

Possibilities to measure the concentration of sodium dithionite in textile applications by means of amperometric sensors

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Abstract

By using linear sweep voltammetry and chronoamperometry at a rotating disc electrode it was found that sodium dithionite can be oxidised at several electrode materials. At platinum, palladium, glassy carbon and gold an oxidation reaction was observed that showed promising characteristics for analytical purposes and sensor development. The limiting current signal at a potential of +0.3 V vs. SSE is proportional to the concentration of sodium dithionite, the electrode reacts almost immediately on a change of concentration of sodium dithionite and experimental proof is given that the electrode is stable for at least 3 days without recalibration. The electrode can be calibrated by a one point calibration because the calibration curve is linear and goes through the origin.

Introduction

Hydrogen peroxide and sodium dithionite (or sodium hydrosulphite) belong to the most important chemicals used in the textile industry. Sodium dithionite is primarily used as reducing agent for the reduction of vat dyes and sulfur containing dyes [1-3]. The purpose of this reduction reaction is to form the leuco components of the mentioned dyes, which are soluble in water and have a great affinity for the textile fabric. Sodium dithionite is also used to optimise the colour fastness, which can be achieved by a reductive decomposition of the excess of dye stuff that is adsorbed at the surface of the textile (especially used for polyester fibres)[4-6]. Other applications of sodium dithionite as reducing agent can be found in the removal of pigments on textile that has been dyed in a wrong way and in the reduction of residual hydrogen peroxide (after bleaching) as a pre-treatment for the dye process with reactive dyes.

Besides its use as reducing agent, sodium dithionite is also used as a bleaching agent in reductive bleaching processes. Examples are bleaching of mechanical paper pulp [7-10] and the bleaching of cotton and wool. It especially reduces carbonyl and alcohol functional groups, which are responsible for the colour of the textile fabric. Unfortunately these processes are not 100 % effective. Therefore a reductive bleaching process is often preceded by an oxidative one (with hydrogen peroxide, sodium hypochlorite or sodium chlorite) [11-14].

Sodium dithionite is relatively unstable [15-18] and tends to react with oxygen. This means that in textile processes where sodium dithionite is involved it is common practice to use a large excess of sodium dithionite to be sure that the concerned treatment is quantitative. Because sodium dithionite itself and its reaction products (sulphite and sulphate) are important pollutants, highly polluted waste water is obtained, containing no dissolved oxygen. A method to measure the concentration of sodium dithionite on line could result in a more efficient use of sodium dithionite and less waste. Measurement and control of the concentration of sodium dithionite also would have a positive influence on the quality of the textile fabric.

At present several methods have been described for the determination of sodium dithionite but none of them gives satisfying results in an industrial environment. A first method, based on a selective titration [19-21], is relatively complicated and takes a lot of time (response time of at least 60 minutes) and effort (expensive). The sample is titrated with iodine after addition of formaldehyde and acetic acid. These compounds are used

to form complexes with sulphite to obtain a selective titration. Besides the above mentioned drawbacks, the precision of this method is relatively low.

A second type of titration based on methylene blue is fast and quantitative but shows no selectivity for sodium dithionite. In this case sulphite, sulphide and thiosulphate present in solution are also titrated.

A third method involves the measurement of the redox potential [22-23] and determination of the sodium dithionite concentration using the equation of Nernst. The authors who described the method did not take into account that the Nernst equation can only be used in equilibrium conditions. Because of the irreversibility of the redox couple $S_2O_4^{2-}/SO_3^{2-}$ this equilibrium condition is never fulfilled, and this method must lead to wrong results because of fundamental reasons.

Measurement of the redox potential during a titration can however be useful when not the potential itself but its variation as a function of degree of progress is taken into account. A relatively simple and fast method has been described using $[Fe(CN)_6]^{3-}$ as titration reagent and a platinum electrode for the potentiometric detection of the endpoint.

In this paper amperometric sensors are described for the on line measurement of the concentration of sodium dithionite with high precision, accuracy and small response time (less than 0.5 s).

Experimental

As working electrodes (WE) use was made of micro disc electrodes. The diameters of those electrodes were 0.5 mm for platinum, 4 mm for gold, 4.2 mm for glassy carbon and 1 mm for palladium, rhenium titanium and zirconium. The reason for using electrodes with a relatively small surface area is to avoid ohmic drop (IR-drop) effects, which can disturb the experimental results drastically. Fig. 1 shows how working electrodes were constructed. A rod of the electrode material (fig.1, a) is positioned on a copper piece (fig. 1, b). To make electrical contact, a thin layer of silver epoxy is used. Then the whole body is immersed in epoxy resin (Epofix kit, Struers) using a holder piece (fig. 1, c) made from PVC[®]. After 48 hours (when the epoxy resin has hardened) the holder is removed and the excess of resin is turned away from the tip of the electrode material (fig. 1, d). From every electrode material used in this investigation, at least 2 electrodes were prepared in this way. A Ag/AgCl/saturated Cl⁻ electrode (SSE, $E_{ref} = +0.222$ V vs. standard hydrogen electrode) from Jumo and a graphite rod from Le Carbone Lorraine acted as reference electrode (RE) and counter electrode (CE) respectively. These electrodes were used in a so called potentiostatic setup. For the measurement of pH and temperature use was made of respectively a glass electrode from Schott and a Pt100 from Jumo.

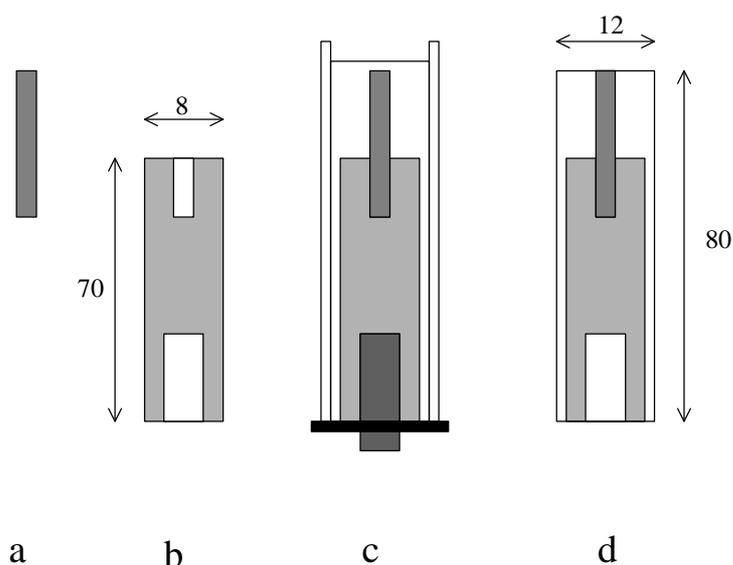


Figure 1 : Scheme of the construction of the working rotating disc electrode. (a) rod of electrode material, (b) copper piece, (c) piece holder for the electrode body and (d) electrode body immersed in epoxy resin. Dimension are given in mm.

With the aid of a potentiostat (PGSTAT10 from Eco Chemie with GPES4.5 software package) it is possible to control the potential of the working electrode with respect to the constant potential of the reference electrode. Therefore a potential difference is applied between WE and CE ($\Delta E_{WE/CE}$) in such a way that the desired potential difference between WE and RE ($\Delta E_{WE/RE}$) is obtained. $\Delta E_{WE/RE}$ can be kept constant (chronoamperometry), varied continuously with time (linear sweep voltammetry) or changed in steps (pulse voltammetry).

The electrochemical activity of the surface of the WE can vary considerably during prolonged contact with air (especially for glassy carbon and less noble metals). Therefore before all experiments the electrode surface was polished to obtain an electrode with optimal and reproducible electrochemical activity. First the surface was smoothed with sand paper (Struers, type 1200 grit) during 15 seconds on a Planopol-2 polishing machine from Struers. To burnish this relatively rough surface it was further polished with Al_2O_3 -powder (Buehler) of 1, 0.3 and 0.05 μm particle size for respectively 5, 10 and 20 minutes. Finally the electrode surface was subjected to ultrasonic cleaning (Branson 3210) for 2 minutes.

The working electrode was rotated with the aid of a RRDE636 rotating system of EG&G Princeton Applied Research. A Lauda MGW20 thermostat was used to obtain a constant temperature in the electrochemical cell. This cell with a capacity of 150 mL was home made from Teflon[®]. A pH-meter from Orion (type 420A) was used for measurement of pH and temperature.

All reagents used were of analytical grade and were obtained from Fluka. Solutions were prepared with double deionised water using a Milli-Q ion exchanger system. All electrode materials were of 99.99 % purity and were obtained from Goodfellow. Nitrogen (L'oxyhydrique, Azote 5.0) was purged through the solution to remove oxygen.

All the experiments were carried out at a pH value of 12.8.

Results

In a first series of experiments the electrochemical behaviour of sodium dithionite was investigated by continuous variation of the potential of the working electrode from a starting potential, where dithionite does not react, to a more positive end potential (linear sweep voltammetry) and simultaneous measurement of the electrode signal (an electrical current). This current is the result of an electrochemical reaction of sodium dithionite at the electrode surface. A positive current is obtained when an oxidation reaction occurs (electrons are released by sodium dithionite to the electrode) a negative current corresponds to a reduction reaction (electrons taken up by sodium dithionite from the electrode). This results into a current potential curve. The scan rate (rate of variation of the potential) was kept constant at 50 $mV s^{-1}$ and the working electrode was rotated at a constant rate of 1000 rotations per minute (rpm). Rotation of the working electrode with a rate of at least 200 rpm is important to obtain steady state conditions, which result into time independent electrode signals that are very useful for analytical purposes.

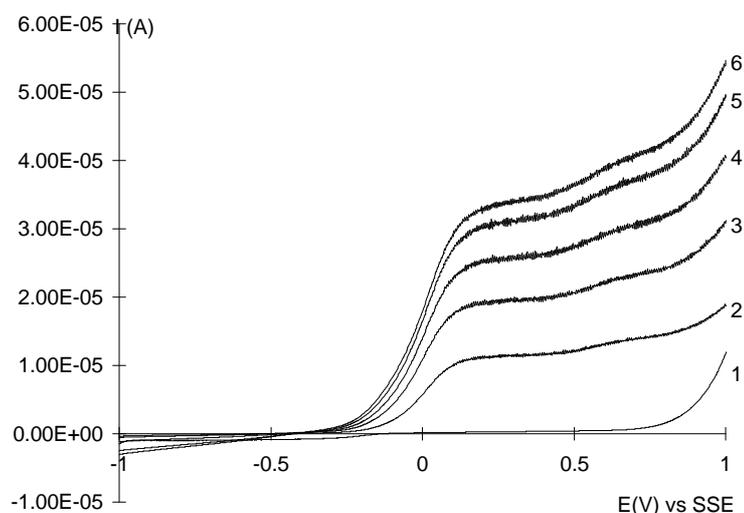


Figure 2 : Current potential curves of the oxidation of sodium dithionite at a platinum rotating disc electrode in alkaline solution (pH = 12.8) for sodium dithionite concentrations of (1) 0, (2) $9.57 \cdot 10^{-3}$, (3) $1.64 \cdot 10^{-2}$, (4) $2.15 \cdot 10^{-2}$, (5) $2.55 \cdot 10^{-2}$ and (6) $2.87 \cdot 10^{-2} \text{ mol L}^{-1}$; $T = 298.0 \text{ K}$.

In fig. 2 current potential curves are shown for the oxidation of sodium dithionite at a platinum electrode for different concentrations of sodium dithionite. At glassy carbon and palladium as electrode material similar curves were obtained. It can be seen that two waves occur which indicates that the oxidation of sodium dithionite takes place in two steps with formation of a relatively stable intermediate product. Only for the first wave a well defined so called limiting current plateau is present (at $E = 0.15$ to 0.4 V vs. SSE). Within the potential range of this plateau, the limiting current is independent of potential and time (steady state condition is obtained) and increases linearly with the concentration of sodium dithionite. This is shown in fig. 3, where relations between limiting current and concentration of sodium dithionite are given for the oxidation of sodium dithionite (first wave) at the surface of a platinum, palladium, glassy carbon and gold electrode.

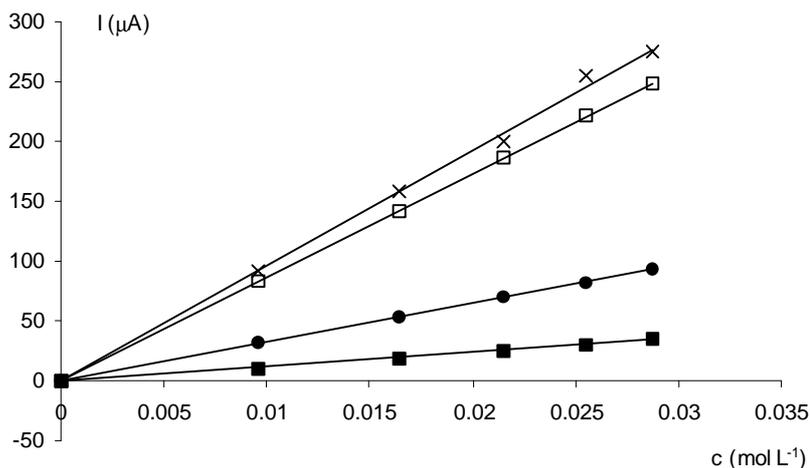


Figure 3 : Calibration curves of sodium dithionite when the oxidation currents measured at a potential of 0.3 V vs. SSE at a rotating disc electrode (1000 rpm) of (x) platinum, (x) glassy carbon, (●) palladium and (■) gold electrode.

The current potential curves obtained at a rotating gold electrode are somewhat different (fig. 4). Besides the oxidation reaction of sodium dithionite (second and third wave in the oxidative region) an additional oxidation reaction (at -0.4 V vs. SSE) and a reduction reaction (at -1.3 V vs. SSE) are observed. It is assumed that these reactions are related to each other because they only occur at the surface of a gold electrode. Remarkably is that, despite rotating the electrode at 1000 rpm, the reduction reaction does not result into a limiting current plateau but into a peak. The relationship between limiting current and sodium dithionite concentration for the oxidation of sodium dithionite (second oxidation wave in fig. 4, $E = 0.3$ V vs. SSE) is also given in fig. 3.

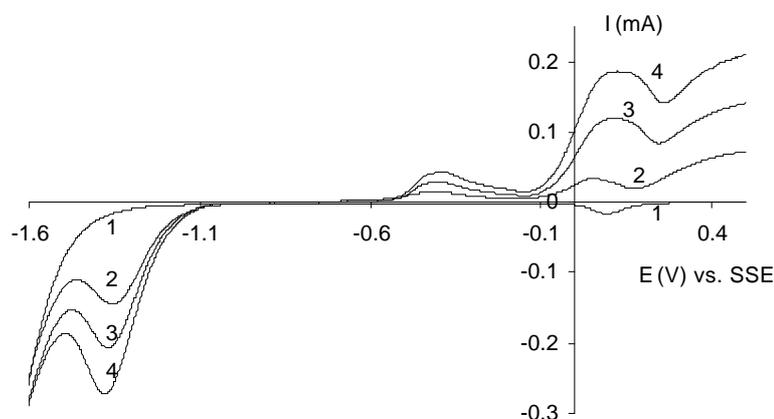


Figure 4 : Current potential curves of sodium dithionite at a gold rotating disc electrode in alkaline solution ($pH = 12.8$) for sodium dithionite concentrations of (1) 0, (2) $9.57 \cdot 10^{-3}$, (3) $1.64 \cdot 10^{-2}$ and (4) $2.15 \cdot 10^{-2}$ mol L⁻¹.

At a rhenium, titanium and zirconium electrode only oxidation reactions of sodium dithionite were observed but they resulted into bad defined limiting current plateaus. The nature of these plateaus appeared to be strongly disturbed by the formation of metal oxides (= oxidation of the electrode surface itself).

In a second series of experiments the rotation rate of the working electrode was varied while a constant value of the scan rate (50 mV s^{-1}) and of the concentration of sodium dithionite ($2.87 \cdot 10^{-2} \text{ mol L}^{-1}$) was maintained. The current potential curves obtained at a platinum electrode are given in fig. 5. Current potential curves obtained at glassy carbon, palladium and gold electrodes are not given because of the similarity with those obtained at platinum. The limiting current of the first oxidation wave of fig. 5 (second one for gold) varies linearly with the square root of the rotation rate ω ($= (2\pi N)/60$, N in rpm) of the electrode as is shown in fig. 6 for platinum and glassy carbon electrodes. At palladium and gold relationships approaching linearity were found but the standard deviation was too high to make a reliable interpretation of the results. The second oxidation wave (third one for gold) did not obey this relationship, which means that a more detailed investigation must be made concerning the kinetics and mechanism of the observed oxidation reaction.

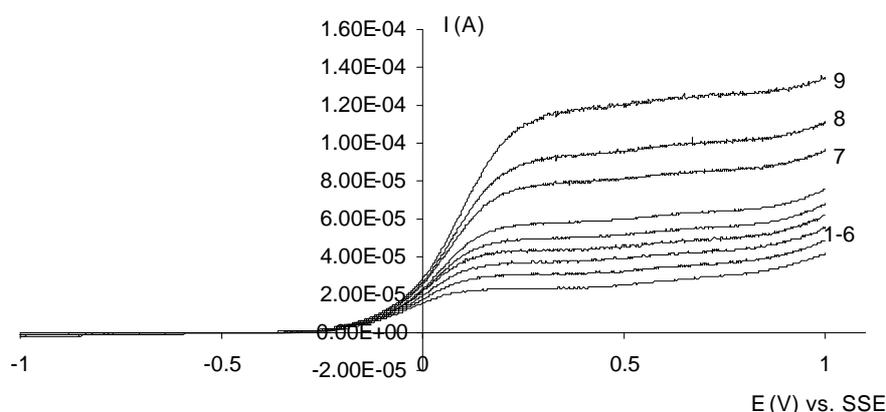


Figure 5 : Current potential curves of the oxidation of a $2.87 \cdot 10^{-2} \text{ mol L}^{-1}$ sodium dithionite solution at the surface of a platinum rotating disc electrode (pH = 12.8, T = 298.0 K) at various rotation rates of the electrode. (1) 250, (2) 500, (3) 1000, (4) 1500, (5) 2000, (6) 2500, (7) 3000, (8) 4000 and (9) 4500 rpm.

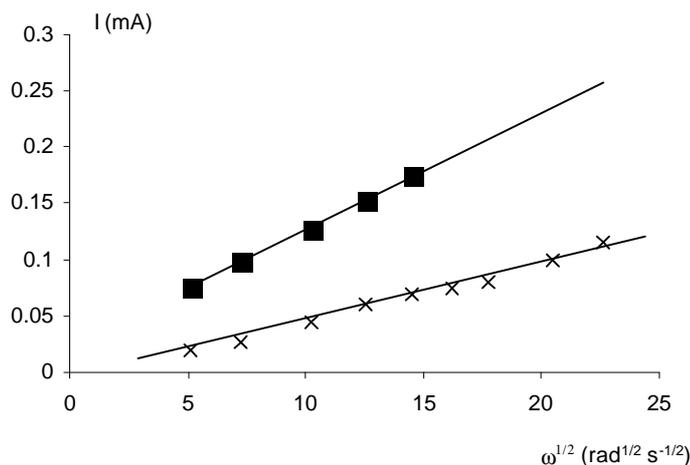


Figure 6 : Relationship between the limiting current and the square root rotation rate of the disc electrode for the oxidation of sodium dithionite at $E = 0.3 \text{ V vs. SSE}$ (pH = 12.8, T = 298.0 K) at (x) platinum and (•) glassy carbon.

In a last series of experiments the potential of the working electrode was kept constant (chronoamperometry) at a value situated in the limiting current plateau of the first oxidation wave (second one for gold). The electrode signal was measured as a function of time. Again the results of these experiments are only given

for platinum as electrode material (fig. 7), because that the results at palladium, glassy carbon and gold are similar. The constant potential was chosen in the middle of the limiting current plateau ($E = 0.30$ V vs. SSE) where a drift of the potential of the reference electrode within the range of potentials of the limiting current plateau (± 100 mV) does not affect the value of the limiting current. At the chosen potential the limiting current was measured (continuous line in fig. 7). Simultaneously at selected points in time a sample of the solution was taken for determination of the sodium dithionite concentration by titration (black squares in fig. 7). In part a of fig. 7 the sodium dithionite concentration was increased in several steps in the absence of oxygen. The electrode reacts almost immediately (in less than 0.5 s) on the variation of concentration. In part b the current signal was followed without further additions of sodium dithionite. The decrease of the limiting current is not caused by a drift of the electrochemical activity of the platinum electrode but by the natural decomposition of sodium dithionite. This can be seen from the titration results that show a proportional drop of the sodium dithionite concentration. In part c the cell solution was left in contact with the air, so oxygen could enter the solution. From the current decay and titration results a fast decrease of the sodium dithionite concentration was observed, induced by reaction with oxygen. Fig. 8 shows the calibration curve for the platinum electrode obtained by linking the limiting currents of fig. 7 (left scale) with the titration results (right scale). As the relation is linear, it is clear that amperometry can be used for the continuous monitoring of dithionite concentrations.

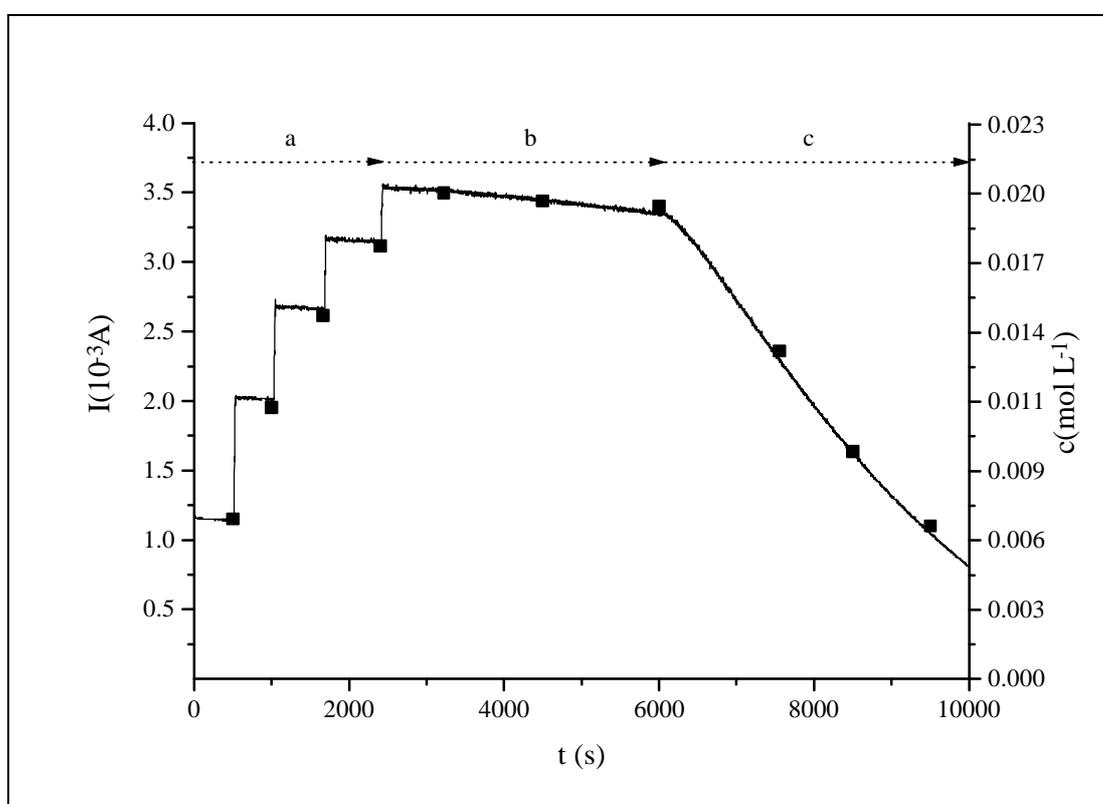


Figure 7 : Currents (left scale, continuous line) measured during chronoamperometric oxidation of sodium dithionite at $E = 0.3$ V vs. SSE at the surface of a platinum rotating disc electrode at a $\text{pH} = 12.8$ and $T = 298.0$ K. At certain points in time (marked \cdot) dithionite concentrations (right scale) were determined by titrations.

Similar experiments were done over a longer period of time. These results obtained indicate that no current drift is observed and that recalibration of the working electrode is not necessary during a period of time of at least three days.

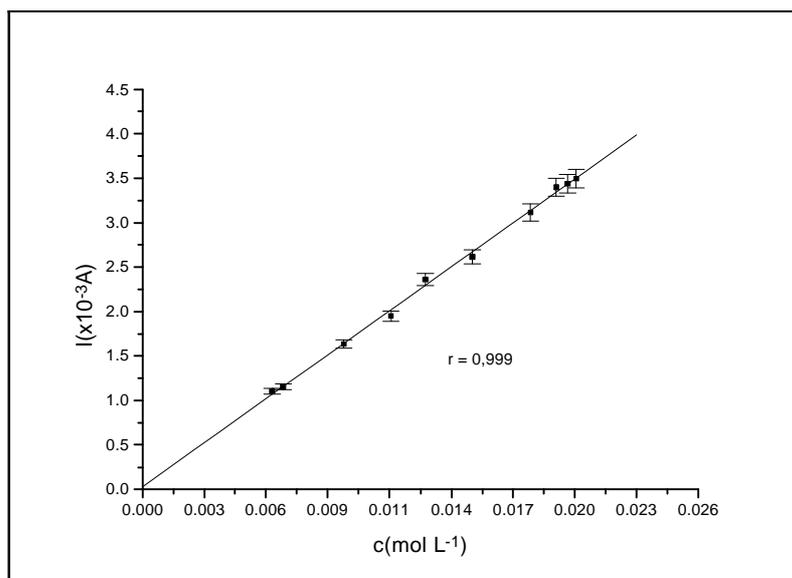
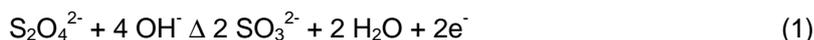


Figure 8 : Chronoamperometric calibration of sodium dithionite at a platinum rotating disc electrode (N = 1000 rpm) obtained from the results shown in fig. 7.

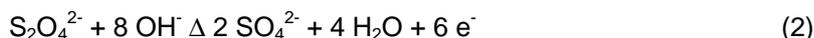
Discussion

For sensor development it is important to obtain a constant and reproducible electrochemical activity of the electrode surface and output signals that are independent of time and proportional to the concentration of the analysed compound. These requirements eliminate rhenium, titanium and zirconium as possible sensor electrode materials for the chronoamperometric monitoring of dithionite concentrations.

At platinum, palladium, glassy carbon and gold as electrode material promising results were obtained using the first of the two oxidation waves observed for sodium dithionite (fig. 2). Recently it was found that the first oxidation reaction at a platinum electrode corresponds to [24] :



while the second wave meets :



For analytical purposes preferably the first wave should be used. Its limiting current plateau is better defined within a wider potential range than is the case for the plateau of the second wave and only for the first wave at platinum a linear relationship between limiting current and square root of rotation rate of the electrode was obtained that passes through the origin (fig. 6). A gold electrode an additional oxidation reaction and a reduction reaction were observed. The peak form of the reduction wave instead of the occurrence of a limiting current plateau can be explained by coverage of the electrode surface with a stable reaction product, such as sulphur. It is assumed that at more positive potentials the deposited (possibly sulphur) layer will be re-oxidised resulting in the additional oxidation wave at $E = -0.4 \text{ V vs. SSE}$.

According to Levich [25] a transport controlled limiting current at a rotating disc electrode should obey

$$I_l = 0.62nFAD^{2/3} \nu^{-1/6} \omega^{1/2} c \quad (3)$$

where I_l is the limiting current (mA), n the number of electrons exchanged in the reaction, A the surface area of the electrode (cm^2), D the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), ν the kinematic viscosity ($\text{cm}^2 \text{ s}^{-1}$), ω the rotation rate of the electrode (s^{-1}) and c the concentration of the electroactive component (mol L^{-1}). This equation predicts a linear relationship between the limiting current and the concentration of the reacting species and between the limiting current and square root of the rotation rate. The results shown in figs. 3 and 6 for the oxidation of dithionite at platinum indeed obey these relationships.

The fact that the calibration curve is linear and passes through the origin reduces the procedure to calibrate the electrode to a one point calibration. The origin can be used as a second point.

The use of the calibration curve in additional experiments, only done at a platinum rotating disc electrode, showed that the electrode signal (limiting current at $E = 0.3 \text{ V vs. SSE}$) follows the variation of the concentration of sodium dithionite (determined by titration) quite well within an error range of 3 %. The response time is short (less than 0.5 s), which opens the possibility for on line and continuous measurement and for a precise control of the sodium dithionite concentration

Conclusion

This study of the voltammetric behaviour of sodium dithionite at various electrode materials show that platinum is a promising electrode material for an amperometric sensor that allows on line and precise measurement of the concentration of sodium dithionite in alkaline solution. Investigations are under way to study how the stability of the electrode and its amperometric output signal is affected by pH, temperature and the presence of other compounds in solution. A precise and undisturbed measurement is needed for controlling the sodium dithionite concentration at an optimal value. Only then the best quality of the treated textile can be obtained, combined with the most effective consumption of sodium dithionite and produced the minimal amount of polluted waste water.

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