Pure & Appl. Chem., Vol. 60, No. 10, pp. 1535–1548, 1988.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
SUBCOMMITTEE ON ENVIRONMENTAL ANALYTICAL CHEMISTRY*†

Interpretation of Speciation Measurements: A Case Study

DIRECT POLAROGRAPHIC DETERMINATION OF O_2, Fe(II), Mn(II), S(−II) AND RELATED SPECIES IN ANOXIC WATERS

Prepared for publication by

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† Title 1985–87: Subcommittee on Electroanalytical Methods of Environmental Trace Analysis of the Commission on Electroanalytical Chemistry

Interpretation of speciation measurements: a case study. Direct polarographic determination of O_2, Fe(II), Mn(II), S(−II) and related species in anoxic waters

Abstract Direct polarographic measurements of naturally anoxic waters can readily determine Fe(II), Mn (II), S(-II) and dissolved O_2. Procedures for collecting and handling samples are described and the results from different studies are systematically discussed and evaluated. The unique capabilities of polarography to distinguish between soluble, colloidal and particulate species have led to the characterization of the time dependent formation of colloidal, complexed and solid phase forms of FeS in natural waters, and to an appreciation of the complicated distribution of various oxidation states of Mn and Fe between particulate and colloidal fractions.

1. INTRODUCTION

Waters which are devoid of oxygen and so termed anoxic occur commonly in nature. Anoxic conditions usually arise when water is isolated from the atmosphere, and oxygen is consumed by the decomposition of organic matter. Some thermally stratified lakes and fjords may have bottom waters which are permanently or seasonally anoxic, as have a few deep oceanic trenches and seas (e.g. the Black Sea). The sediments of most lakes, rivers and seas are mainly comprised of water (80-95%) and usually lack oxygen. Similarly the interstitial waters of many soils are anoxic and although consumption of oxygen in groundwaters is usually slow, they may be isolated for sufficiently long times for the oxygen to be completely removed.

When an element has more than one oxidation state the more reduced form is often stable in the absence of oxygen and the more oxidized one in its presence. Thus Fe(II), Mn(II) and S(-II) are stable in anoxic waters but are readily oxidized by oxygen (refs. 1,2). These three reduced elemental forms are readily determined by polarography (ref. 3). Anoxic waters are ideally suited to voltammetric analysis because there is no need to bubble with inert gas to remove the unwanted oxygen signals. Under favorable conditions measurements may be made directly on untreated waters and so valuable information is gained about the in situ chemical speciation.

Although there are other elements which undergo redox transformations in anoxic waters this paper is restricted to oxygen, iron, manganese, sulfur and a few related species. These are all abundant in nature and so can usually be measured by direct polarographic techniques without recourse to pretreatment procedures, as used for example in stripping techniques. More than a decade has passed since polarography was first used to measure iron and manganese in anoxic lake water (ref. 4), and in that time voltammetric techniques have been used increasingly to study diverse situations. It is now an appropriate time to take an overview of progress to date, to consider how practical problems have been overcome, and how progress may be made in the future.

2. SAMPLING AND HANDLING

2.1 Major difficulties

The type of procedures used for collecting a sample of anoxic water and subsequently manipulating it prior to measurement depend on whether there is a requirement for information concerning the chemical speciation of the sample. If there is, care must be taken to perturb the sample as little as possible from its in situ state, but if only simple analysis is required more flexibility in sample treatment can be tolerated. As voltammetric techniques are particularly well suited for speciation studies sampling and subsequent handling of an undisturbed sample will be considered.

Two major problems have to be overcome:

(1) Oxidation by O_2: some of the dissolved reduced species are very susceptible to oxidation so the anoxic conditions must be strictly preserved. At pH 7 and 20° C the half-life

of Fe(II) in air-saturated freshwater is 36 minutes, whereas at pH 8 in freshwater and seawater it is 0.4 and 7 minutes, respectively (ref. 5). The oxidation of Mn(II) (ref. 6) and S(-II) (ref. 7) usually proceeds more slowly (days), but can be accelerated by catalysis.

(2) Losses of soluble gaseous species: Gas solubility is, according to Henry's Law, related to the partial pressure in the overlying atmosphere. As normal air contains negligible sulfide, in an open system there will be a continuous loss of sulfide from solution. The pH of most natural waters is controlled by the partial pressure of carbon dioxide and most anoxic waters - due to a production of CO_2 by oxidation of organic material - contain an excess of CO_2. On exposure to air this is released to re-establish equilibrium with the partial pressure of CO_2 in the atmosphere, and consequently the pH of the solution rises.

2.2 Sampling procedures

To overcome volatility problems samples have been collected in sealed containers which also exclude oxygen. Davison (refs. 8, 9) has collected samples using a peristaltic pump. The water was transferred, by continuous flushing in a bubble free stream, into 100 ml glass bottles fitted with glass taps (Fig. 1). On returning to the laboratory the bottles were connected via plastic tubing to a pre-degassed polarographic cell modified to act in a flowing mode. The sample was transferred from the bottle to the measuring cell by simple gravity feed. Comprehensive tests showed that using this procedure there was no discernable contamination by dissolved oxygen (detection limit 15 µg/l), whereas use of a Ruttner sampler or of a Friedinger sampler (refs. 3, 10) introduced measurable amounts of oxygen (refs. 8, 9), even when samples were collected as recommended for determining oxygen by Winkler titration (ref. 8) and transferred to a polarographic cell in a glove box filled with an inert gas.

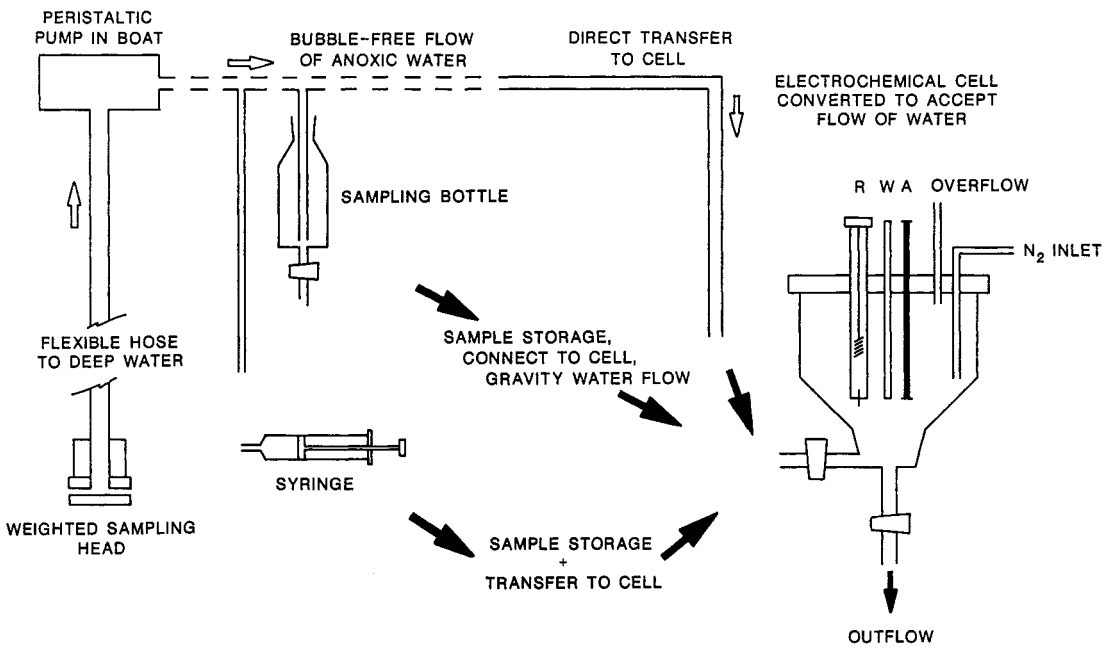


Fig. 1. Schematic representation of sampling and handling procedures usable for polarographic determinations in anoxic waters.

Liden (ref. 12) used a multiple syringe sampler to collect anoxic water from an ice covered lake. The remotely triggered syringes were filled slowly to prevent pressure changes which could effect the dissolved gases. The syringes were then stoppered and stored in glass tubes containing an oxygen consuming buffer. Within a few hours the sample was transferred directly to the measuring cell which was blanketed with argon.

Syringes have also been used to collect pore water samples from lake sediment cores (ref. 13). A sealed filter unit was incorporated in the syringe and the filtered sample transferred to the polarographic vessel within 2-3 minutes of taking the sample. The polarographically measured iron and manganese decayed very rapidly and then levelled out. A plateau value for Mn(II) of 95% of the initial value was reached in 5 minutes and for iron

TABLE 1. Polarographically measurable (DPP) Mn(II), Fe(II) and S(-II) determined in the field and after sample storage using two different sampling techniques.

Species	Sampling procedure		
	Field determination	Syringe-sampler	Winkler bottles
Mn(II) (μM)	8.1 ± 0.5	8.2 ± 0.4	8.3 ± 0.4
Fe(II) (μM)	27.9 ± 5.4	32.9 ± 7.8	33.9 ± 6.2
S(-II) (μM)	11.4 ± 1.9	1.7 ± 0.3	5.0 ± 4.4

concentrations given are the average values computed from 5 replicate samples. Error interval is ± ts, where t is the student t for a 95% confidence level and s is the sample standard deviation.

the plateau, between 80% and 95% of the initial value depending on the conditions, was reached in 100 minutes. Experiments showed that these changes were not linked to loss by oxidation, or to a pH shift due to CO_2 removal. They were exaggerated by stirring, suggesting that they may be brought about by particle interactions.

Although storage of the sample in sealed containers for a few hours may be suitable for the determination of iron and manganese it is unsuitable if sulfide is present. De Vitre and Buffle (refs. 14, 15) have compared direct in the field polarographic determinations with results obtained by collecting samples in completely filled, airtight, plexiglass syringes or Winkler bottles followed by sample storage (6-8 hours) and laboratory measurements. In the former case, they performed their measurements on a platform floating on the lake, and used a peristaltic pump to supply the water sample directly to the polarographic cell. Prior to measurement the pre-degassed cell was flushed with at least four times its volume of sample and was completely filled to obviate the need for a blanketing inert atmosphere, so minimizing volatilization losses. The direct in the field determinations for both Fe(II) and S(-II) were significantly different from the values measured in the laboratory using either of the two above mentioned sampling procedures (see Table 1). Very large losses of sulfide - up to 80% - occurred in the case of laboratory measurements when either Winkler bottles or syringes were used. The Fe^{2+} concentration was also wrong, neither oxidation nor a change in pH could account for the differences observed. They were explained by recording the polarographic S(-II) and Fe^{2+} peaks directly in the field as a function of time. The former was found to decrease very quickly (approx. 25% after 10 min., 50% after 1 hour; see Fig. 2). These losses of S(-II) in airtight completely filled containers were attributed to the formation of gas microbubbles on the walls of the containers, due to a pressure change. A simultaneous change in the Fe^{2+} peak can occur in conditions where Fe(II)-S(-II) complex species exist in solution (ref. 15). Losses of S(-II) produce a shift in the corresponding equilibrium towards decomplexation and therefore an increase in the Fe^{2+} peak compared to the initial state.

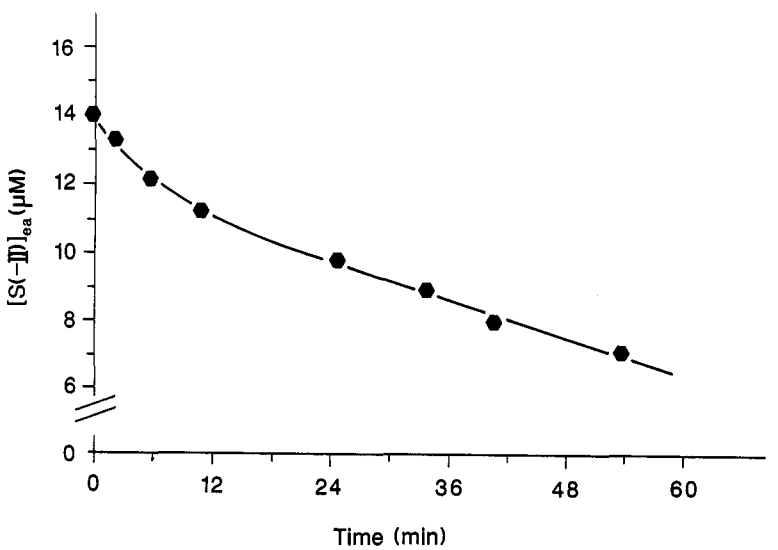


Fig. 2. Change in the DPP measurable sulfide concentration as a function of time after sampling. The measurements were performed directly in the field (Lake Bret, VD, Switzerland), in a completely filled polarographic cell (pH = 7.1, T = 19 ± 3 °C).

2.3 Sample storage

When sample storage is unavoidable it is in principle important to store and transport the samples, prior to measurement, in the dark to avoid photosynthetic processes (ref. 16) and consequently consumption of CO_2 resulting in a change in pH. Respiration processes may occur in the dark, but the resulting pH change is usually less dramatic than for photosynthesis. Exposure to light can initiate photochemical reactions (ref. 17) including changes in the oxidation state of iron and manganese and can promote the conversion of sulfide to sulfate (ref. 18) if the appropriate micro-organisms are present. In practice, however, samples exposed to light are seldom measurably different from their dark controls (Davison: unpublished results).

Samples should also be stored at the in situ temperature to avoid thermally induced changes in the species distributions (see below).

Finally it should be noted that in samples containing both Fe(II) and S(-II), and when the ionic product is close to or exceeds the solubility product of FeS, colloidal particles - invisible to the naked eye - may slowly form within hours, resulting in a slow decrease in the concentration of polarographically measurable Fe(II) and S(-II) species. In the above-mentioned case sample storage must be avoided and determinations carried out directly in the field.

3. GENERAL EXPERIMENTAL CONSIDERATIONS

3.1 Temperature

The in situ temperature of most anoxic waters is lower than normal laboratory temperatures and in some cases, for example in deep lakes, the pressure may be elevated by a few atmospheres. Changes in temperature may produce changes in the value of equilibrium constants, altering the pH and the equilibrium concentration of ionic species. In carbonate buffered systems the pH decreases by ca. 0.1 for a 10° C increase in temperature (refs. 19, 20). Furthermore, for most electrode reactions each 1° C change in temperature alters the SDC (Sampled Direct Current polarography) current by 1-2% (ref. 21) and cathodic sweep voltammetric currents by 5-10%. Therefore during sample storage and the polarographic measurement the temperature should be maintained at the in situ value of the sample if representative speciation measurements are desired.

3.2 Inert blanketing gas, degassing and pH buffering

Ideally, polarographic measurements should be made in a completely filled airtight cell, excluding any gaseous exchange with an inert blanketing atmosphere. This is particularly important for samples containing sulfide (to avoid losses by volatilization). Even if sulfide is absent however, it prevents the exchange of CO_2 and any resultant changes in pH. Should oxygen be present, it may be necessary to degas the sample. In these cases one must take into account that the pH of bicarbonate buffered water samples is finely poised with respect to the partial pressure of carbon dioxide. Therefore to avoid any shift in pH, the gas used to blanket the solution, or to deoxygenate it, must contain CO_2 at the partial pressure corresponding to the CO_2 concentration in the sample. Ar/CO_2 or N_2/CO_2 mixtures have been used at total gas flow rates of 100-400 ml min^{-1}. It is convenient to measure the pH of the solution to assess the gas balance, and, rather than introducing the electrode into the polarographic cell, it can be placed in a twin (dummy) cell fed by a parallel gas stream. Often the partial pressure of CO_2 is set at the average value for air of $3.3.10^{-4}$ atm (ref. 1), but as mentioned above if very fine pH control is required it must be at the partial pressure of the solution. This can be achieved by measuring the pH of an extra sample and then tuning the gas mixture to maintain that value (ref. 5).

In many cases (O_2, S(-II) and complexed forms of Fe(II), for example) the concentration of polarographically measured species is linked to pH through some chemical reaction. It is then very important to maintain a constant pH, not only in the bulk of the solution but also at the electrode surface (ref. 22), since the electrode process itself may induce important local pH changes, and consequently drastic changes in the species present in the diffusion layer. This may strongly affect the potential, current and width of the peak. Such effects can only be avoided by ensuring that the pH buffer capacity of the solution is at least ten times greater than the concentration of the polarographically measured species. These conditions are generally fulfilled by using the above mentioned HCO_3^-/CO_2 system with samples containing a concentration of at least 0.3 mM of hydrogen carbonate.

3.3 Electrodes

Reported measurements of anoxic waters have been carried out with conventional polarographic equipment. The techniques have been restricted to differential pulse polarography (DPP), normal pulse polarography (NPP) and polarography with current sampling (SDC). All workers have used renewable mercury electrodes with mechanical drop dislodgement, either with

classical continuous feed (refs. 4, 15) or as an intermittant static drop (ref. 12). Both silver chloride and calomel reference electrodes have been successfully used. Platinum wire is well accepted as the auxiliary electrode.

3.4 Swamping electrolyte

Addition of a swamping electrolyte should be avoided since this may lead to a change in the equilibrium conditions. In this respect seawater is an ideal medium for polarography because its high ionic strength (0.7 M) ensures an adequate concentration of swamping electrolyte. Freshwaters are much more dilute: hard waters have typical ionic strengths of 5-10 mM and soft waters are usually 1-2 mM, and in some cases lower (ref. 23). Usually the measured species are at concentrations of less than 10 μM (i.e., at least 100 times lower than the natural electrolyte concentration), and so migration currents are negligible even without addition of an external electrolyte. When concentrations of the analyte exceed 0.1 mM, as Fe(II) does in some cases (ref. 3), migration currents may have to be considered.

In very dilute solutions the effective resistance between the working and the reference electrode may be appreciable (10-100 kΩ), which in solutions containing high concentrations of Fe(II) and Mn(II), where the current can be as great as 1 μA (ref. 24), can lead to potential shifts of 10-100 mV due to ohmic drop problems (ref. 25). The diffusion limited height of a DC or NPP polarographic wave is not affected by resistive problems and, providing account is taken of the potential shift, the measured current will increase linearly with concentration. Therefore when using SDC or NPP, a possible ohmic drop is not an important problem for S(-II), Mn(II), Fe(II) and O_2 measurements since generally only the currents are used to compute concentrations. DPP, however, is sensitive to possible ohmic drop problems, peaks are broadened, and the current depressed, resulting in non-linear calibration curves. Note however that values of ohmic drop of 10-100 mV represent the worst possible cases: for most measurements ohmic drop effects are negligible.

High solution resistance has another detrimental effect on modulation techniques. It increases the RC decay constant and so prolongs the time, after application of a pulse, required to separate the faradaic and the capacitive components of the current. Techniques which use relatively long measuring times (50-100 ms) such as DPP are little affected, but the distortion of rapid staircase or square wave polarograms can be appreciable (ref. 26). A more detailed discussion on the minimum acceptable ionic strength is given in ref. 27.

3.5 Calibration curves

Calibration curves should, as far as possible, be prepared in the same medium used to perform the measurement. Providing the conditions, including the performance of the electrodes, remain constant, calibration curves should not change. Direct current polarograms always give linear calibrations over all concentrations ranges, and to a large extent, irrespective of the media. DPP polarograms are dependent on the reversibility of the electrode reactions which may be influenced by medium changes. Other complicating factors, such as solution resistivity, can also operate and produce curved calibrations. Typical DPP and SDC polarograms are shown in Fig. 3 and the individual features of the peaks and waves are discussed in the succeeding sections.

4. OXYGEN

Although this work primarily addresses measurements in anoxic waters, there is still a requirement to measure oxygen. It is useful for testing sampling and handling procedures and for distinguishing, both temporally and spatially, the limits of anoxia. Thus, in lakes, anoxic conditions may develop seasonally and so the depth of water which is anoxic may continually change (ref. 15, 28-30).

The electrode reactions for the reduction of oxygen at a dropping mercury electrode are well established (ref. 31). In neutral or alkaline media they are:

$$O_2 + 2H_2O + 2e = H_2O_2 + 2OH^- \quad (1)$$

$$H_2O_2 + 2e = 2OH^- \quad (2)$$

The first reaction has a half wave potential of -0.50 V versus the sat. calomel electrode and the second occurs at -0.90 V (ref. 32). Dropping mercury electrodes were frequently used for measuring oxygen in natural waters (refs. 33, 34) until the mid-sixties when, because of ease of use, membrane covered electrodes became popular. The dropping mercury electrode has a higher sensitivity than most commercially available membrane electrodes and can therefore be of particular use for precise determination of low concentrations (3.0 μM, i.e., 0.1 mg/l). The first wave is normally used, since the second wave is broad due to irreversibility. Direct current polarography, especially using mechanical drop dislodgement and current sampling, provides an easy means of measurement. The current of the diffusion limited plateau is usually measured at a preselected voltage. Ideally it should be prior to the second wave, which increases from about -0.70 V. In sulfide free solutions anywhere between

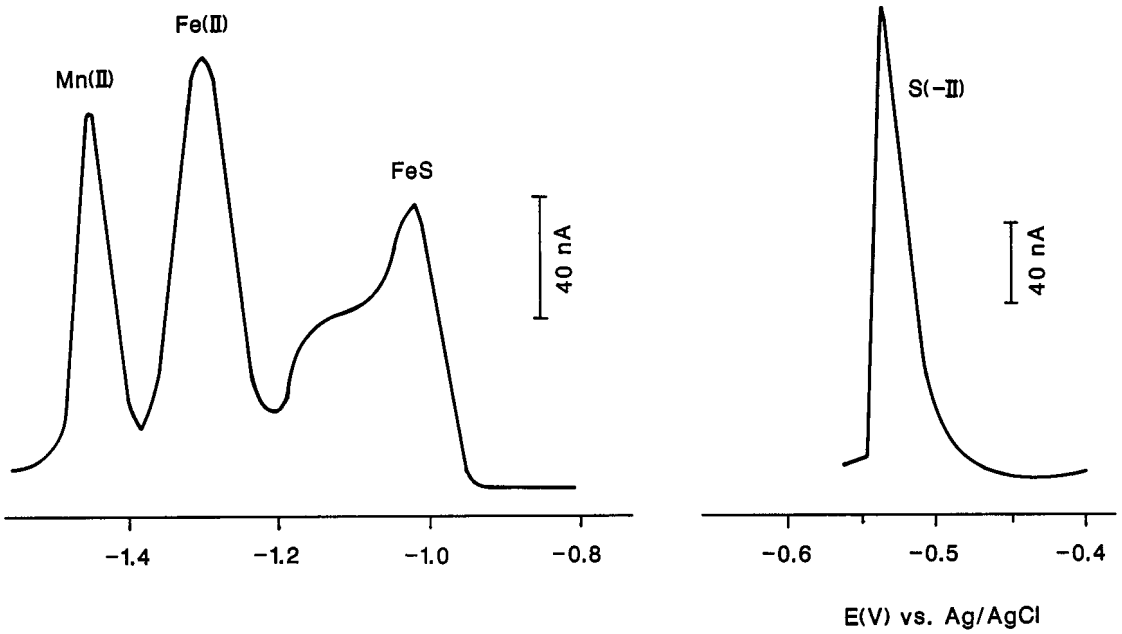
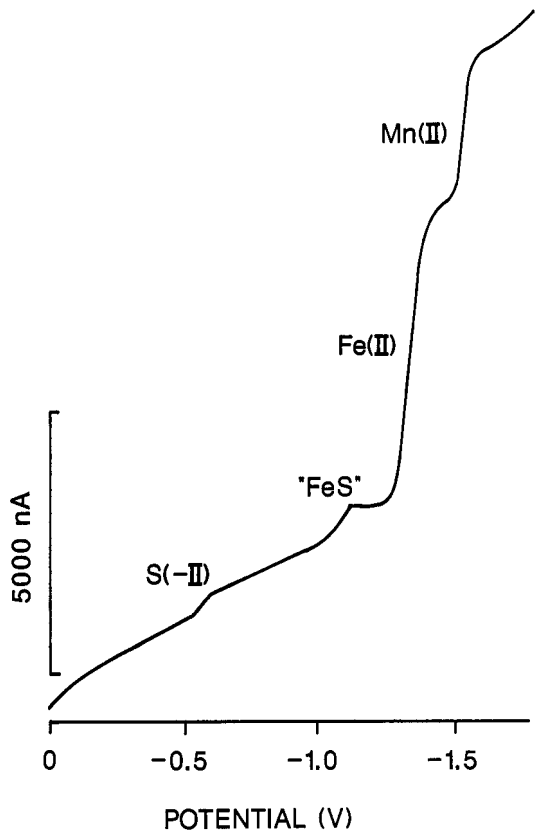


Fig. 3a (above) Typical DPP polarogram of anoxic lake water (Lake Bret, VD, Switzerland), pH = 7.2, T = 11° C. Concentrations were : S(-II), 10.1 µM : Fe(II), 54.4 µM; Mn(II) 10.4 µM.

Fig. 3b (side) Typical SDC polarogram of anoxic lake water (Esthwaite Water, Windermere, UK), pH = 7.1, T = 20° C. Concentrations were : S(-II), 5.1 µM; Fe(II), 96 µM ; Mn(II) 46 µM.



-0.40 V and -0.60 V may be selected. In the presence of sulfide O_2 measurements must be performed after the sulfide signal which is also at about -0.60 V (ref. 3). Since this signal is anodic, DC current measured at a more negative potential is not affected by it. Note that this problem does not exist with DPP which is the prefered technique in the presence of S(-II). Another good reason for selecting a fairly negative potential when using SDC polarography is that the current is more likely to be free from maxima due to

surface phenomena at the electrodes (ref. 32). These artificially enhance the current in an unpredictable way. In freshwaters when short (1s) drop times are used they only tend to occur between -0.10 and -0.40 V. Although the maxima can easily be removed by adding surfactants, this would interfere with the speciation so manipulation of conditions, such as potential and drop time must be used instead.

Calibration is best performed in the medium in which oxygen is being determined. Fixed aliquots of a concentrated standard solution should be added to a stirred solution which is initially free of oxygen, and the polarogram recorded within 2 minutes to avoid loss by volatilization. The standard solution should be kept in full sealed glass containers; a micrometer syringe assembly is ideal because it can be used for storage and for making known additions. Air saturated water can be used as the standard solution. The oxygen content is preferably determined by Winkler titration (ref. 35) either in the stock solution or in the polarographic solution by taking samples from the polarographic cell itself, immediately after measurement. In this case use of a cell as described in Fig. 1 is particularly convenient. Oxygen concentration can also be checked against documented saturated concentrations (ref. 34).

The precision (standard deviation) of the SDC determination of oxygen was reported to be 0.6 μM (0.019 mg/l) for seawater (ref. 32) and 0.3 μM (0.009 mg/l) for freshwater using optimal sampling procedures (ref. 8) which enabled as little as 0.5 μM (0.016 mg/l) to be detected in the latter case.

5. MANGANESE

Although manganese has three common oxidation states only Mn(II) is soluble in aqueous solution, Mn(III) and Mn(IV) being completely hydrolysed and present as non-stoichiometric oxides (ref. 1). Manganese is an ubiquitous and abundant metal (ref. 36) which can, in anoxic water, reach concentrations of 0.1 mM (ref. 37). Concentrations of Mn(II), of up to 1 μM commonly occur in oxygenated waters (ref. 38). They are due either to anthropogenic input or to the photochemical production of Mn(II) (ref. 39) and its relatively slow rate of oxidation, which, depending on catalytic effects, has a half-life of 1-100 days (refs. 6, 15, 40).

Electrochemical measurement is based on the reduction of Mn(II) to the metal. The reaction (refs. 41, 42)

$$Mn(II) + 2e = Mn^{\circ} \qquad (3)$$

is easily measured by SDC or DPP. The peak potential, versus the saturated calomel electrode, occurs at -1.5 V in seawater (refs. 43, 44) and between -1.49 and -1.56 V in various freshwaters (refs. 4, 15). Note that Cr(III) in anoxic waters is reduced at a similar potential. If the simultaneous presence of Cr(III) is suspected the solution composition must be modified to resolve the signals (ref. 45). In some freshwaters maxima may develop using SDC, but only near the start of the diffusion limited plateau. There is rarely any need to resort to adding surfactants (ref. 46) or raising the temperature (ref. 47) to overcome the problem.

Calibration using SDC is simple because the curve is linear over all concentration ranges. Additions of aliquots of a degassed stock solution of Mn(II) to lake water and to a synthetic solution of 1 mM $NaHCO_3$ plus 1.16 mM KCl result in identical calibration curves (ref. 4). Nevertheless internal calibration directly in the studied medium is best. Because measurements using SDC are not influenced by the electrode reaction it should be the preferred technique for concentrations above the detection limit of 2 μM, although admittedly the wave heights are a little more difficult to measure than DPP peaks. DPP should be used in the concentration range 1.10^{-7} to 2.10^{-6} M, although calibration curves tend to be slightly convex at the high concentration end. In low ionic strength freshwaters, the curvature has been attributed to the high solution resistance depressing larger currents (ref. 4). However, curvature was also observed in seawater (ref. 43) so there may well be a change in the electrode reaction at higher concentrations of manganese. Different procedures have been used to calibrate the measurements. Several workers (refs. 3, 15, 29, 30) simply prepared calibration curves by adding manganese to a sample of manganese free lakewater, however care must be exercised to ensure that the lakewater does not contain particulates or dissolved organic compounds capable of adsorbing and/or complexing the added Mn. Furthermore the adsorption of Mn onto the polarographic vessel's walls can lead to concave calibration curves at low Mn concentrations (see Fig. 4). Knox and Turner (ref. 43) fitted a convex calibration to two straight lines, above and below 3 μM, and combined this information with standard additions to the sample being measured. Detection limits for Mn(II) determined by DPP have been cited between 0.05 μM for freshwater (ref. 48) and 0.2 μM for seawater (ref. 43). However due to the above-mentioned adsorption losses and complexation of Mn(II), caution must be exercised when applying these detection limits.

Manganese has also been measured in natural waters using anodic stripping voltammetry, ASV, with detection limits of 10^{-10} to 10^{-9} M, depending on the type of working electrode

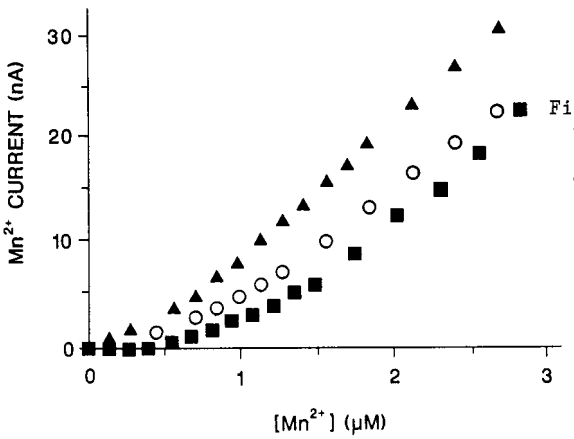


Fig. 4. DPP calibration curves for Mn(II) in various media. ▲: untreated lakewater (Lake Bret, VD, Switzerland); ■ : 0.02 M $NaHCO_3$; ○ : 0.1 M KCl + 5.10^{-3} M $NaHCO_3$. In all cases, T = 20° C, pH = 7.9. The initial non-linear parts of the curves are due to adsorption of Mn(II) on the polarographic cell walls.

(refs. 38, 49, 50). It is readily stripped from mercury at the fairly slow scan rate used for differential pulse anodic stripping voltammetry, DPASV, (ref. 51). One major problem is the very negative (ca. -1.7 V) deposition potential which, in the neutral pH of natural waters, has to be carefully selected to avoid interference from the reduction potential of hydrogen. Furthermore, adsorption of organic compounds on the electrode surface may also distort ASV peaks in natural waters, so that DPP should be used preferably when the concentration of Mn(II) is greater than 10^{-7} M.

6. IRON

6.1 Fe(II) peaks

Iron has two common oxidation states. In neutral solutions Fe(II) is soluble, whereas Fe(III) occurs as a variety of oxyhydroxides (ref. 1). As the second most abundant metal in the earth's crust, iron is present in almost all waters and under anoxic conditions Fe(II) can occur at concentrations exceeding 0.1 mM (ref. 37). It can also occur at lower concentrations (1 μM) in well oxygenated waters if they are sufficiently acid or if photochemical reactions occur (ref. 52).

Fe(II) is usually determined (ref. 4) by its irreversible reduction to the metal (equation 4).

$$Fe(II) + 2e = Fe \quad (4)$$

In principle it is also possible to measure Fe(II) by its oxidation to Fe(III) (equation 5), refs. 53-55:

$$Fe(II) = Fe(III) + e \quad (5)$$

However the potential for this reaction is very dependent on pH and the presence of complexing agents. Furthermore, in untreated natural waters the reaction occurs at potentials which are too positive to be measured by a mercury electrode (ref. 55).

The DPP peak potential for the reduction of Fe(II) has been measured at -1.35 V in freshwater (ref. 3, 15) and -1.45 V in seawater (ref. 44). The potential cannot be stated very precisely as it depends on pH and the concentration of Fe(II), possibly because $FeOH^+$ is the species which is reduced (ref. 56). SDC polarography is slightly less sensitive for the reduction of Fe(II) than for Mn(II) (ref. 4). The DPP signal for Fe(II) is only one third as sensitive as for Mn(II) and the peak half-width is larger (90-110 mV as compared with 60-70 mV). These are clear indications of a degree of irreversibility in the reduction of Fe(II). The DPP peak is higher and much narrower in low ionic strength solutions.

Calibration procedures for Fe(II) in natural waters are similar to those for Mn(II) (refs. 4, 12, 15). The only surprise is that in anoxic lake water the DPP calibration is closer to linearity than the comparable manganese curve (refs. 12, 15) or that of Fe(II) in a solution of synthetic lake water (ref. 4), which simplifies calibration procedures. Detection limits are 2 μM for SDC (ref. 4) and 0.1 μM for DPP (ref. 48).

In the presence of S(-II) and Fe(II), in conditions where the ionic product is greater than or equal to 1/4 of the solubility product (ref. 15), an iron SDC prewave at ca. -1.0 V may be observed (Fig. 3). It corresponds to a DPP prepeak (Fig. 3) and is due to the reduction to Fe° of a labile FeS complex (most probably Fe_2S_2) which also adsorbs slightly on the electrode (ref. 15, 57). This adsorption may influence the current measured at -1.0 V, but

by correctly choosing the experimental conditions (in particular a short drop time) the height of the corresponding wave (or peak) may be used to measure the concentration of $Fe_2S_2^\circ$. Note that this complex does not influence the DPP peak at -1.35 V which is proportional to the sum of Fe^{2+} and all labile species except $Fe_2S_2^\circ$ (refs. 15, 57).

The electrochemistry of iron is generally very complicated. For example, in non environmental conditions, it was observed that if iron is reduced in the presence of iodate and either perchlorate or nitrate a maximum is produced (refs. 58, 59). The reduction of iodate at -1.1 V produces hydroxyl ions which react with Fe(II) to form colloidal $Fe(OH)_2$ at the electrode surface. The $Fe(OH)_2$ reduces either nitrate or perchlorate at potentials near to the start of the Fe(II) reduction wave, but at more negative potentials direct reduction of Fe(II) out-competes the reaction with hydroxyl ions. No further nitrate or perchlorate is reduced and the current is appropriate to the simple reduction of Fe(II). It must be noted, however, that this catalytic reaction, which has been used to determine nitrate or perchlorate (ref. 60) is unlikely to occur in natural water owing to an absence of any efficient electrolytic generation of hydroxyl ions.

6.2 Fe(III) peaks

It is also possible to reduce Fe(III) at a mercury electrode. When the pH is between 2 and 3 hydrolysed species are produced. The simplest ones, which are in rapid equilibrium with aqueous Fe^{3+}, are reduced at ca. +0.20 V versus the SCE whereas higher molecular components are reduced via an adsorption step at ca. -0.05 V (refs. 61, 62). When the hydrolysed species are formed in the pH range 3-8, in the presence of complexing agents and in conditions where no precipitation occurs, the $E_{1/2}$ of the latter wave shifts towards negative values with a slope of -98 mV/pH. At pH 7, the value of $E_{1/2}$ is ca. -0.40 V (ref. 29). In most natural waters the hydrolysis of Fe(III) is so complete at the nearly neutral pH that the concentrations of the electroreducible species are generally undetectable. However, in special cases hydrolysed species of Fe(III) can be stabilised by natural complexing agents. In fact direct measurements in neutral lake water (refs. 15, 63), often reveal a small (10-50 nA) DP signal at -0.35 V to -0.40 V which can increase as the total concentration of Fe(III) increases (ref. 63). If these small currents, corresponding to an equivalent concentration of $5\text{-}20.10^{-7}$ M, are due to an Fe(III) component it only represents a small fraction of the total Fe(III) ranging from 2.10^{-6} to 2.10^{-5} M. Polarographic measurements of Fe(III) at -0.20 V have also been performed on neutral waters which have a high concentration of humic substances (ref. 64).

Anodic stripping voltammetry has also been used to determine the hydrolysed products of Fe(III), directly at a mercury/graphite electrode (ref. 65), and on Hg HMDE (refs. 66, 67).

7. SULFIDE

Hydrogen sulfide is a dibasic acid which, at a partial pressure of 1 atm, dissolves readily in water to a concentration of 0.12 M at 20° C (ref. 68). The first dissociation constant is close to $pK_1 = 7.0$ at 25° C and the second has a pK_2 greater than 14 (ref. 69). S(-II) may also combine with sulfur to form electroactive polysulfides S_x^{-2} whose stability constants are given in Table 2. It may be shown, however, that in most cases, their contribution to the total sulfide concentration is negligible (ref. 29). Thus below pH 7 the dominant solution species is H_2S, whereas above pH 7 it is HS^-. However as the equilibria

$$H_2S = HS^- + H^+ = S^{-2} + 2H^+ \qquad (6)$$

occur very quickly the electroactive species can be considered to be S^{-2}.

TABLE 2. Conditional stability constants of polysulfides. (adapted from ref. 97)

	log K_s
$1/4\ S_8^\circ + HS^- = S_3^{2-} + H^+$	- 12.5
$3/8\ S_8^\circ + HS^- = S_4^{2-} + H^+$	- 9.5
$1/2\ S_8^\circ + HS^- = S_5^{2-} + H^+$	- 9.4
$5/8\ S_8^\circ + HS^- = S_6^{2-} + H^+$	- 9.6

At potentials more positive than ca. -0.6 V sulfide reacts with mercury to form mercuric sulfide.

$$Hg + S^{-2} = HgS + 2e \qquad (7)$$

At more negative potentials the reverse reaction occurs, with Hg(II) of HgS being reduced back to mercury. These reactions have been widely used for the analytical determination of sulfide (refs. 70-75). The kinetics and mechanism of formation of initial and successive layers of HgS on the mercury surface have been well studied (refs. 76, 77).

The measured current is due to the formation of HgS at each fresh mercury drop. However, at high sulfide concentration, when using conventional polarography (ref. 73) or DPP (ref. 72) modification of the mercury surface by the formation of insoluble films of HgS can result in multiple signals which are unsuitable for analytical work. There have been several

suggestions for overcoming these problems, all based on restricting the formation of mercury sulfide to low surface concentrations, presumably corresponding to less than a monolayer coverage (refs. 73-75).

If a stationary electrode is used to measure sulfide the potential must be scanned anodically so that the mercuric sulfide film is formed during the scan rather than initially. With polarographic techniques which use a new drop each time the potential can be scanned in either direction, but an anodic scan is preferable in solutions containing relatively large concentrations of S(-II).

The high sensitivity of DPP can be exploited when S(-II) is less than 10^{-6} M (refs. 15, 72, 78). The most elegant approach, however, to avoid insoluble film formation is to use NPP (refs. 74, 75, 78, 79), holding the initial potential in the region where HgS does not form, e.g., -0.80 V, and scanning the potential in a positive direction. While the drop is growing no HgS is formed, but at the end of drop life, when the pulse is applied, sulfide reacts with the surface. The short duration of the pulse ensures that multi-film formation does not occur.

Calibration of the normal pulse technique is easy as the same calibration curve is obtained whatever the solution, from 0.4 M NaOH, to lake water of low ionic strength (0.001 M) (ref. 78). Sodium hydroxide solutions are useful for calibration because they maintain H_2S at a low partial pressure and prevent loss of volatile sulfide which readily occurs from neutral solutions. However, when sodium hydroxide is added to lake water to overcome volatility problems care should be exercised since raising the pH may remove sulfide from solution by inducing the precipitation of heavy metal sulfides (ref. 12). Standard solutions, prepared by dissolving $Na_2S.9H_2O$ in water, are quite alkaline and stable for at least 1 week if well stoppered. By using large (~1 g), well formed, single crystals which are quickly washed and tissue dried prior to accurate weighing, 10^{-3} to 10^{-2} M stock solutions can be prepared. Secondary standardization by iodometric titration is however recommended.

Calibration in the case of DPP is more delicate. The mechanism of reduction appears to depend on concentration, and the response of additional spiked sulfide may be influenced by the equilibration time with the solution (ref. 78). DPP is most appropriate for measuring low concentrations when NPP is insufficiently sensitive. The shape of the DPP signal can be used to verify that the electrode reaction is not complicated by extraneous effects (ref. 80). 5.10^{-7} M is a reasonable detection limit for NPP, whereas DPP can be usefully used in the range 1.10^{-7} to 2.10^{-5} M (refs. 15, 78). For DPP calibration can be accomplished by adding small aliquots of a slightly alkaline sulfide solution to the water being measured. DeVitre (ref. 15), for instance found that a linear calibration curve for S(-II) concentrations between 1 and 20.10^{-6} M may be readily obtained by adding suitable aliquots of a stock sulfide solution at pH 11 to anoxic sulfide free lake water. To ensure solution homogeneity the solution was magnetically stirred before measuring the DPP peak. If necessary the pH was adjusted using a N_2/CO_2 gas mixture in order to perform all the measurements at a fixed pH. Immediately after recording the signal an aliquot was withdrawn and the total sulfide concentration determined by the methylene blue colorimetric procedure. By repeating this sequence a linear calibration curve was obtained at the natural lake conditions.

These techniques have been used for the direct measurement of sulfides in lakewaters (refs. 3, 12, 15, 29, 30, 78), the pore waters of marine (ref. 81) and freshwater (ref. 13) sediments, waste waters (ref. 79) and industrial solutions (refs. 82, 83).

Sulfur species other than sulfide, which may be particularly important in marine waters (ref. 81) may also be measured polarographically, but after an appropriate chemical treatment (refs. 15, 29, 30, 81-85). Like sulfide, polysulfide, sulfite, thiosulfate, elemental sulfur and some organic-S containing compounds react anodically, oxidizing mercury to mercuric ions. The conditions and potentials at which the above mentioned species may be analytically determined is given in Table 3.

8. PROGRESS TO DATE

Direct polarographic measurements of anoxic waters have mainly been used for analytical determinations of Fe(II), Mn(II), S(-II) and dissolved O_2 in lakewaters (refs. 3, 4, 8, 9, 12-15, 20, 24, 28-30, 48, 78, 86-90), but estuarine waters (ref. 43), waters from an anoxic marine basin (ref. 44) and waters of marine (ref. 81) and freshwater (refs. 13, 48) sediments have also been analysed. Polarography is particularly appropriate for samples which are already devoid of oxygen and where, consequently, direct measurements of undisturbed natural samples are possible. In particular this has been used to estimate (ref. 15, 30, 91):

- the proportion of particulate, colloidal and small electroactive species;
- the conditional solubility product of FeS in natural conditions based on measurement of true ionic concentrations;
- the chemical evolution of the sample's composition with time due to the formation of colloidal and complexed labile forms of "FeS" and the loss of sulfide due to volatilization.

TABLE 3. Principal reactions used to determine sulfur species using voltammetric techniques.

Reaction	Medium	Technique	Potential[a]	Reference
$Hg^{\circ} \overset{2e^-}{=\!=} Hg^{2+}$ + $2S_2O_3^{2-} = Hg(S_2O_3)_2^{2-}$	Cl^-	SDC/DPP/LSV	-0.12[b]	81
	Ac/AcH, pH=4.7	AC	-0.26[c]	82
$Hg^{\circ} \overset{2e^-}{=\!=} Hg^{2+}$ + $SO_3^{2-} = Hg(SO_3)_2^{2-}$	Cl^-	SDC/DPP/LSV	-0.60[b]	81
	Ac/AcH, pH=4.7	AC	-0.67[c]	82
$Hg^{\circ} \overset{2e^-}{=\!=} Hg^{2+}$ + $HS^- = HgS_{ads} + H^+$	Cl^-, pH=10-12	SDC/DPP/LSV	-0.68[b]	81
	HCO_3^-, pH=7	NPP,DPP	-0.58[c]	15,29,78
$Hg^{\circ} \overset{2e^-}{=\!=} Hg^{2+}$ + $S_x^{2-} = Hg_{ads} + (x-1)S^{\circ}$	Cl^-, pH=10-12	SDC	-0.68[b]	81
$S_x^{2-} + xH_2O \overset{2(x-1)e^-}{=\!=} xHS^- + xOH^-$	NO_3^-/HCO_3^-, pH=9.5	SDC	-0.68[b]	98
$1/8\ s_8 + Hg = HgS_{ads}$	EtOH/H_2O 1:1	CSV	-0.35[c]	29
$HgS_{ads} \overset{2e^-}{=\!=} Hg^{\circ} + S(-II)$	pH=2.2			

a- rel. to sat. calomel electrode, b- half-wave potential, c- peak potential.

The above-mentioned studies exploit the abilities of polarography to determine a unique oxidation state and to distinguish between soluble, colloidal and particulate species. This capability has also been used in laboratory adsorption studies of lead (ref. 92) and manganese (ref. 15). This type of analytical application is important since it is becoming increasingly clear that small colloidal particles which can pass through very fine filters (0.1 μm) (refs. 15, 38, 93, 94) can commonly occur in natural waters. It is common practice to use filtration to distinguish the insoluble forms (presumed to contain only the higher oxidation states) of iron and manganese from the soluble forms (supposed to be only aquated Fe(II) and Mn(II)). Polarography measures either the aquated forms or possibly very small labile colloidal species and therefore gives a different and complementary answer compared to separation by membrane filtration (ref. 15, 38, 43). Their combined use (ref. 15) showed that in lake water, for instance: (1) colloidal sized Fe(III) (with a size less than 0.45 μm) frequently occurs and that it can represent a significant fraction of total iron at a given depth, and (2) that a significant proportion of Fe(II) in a 0.45 μm filtered sample of hypolimnetic water is in fact present as a labile FeS complex.

In order to correctly interpret the results of direct polarographic measurements possible contributions of small colloidal species must be considered. For instance, Fe(III) species can be reduced as small colloids (refs. 61-63). Although Mn(II) and Fe(II) are not subject to strong complexation effects (ref. 2) there is evidence for their being associated to small colloids (refs. 14, 38, 43), in particular as FeS (refs. 3, 63, 29, 30). Sulfide measurements also include polysulfides (ref. 18) as shown in Table 3. The problem of the contribution of colloidal species to the polarographic current is discussed in reference 22 and has been addressed in a theoretical paper by Van Leeuven et al. (refs. 95, 96). The qualitative conclusions important for the present work are briefly presented below.

If colloids contribute to the polarographic current, it will be decreased compared to the current for simple ionic species for two reasons:

(1) their smaller diffusion coefficient will slow down the transport to the electrode;
(2) the colloidal form of the electroactive species must dissociate prior to reduction and the kinetics of such a dissociation step are generally slow.

At present, to our knowledge, no information on the dissociation kinetics of possible colloidal forms of iron, manganese and S(-II) species has been published). On the other hand, the effect of a smaller diffusion coefficient can be assessed in the following manner (ref. 22). Polarographic currents are proportional to the square root of the diffusion coefficient which for "compact" particles is inversely related to the radius of the

diffusing electroactive species (Stokes-Einstein). Therefore, it is possible to estimate the current due to a fully labile colloidal species with a radius of 50 nm as equal to ca. 8% of the current due to an equivalent concentration of an ionic species with a radius of ca. 0.3 nm. This proportion will be even smaller for slowly dissociating colloids. Any particle with a radius greater than or equal to 50 nm is for practical purposes therefore electroactively inert, and so 50 nm can be considered as the upper size limit for colloidal particles to be detected polarographically.

During the past decade rapid progress has been made in the direct use of polarography to study naturally anoxic systems. The next decade is likely to witness increased and more diverse applications, and a more detailed understanding of the measured quantity.

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