or oxidized at the electrode can also act as surface active substances. The A.C. polarographic recording then consists of both faradaic and adsorption-desorption peaks that can sometimes coalesce.

Adsorptive stripping analysis

Electrochemical stripping analysis consists of prior electrolytic accumulation of a metal ion at the electrode, followed by recording of the voltammetric curve of the amalgam or surface layer formed; this is now a classical method for the determination of trace concentrations, especially of heavy metals.

The substance can be accumulated at the electrode surface on the basis of other principles or properties of the substance, such as the adsorption of surface active substances (ref.14). If the substance is electroinactive (tensides, alkaloids), the corresponding tensammetric peak is studied on the voltammetric curve. When reducible surface active substances are present, such as metal complexes or organic compounds, then the trace determination of a number of trace metals, such as U, Ni, etc., as well as a large number of organic compounds, such as various pesticides, pharmaceuticals, alkaloids, etc., can be carried out. The recorded peak then belongs to the reduction of the adsorbed compound.

In adsorptive stripping analysis, the peak height depends on the length of the accumulation period (attaining a limiting value when the electrode surface is covered with the adsorbate), on the convection conditions in solution and on the potential at which accumulation is carried out. Additional factors include the surface properties of the compound, the surface area of the electrode and some instrumental parameters.

Adsorptive stripping voltammetry is a very promising method. Electroinactive organic compounds can be studied down to concentrations of about 0.1 mg L^{-1}; the detection limit for reducible organic compounds is as low as 0.1 μg L^{-1}. This method thus permits trace determination of organic compounds at concentrations where other physico-chemical methods are often no longer useful. A further advantage is the quite inexpensive instrumentation: in principle, a classical polarographic arrangement can be used. This method is quite universal as a great many organic compounds exhibit surface activity. However, it should be noted that other surface active substances that can also be present as impurities in the sample can interfere in the measurement.

Measurement of charging currents

The polarographic determination of surface active substances can be carried out by measuring the charging current. Optimal conditions are attained where this current is large, for example when using the Kalousek commutator (ref.15) (this method is also termed Kalousek Polarography), permitting fast, discontinuous changes in the applied voltage at the electrode: in one cycle, the electrode is polarized to a potential that increases constantly with time; in the second cycle, an auxiliary potential is applied (this value is arbitrary). As the electrode is charged periodically to various potentials, the charging current also increases. Changes in the capacity of the electrode double layer as a result of adsorption or desorption of the surface active substance thus lead to considerable changes in the charging current. The measured effect can be increased through prior accumulation by adsorption of the substance at the electrode (ref.16).

Other methods can be used in analytical chemistry to study capacity effects, such as chronopotentiometry, cyclic derivative chronopotentiometry, oscillographic polarography with alternating current, etc. (ref.1).

3. DETERMINATION OF SURFACE ACTIVE SUBSTANCES IN WATER

Determination of surface active substances in water is especially important as these substances are often indicators of pollution. The following text gives examples of the application of the determination of surface active substances in water (distilled, potable, etc.) using various electroanalytical methods, especially those derived from polarography.

As was mentioned in the introduction, the measurement of surface active substances in water on the basis of their ability to suppress oxygen maxima was one of the first applications of polarography after its discovery (ref.1). However, the method of suppression of polarographic maxima is nonspecific and gives only a general picture of the surface activity of the sample. Nonetheless, as will be seen, this method has been the subject of renewed interest over the years.

Undefined surface active substances

A sensitive tensammetric method for the determination of traces of surface active substances in distilled, potable and untreated waters is described in ref.17. This method is based on measurement of the decrease in the differential capacity as the result of the adsorption of surface active substances at a hanging mercury drop electrode on the basis of the A.C. polarogram in the potential range from +0.4 to -1.2V (vs. the SCE). In stirred solutions the surface active substance is first accumulated at the surface of the electrode at a potential of -0.6V. The ratio of the decrease in the charging current after accumulation to the maximal current (in "pure" solutions) is proportional to the concentration of surface active substance in the range from 10 to 300 μg L^{-1}. Water or solutions with higher contents of surface active substances must be diluted prior to the determination. Rokafenol N-10, Triton X-100 or Na-dodecyl-sulphate can be used as models or standard surface active substances for comparative measurements. Water with concentrations of surface active substance higher than 300 μg L^{-1} can be analyzed without previous accumulation on the electrode. Prior to analysis, water samples should be acidified with HClO$_4$ to a concentration of 0.1 mol L^{-1}.

The content of pyrogenes (dead microorganisms and the products of microbial metabolism) in distilled water for preparation of innoculations can be determined on the basis of suppression of maxima of the second kind (ref.18). The most useful base electrolyte is 1M NH$_4$Cl + 1mM CdCl$_2$. A polarographic capillary with the following parameters should be used: mercury flow rate 3.5 mg s^{-1}, capillary diameter 0.08 mm. The base electrolyte solution must first be purified by addition of active carbon, which removes the last traces of surface active substances. Under these conditions, the maximum formed on the cadmium wave can be affected by as little as 0.1 mg L^{-1} gelatine - employed as a comparative standard.

A number of methods have been developed for the determination of surface active substances in sea water, based on the suppression of polarographic maxima or on measurement of the charging current using the Kalousek commutator. One of these methods is based on the suppression of the polarographic maximum of oxygen (ref.19). The surface active sample of sea water is evaluated by comparison with the calibration curve for a "synthetic" sample of sea water containing Triton X-100. Suitable dilution of the sea water samples by distilled water yields the surface activity equivalent to Triton X-100 in the concentration range from 0.1 to 0.3 mg L^{-1}. (Water samples taken in the vicinity of the shore of the Adriatic Sea have a surface activity equivalent to 0.2 to 5 mg L^{-1} Triton X-100). Surface active substances have been determined in samples from the sea surface and immediately below the surface using suppression of the polarographic maximum of mercury (II) or on the basis of measurement of the charging current as described above (ref.20). In the former case, 10^{-3} mol L^{-1} HgCl$_2$ is added to the sea water sample and the height of the maximum at -0.3V (vs. Ag/AgCl) is measured. The presence of surface active substances once again decreases the height of this maximum; Triton X-100 is used for calibration. In measurement of the charging current using the Kalousek commutator, the surface active substances are first accumulated on a hanging mercury drop electrode over a period of several minutes at -0.6V (vs. the SCE); then the electrode is polarized to more negative potentials. This potential is periodically switched to a value of -0.6V (with a frequence of 64 Hz) and to a smoothly increasing voltage; the charging current is recorded as a function of the potential of the electrode. The presence of surface active substances appears as a decrease in the charging current over a broad potential region. At a given potential value, this current decrease is a function of the concentration of the surface active substance. Triton X-100 is used as a model substance in the preparation of the calibration curve for the determination.

The cited work (ref.20) discusses results obtained in the analysis of samples of sea water collected on the shore about one mile from the pollutant source, as well as samples of water polluted by industrial or city wastes, and samples of water polluted by crude oil products. It was found that the polluted shore waters contain surface active substances at concentrations equivalent to 0.2 to 0.8 mg L^{-1} Triton X-100. Values of up to 10 mg L^{-1} were found for water samples polluted by crude oil products or water samples during the vegetative period of phytoplankton (ref.21). The values for water samples below the surface were one order of magnitude lower. The degree of suppression of the polarographic maximum thus corresponds basically to the overall content of surface active substances in the water (ref.22). Charging current measurements have also been used to study water pollution in ports (ref.23).

Tensides

All the above methods have also been used to study the content of uncharged tensides and anionic type tensides in waste waters (ref.24). The suppression of the polarographic maximum of mercury (II) (in 0.55M NaCl) was used to evaluate the total amount of tenside present in waste waters from large laundry facilities. The method of measuring the charging current using the Kalousek commutator was also employed to determine the detergent content in hospital waste waters. These waste water samples had to be diluted so that the detergent content was in the concentration range from 0.05 to 5 mg/Kg for measurement of polarographic maxima or 0.1 to 0.7 mg/Kg for charging current measurements. The comparative standard was

Triton X-114 or Na-Lauryl sulphate. The results obtained were in good agreement with those obtained by the spectrophotometric method (based on measurement of the complex with methylene blue).

The detergent content in waters, including waste waters, can also be determined using suppression of polarographic maxima (ref.25).

The tensammetric determination of detergents of the Na-laurylsulphonate and polyethyleneglycol type (in 0.1M NaOH + 0.1M Na_2SO_3) using differential pulse polarography was described in ref. 26. The studied substances were first accumulated on the electrode by adsorption. Methods for the determination of detergents, especially of the polyethyleneglycol type, are described in the book by Jehring (ref.3), providing detailed information on the adsorption capabilities of a number of compounds.

A wide range of uncharged tensides has been determined by derivative chronopotentiometry (refs. 27,28), with special emphasis on fish breeding. The useful concentration range is from 1 to 200 mg L^{-1}. The method can also be used for the classification of detergents according to the length of the hydrophilic polyoxyethylated chain.

Simultaneous determination of uncharged and anionic detergents can be carried out by measuring charging currents using the Kalousek commutator (ref.29). A mixture of Na-dodecyl-sulphonate and Triton X-100 is used as a comparative standard.

A very sensitive method for the determination of various surface active substances such as tetraalkylammonium and dextran salts and crude oil products in water is based on measurement of the electrocapillarity (refs. 7,8,9) under conditions where transport of the substance to the DME is accelerated by convection. The detection limit lies in the concentration range from 10 to 100 μg L^{-1}.

Commercially employed detergents have also been determined after HPLC separation with electrochemical detection following adsorptive accumulation at the electrode (ref.30). An A.C. polarographic analyzer has been designed for continuous measurement of surface active substances in waters (in the concentration range from 0.1 to 20 mg L^{-1}) based on measurement of the alternating charging current, which depends on the concentration of the analyzed substances (ref.31). The instrument carries out measurements of the differential capacity of the electrode double layer prior to and after attainment of adsorption equilibrium. The measurements prior to attainment of adsorption equilibrium correspond to the "empty" solution in the absence of the surface active substance.

Humic compounds

Traces of humic compounds in drinking water can be determined by classical polarographic methods, where the inhibition effect of tri-n-butylphosphate adsorbed at the electrode on the polarographic wave of copper (II) ions is measured (ref.32). The presence of humic components in the sample decreases this inhibition effect. The method can be used for determinations in the concentration range from 0.05 to 1 mg L^{-1}. Humic acid and fulvic acid cannot be distinguished; the presence of aminoacid peptides and polyhydroxy compounds does not interfere in the determination.

Oily substances

The published polarographic methods for the determination of crude oil and derived substances in waters are based on nonspecific measurement of the surface activity. The analysis is further complicated when the water sample is polluted by other surface active substances (tensides, fats, emulsifiers, etc.). The measured effects most often correspond to the content of crude oil products dissolved in water; however, these substances can also be present as emulsions, which also yield a tensammetric peak (usually with a very sharp shape). The height of these peaks exhibits a time dependence on the changes in the stability of the emulsion.

Gosman and Heyrovsky (ref.33) described a suppression effect of crude oil on the polarographic maxima of divalent copper. Crude oil was classified according to various sources according to the sample dilution that produced a decrease in the height of the maximum to half its original height. Similar suppression effects of aqueous extracts of crude oil, heating oils, kerosene and various aromatic and saturated hydrocarbons are described in ref. (34). The suppression of the polarographic maximum of divalent mercury was measured in solutions containing 0.1 mL of a 0.1M $HgCl_2$ solution added to 100 mL of sample. The suppression effect increased for higher crude oil fractions. The effect of these substances on the charging current was also measured using a Kalousek commutator. Crude-oil-type substances dissolved in sea water yielded a measurable effect at the DME at concentrations of 0.02 to 100 mg L^{-1}. Triton X-100 was used in the construction of the calibration curve. Crude-oil-type substances dissolved in water can also be determined using polarographic methods, especially when combined with previous adsorption accumulation of the substances on the surface of a hanging mercury drop electrode (ref.35). The desorption peak is then measured in base electrolyte solutions containing KF or NaOH, with a potential of -1.2V in 1M NaOH

and $-1.4V$ in 5M KF (accumulation is carried out at $-0.7V$, all the potentials are vs. the SCE). Similar results were obtained in synthetic sea water containing crude-oil-type substances. The lower crude oil fraction (to $150^{\circ}C$) yielded a sharp peak in the potential region from $-0.6V$ to $-0.9V$ and the higher fraction yields a peak at a potential of $-1.2V$, which is typical for the presence of crude oil in water. The content of crude-oil-type substances in water can also be determined by electrocapillary measurements of the dependence of the DME drop time on the potential. Adsorptive accumulation at the electrode is also employed here (during growth of the drop). In this method, a solution of the base electrolyte is pipetted into the clean vessel and, after removal of oxygen, the dependance of the drop time of a freely dropping DME (t_o) on the applied potential E is measured (for example, in steps of 100 mV). After addition of the surface active substance (or polluted water), the drop-time measurement is repeated; the solution is stirred during drop growth up to about (t_o - 12)s, when stirring is stopped. Compared to the original t_o -E curve, the new t_o' -E dependence is decreased in the potential range corresponding to adsorption; the greatest changes in the drop time are observed at the potential of maximum sensitivity (i.e. maximal adsorption), E_{max}. When the solution is exchanged for a fresh base electrolyte solution and the dependence of the drop time t_o' on the concentration of surface active substance C is measured at $E = E_{max}$ and with solution stirring up to about (t_o'-10)s, an analytically useful dependence is obtained. The parameters of the curve are characteristic for the given system and given arrangement, as they correspond to the dependence of the surface tension on the concentration.

The concentration dependence of the output signal, i.e. the height of the adsorpion/desorption peak or the change in the drop time in electrocapillary measurements can be measured using a series of standard solutions, with a defined volume percent concentration of a saturated solution of the given sample of crude oil or crude oil product in the base electrolyte solution. This approach, of course, assumes knowledge of the source or product producing pollution of the water sample. The height of the tensammetric peak in the region around $-1.2V$ and the change in the drop time at E_{max} can also be compared with the corresponding quantities for sodium dodecylbenzenesulphonate (DBS), used as a comparative standard, obtained under the same conditions. The shape of the tensammetric peak of DBS at $-1.1V$ and that of the electrocapillary curve of DBS are similar to those for crude oil products and measured changes in the concentration range from 1 to 8 μmol L^{-1} are roughly a linear function of the concentration. In this way, the concentration -or, rather, the surface activity which is important ecologically - of crude-oil-type substances in water can be related to the concentration of DBS. Electrocapillary measurements can be used to characterize the surface activity of samples without use of a comparative standard, in terms of the relative change in the drop time or relative interfacial tension between mercury and the solution.

Other organic compounds

Waters can be polluted by a great many substances that were not mentioned in the previous text. These include particularly pesticides, various nitrocompounds, polychlorinated biphenyls, etc. The determination of these substances can also be based on adsorption phenomena, especially using adsorptive stripping voltammetry, discussed in Sect. 2. Adsorptive stripping voltammetry can serve for trace determination of some pesticides like paraquat (ref.36) and pesticides with nitro- or triazine groups (ref.37). Paraquat can be accumulated at the hanging mercury electrode at $-0.6V$ (vs. the SCE) in acetate buffer pH 4.6, and the peak can be measured at $-1.15V$ (SCE). Polychlorinated biphenyls may appear in natural and waste waters as the result of industrial activity. These compounds can be determined after adsorptive accumulation at $-0.4V$ (vs. Ag/AgCl) in Britton-Robinson buffer pH 5 to 6 containing 20% methanol (ref.38). The method can be used in the concentration range 0.01 to 1 mg L^{-1}. Cyanuric acid and its chlorinated derivatives are used in dyestuff production or for disinfection of water and can be determined in waters using the combination of cathodic and adsorptive stripping voltammetry (ref.39). The detection limit is 10 μg L^{-1}, and chlorides do not interfere.

Determination of some trace metal ions

The adsorptive stripping analysis of some metals can be carried out by using complexing agents to form complexes that are adsorbed on the electrode surface; the reduction peak of the adsorbed compound is then measured. This approach permits sensitive determination of elements that are impossible or very difficult to determine by anodic stripping voltammetry (such as Ni, U, V, Mo, Fe, etc.).

For example, uranium can be determined down to a concentration of 2.10^{-9} mol L^{-1} after adsorptive accumulation of its pyrocatechol complex (ref.40). The base electrolyte is an acetate buffer with pH 4.7 and the accumulation potential is $-0.1V$ (vs. Ag/AgCl); the peak potential equals $-0.35V$. A similar method is described in ref. (41). Nickel can be determined in water, biological materials, foodstuffs, etc. after accumulation of the Ni-dimethylglyoximate complex at a mercury electrode (ref.42). The detection limit for the determination of Ni^{2+} in water is 1 μg L^{-1}. Silica in drinking, sea and boiler water can be determined after accumulation as silicomolybdate (ref.43).

4. CONCLUSIONS

When consideration is given to the capabilities of polarography for the study of surface active substances, it should once more be emphasized that a great many methods, and especially those based on suppression of polarographic maxima, are nonspecific and mostly do not permit analysis of a mixture of substances. In many applications, such as the determination of undefined surface active substances in waters, the result obtained corresponds only to the overall content. Nonetheless, the determination of the surface activity of water is often more important than determination of the concentrations of the individual components, because of the toxic effects of surface active substances on living organisms.

The method of adsorptive stripping analysis, both of adsorbable complexes and of electroactive organic compounds, appears very promising, as it broadens the range of trace analysis down to concentrations below 1 μg/Kg (ref.44).

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