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pH Study of the Electrocatalytic SO₂ Detection at a Glassy Carbon Electrode Modified with Iron(II)tetrasulfophthalocyanine

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Abstract. The electrocatalytic determination of SO₂ is studied as a function of pH at a glassy carbon electrode modified with iron(II)tetrasulfophthalocyanine $([Fe(II)TSPc]^{4-})$. It was found in the literature that depending on pH, $SO_2 \cdot xH_2O$, HSO_3^- and/or SO_3^{2-} are the main compounds in solution, that these compounds behave differently at the electrode surface, and that the condition of the electrode surface is stable over the entire pH-range. The use of $SO_2(g)$ or sodium sulfite as starting material did result in identical curves except in the pH range from 7.5-9.0. A possible explanation could be given by proposing that $SO_2 \cdot xH_2O$ is very unstable in the presence of SO_3^{2-} . In strongly acidic medium, $SO_2 \cdot xH_2O$ is the main compound, which can be oxidized as well as reduced with exchange of two electrons. HSO₃⁻ is the main compound at pH = 4 and can also be oxidized and reduced with exchange of, respectively, two and four electrons. In alkaline solution sulfite is the main compound and can only be oxidized, also under exchange of two electrons. Detection limits are in the range of $4.0 \pm 0.1 \times 10^{-5}$ and 7.5 \pm 0.1 \times 10⁻⁵ mol L⁻¹, dependent of pH and of the type of reaction (oxidation or reduction) used.

Key words: Sulfur dioxide; pH; modified glassy carbon; iron(II) tetrasulfophthalocyanine.

Sulfur dioxide is used in many applications such as organic synthesis [1], in lithium batteries [2] and as a preservative. Besides detection and monitoring of sulfur dioxide in these and other applications, detection is also important for environmental reasons [3]. Sulfur dioxide is a major atmospheric pollutant and has a serious impact on buildings and vegetation as component of acid rain [3].

Dependent of the pH of the solution, sulfur dioxide transforms into bisulfite and/or sulfite according to the following reactions [4].

$$\operatorname{SO}_2 \cdot x\operatorname{H}_2\operatorname{O} \xrightarrow[k_{-1}]{k_1} \operatorname{HSO}_3^- + \operatorname{H}^+ + (x-1)\operatorname{H}_2\operatorname{O}$$
 (1)

$$HSO_3^- \stackrel{k_2}{\underset{k_{-2}}{\longleftrightarrow}} SO_3^{2-} + H^+$$
 (2)

where k_1 , k_2 , k_{-1} and k_{-2} are rate constants and $K_1 = 1.54 \times 10^{-2} \text{ mol } \text{L}^{-1}$ [5] and $K_2 = 1.02 \times 10^{-7} \text{ mol } \text{L}^{-1}$ [5] are the respective equilibrium constants.

Various electrochemical methods based on polarography [6–8], amperometry [9–11], potentiometry [12, 13] and voltammetry [11], at bare and modified electrodes [14] have been described for the detection of sulfur dioxide. Many electrolytes, especially acidic ones like sulfuric acid and perchloric acid, have been employed.

Despite many electrochemical methods that describe the detection of sulfur dioxide, there remains a problem of instability of this compound and the presence of other sulfur containing compounds in

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 SO_2 solutions [15, 16]. At gold and platinum electrodes in alkaline solution the kinetics of sulfur dioxide oxidation and/or reduction are slow [17–19]. However, gold has been used successfully in alkaline solution [11]. Despite the relatively slow kinetics, a suitable potential window could be observed for gold where transport is the rate determining step.

A recent study done by Rea and co-workers [20] discusses important mechanistic aspects of porphyrins electrocatalysis. Chen [21–23] presents results for sulfite oxidation in presence of iron, manganese and cobalt porphyrins and with electrodes modified by metal hexacyanoferrates [24]. Analytical applications involving electrodes modified with electrostatically assembled films containing cobalt tetrarutenated porphyrins were presented before [25], where detection limits below 10^{-6} M sulfite were attained. A similar sensor associated with a diffusion cell was explored for sulfite quantification in wines [26].



Fig. 1. Chemical structure of $[Fe(II)TSPc]^{4-}$



In this paper, the detection of sulfur dioxide is described as a function of pH at a glassy carbon electrode modified with iron(II)tetrasulfophthalocyanine $([Fe(II)TSPc]^{4-})$, Fig. 1, in order to electrocatalyse the reactions of sulfur dioxide and related compounds, and to obtain improvement in the electrode kinetics.

Experimental

Sulfur dioxide (Messer Griesheim) was used as received. Small amounts were bubbled directly in the electrochemical cell. In order to avoid formation of decomposition products in the stock solution before analysis, use of stock solutions was not possible. Sodium dithionite, sodium bisulfite, sodium sulfite and buffer solutions were obtained from Aldrich. The sodium salt of $[Fe(II)TSPc]^{4-}$ was prepared and purified according to established methods [27]. The complex gave satisfactory elemental analysis, UV/Vis and IR spectra. Millipore water was used for the preparation of the solutions. The concentration of sulfur dioxide was determined by taking a sample of the cell solution, treating it with iodine and titrating with sodium thiosulfite [28].

Glassy carbon and platinum electrodes (BAS) with geometrical areas of 0.07 cm² were used as working electrodes. A Ag|AgCl|3 mol L⁻¹ KCl and a platinum wire were used respectively as reference and counter electrodes. Prior to electrodeposition of the [Fe(II)TSPc]⁴⁻, the glassy carbon electrode was polished on SiC-emery paper (type 2400 grid) followed by polishing with alumina (<10 μ m) on a Buehler felt pad. Finally, the electrode was subjected to ultrasonic vibration.

Cyclic voltammetry experiments were carried out in a one compartment, three electrode cell. A BioAnalytical System (BAS) model 100B/W workstation was used. All solutions were purged with nitrogen 5.0 (Messer).

Results and Discussion

Electrodeposition of [Fe(II)TSPc]^{4–} *in pH 7.4 Buffer*

In Fig. 2 the electrodeposition of $[Fe(II)TSPc]^{4-}$ is shown as a function of scan number and was carried

Fig. 2. Voltammetric curves of the electrodeposition of $[Fe(II)TSPc]^{4-}$ at a glassy carbon electrode in pH = 7.4 buffer containing 10^{-3} mol L⁻¹[Fe(II)TSPc]⁴⁻.v = 100 mV s⁻¹. Number of scans is 25

out in a 10^{-3} mol L⁻¹ [Fe(II)TSPc]⁴⁻ solution. Five peaks could be observed during this experiment, all of them were increasing with scan number (some of them increased weakly). This means that indeed $[Fe(II)TSPc]^{4-}$ is depositing onto the surface of the electrode. Extensive research on [Fe(II)TSPc]⁴⁻ was found in the literature [27, 29-34]. The paper of Zecevic et al. [24] was used as reference work to identify the observed peaks. However, their study showed that no peaks were observed in the first scan using [Fe(II)TSPc]^{4–}. Around 0 V vs. Ag|AgCl in Fig. 2 a broad oxidation peak was obtained attributed to Fe^{II}/Fe^{III} oxidation. The return peak for this oxidation was observed at -0.5 V vs. Ag|AgCl (A). A second weak redox couple B is attributed to ring oxidation in the $[Fe^{III}TSPc(-2)]^{3-}$ giving $[Fe^{III}TSPc(-1)]^{2-}$. A relatively large irreversible reduction peak C centered around 0.2 V vs. Ag/AgCl could be identified as

the reduction of oxygen. Despite the fact that the experiments were carried out in solutions purged with nitrogen, oxygen was produced at the electrode surface at the most positive applied potentials. Scanning the potential to a value less positive than the oxygen evolution reaction (up to 1.25 V vs. Ag|AgCl) did not result in peak C. Therefore it could be concluded that this peak was due to oxygen reduction.

Sulfite and Sulfur Dioxide in $1.0 \text{ mol } L^{-1} H_2 SO_4$

Figure 3 shows current-potential curves, recorded at a glassy carbon electrode modified with $[Fe(II)TSPc]^{4-}$, with increasing concentrations of sulfur dioxide in a $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution. Similar curves were obtained for sodium sulfite, which implies that in strongly acidic solution, sulfite is almost completely transformed to $SO_2 \cdot xH_2O$ (Table 1). This also means



Fig. 3. Current-potential curves recorded in $1.0 \text{ mol } \text{L}^{-1} \text{ H}_2\text{SO}_4$ solution for increasing SO₂ concentrations at a glassy carbon electrode modified with $[\text{Fe(II)TSPc}]^{4-}$. SO₂ concentrations are (1) 0, (2) 8.34×10^{-5} , (3) 1.00×10^{-4} , (4) 3.37×10^{-4} , (5) 6.42×10^{-4} , (6) 1.21×10^{-3} and (7) $2.20 \times 10^{-3} \text{ mol } \text{L}^{-1}$. v = 100 mV s⁻¹

Table 1. Actual fractions of SO_2 , HSO_3^- and SO_3^{2-} in solution as a function of pH

K ₁	K ₂	${C_{H}}^{+}\left(molL^{-1}\right)$	pH	Fraction SO ₂ ⁻	Fraction HSO ₃ ⁻	Fraction SO_3^{2-}
1.54×10^{-2}	1.02×10^{-7}	1	0	9.85×10^{-1}	1.52×10^{-2}	1.55×10^{-9}
1.54×10^{-2} 1.54×10^{-2}	1.02×10 1.02×10^{-7}	10^{-2}	1 2	8.67×10^{-1} 3.94×10^{-1}	1.33×10^{-1} 6.06×10^{-1}	1.36×10 6.18×10^{-6}
1.54×10^{-2}	1.02×10^{-7}	10^{-3}	3	6.10×10^{-2}	9.39×10^{-1}	9.58×10^{-5}
1.54×10 1.54×10^{-2}	1.02×10^{-7} 1.02×10^{-7}	10^{10} 10^{-5}	4 5	6.43×10^{-4}	9.93×10 9.89×10^{-1}	1.01×10^{-2} 1.01×10^{-2}
1.54×10^{-2}	1.02×10^{-7}	10^{-6}	6	5.89×10^{-5}	9.07×10^{-1}	9.26×10^{-2}
1.54×10^{-2} 1.54×10^{-2}	1.02×10^{-7} 1.02×10^{-7}	10^{-8}	8	3.21×10^{-8} 5.80×10^{-8}	4.95×10^{-2} 8.93×10^{-2}	5.05×10^{-1} 9.11×10^{-1}
1.54×10^{-2} 1.54×10^{-2}	1.02×10^{-7} 1.02×10^{-7}	10^{-9} 10^{-10}	9 10	6.30×10^{-10} 6.36×10^{-12}	9.71×10^{-3} 9.79×10^{-4}	9.90×10^{-1} 9.99×10^{-1}

that k_{-1} and k_{-2} in reactions 1 and 2 are high. Indeed, by dissolving sodium sulfite in $1.0 \text{ mol } \text{L}^{-1}$ H_2SO_4 the typical smell of SO₂ was detected. However, if a bare glassy carbon electrode is used, illdefined and poorly visible waves were obtained. This is a first indication that $[\text{Fe}(\text{II})\text{TSPc}]^{4-}$ electrocatalyses the observed reactions.

Two main waves IV and V can be observed, attributed to respectively oxidation (reaction 3) and reduction of sulfur dioxide, the latter reaction being discussed further.

$$SO_2 + 2H_2O \xrightarrow{\longleftrightarrow} SO_4^{2-} + 4H^+ + 2e^-$$
 (3)

Besides these main waves, three other waves are observed. Waves I and II are attributed to oxidation of reaction products formed in wave V. This was proved, by cycling the potential between -0.3 and 0.6 V vs. Ag|AgCl where waves I and II were absent. By addition of sodium dithionite to the solution, waves I and II again appeared. This indicates that the reaction product formed in wave V is dithionite. Waves I and II were also observed at a bare glassy carbon electrode after addition of sodium dithionite. Therefore it is not clear whether these reactions are electrocatalysed by $[Fe(II)TSPc]^{4-}$. However, when cycling between -0.3 and 0.6 V vs. Ag|AgCl, wave III still occurred under these conditions, indicating that this wave is attributed to a species in solution.

Both, waves IV and V in Fig. 3, correspond to diffusion controlled reactions, because a linear relationship is obtained between the peak current and the square root of the scan rate. However, the slope of the relationship between the peak current and $SO_2 \cdot xH_2O$ concentration is slightly higher for the reduction than for the oxidation (Fig. 4, curves 1 and 2, respectively). A different number of electrons exchanged in both reactions cannot explain the small peak current differences of these waves. As pointed out earlier, wave III corresponding to curve 3 in Fig. 4 can be attributed to a species present in solution. Moreover, it can be seen that the sum of the peak currents of waves III (curve 3) and IV (curve 2) is equal to the peak current of wave V (curve 1 in Fig. 4). Therefore, it is supposed that wave III corresponds to the oxidation of bisulfite (reaction 4), which is present at about 1.5% of the analytical sulfur dioxide concentration (Table 1). This wave is observed at similar potentials as those for the oxidation of the Fe-metal ion in [Fe(II)TSPc]⁴⁻. Therefore, it is sup-



Fig. 4. Calibration plots of the oxidation and reduction of SO₂ and its related compounds at a glassy carbon electrode modified with [Fe(II)TSPc]⁴⁻. (1) SO₂ reduction in 1.0 mol L⁻¹ H₂SO₄, (2) SO₂ oxidation in 1.0 mol L⁻¹ H₂SO₄, (3) HSO₃⁻ oxidation in 1.0 mol L⁻¹ H₂SO₄, (4) HSO₃⁻ oxidation in pH=4 buffer, (5) HSO₃⁻ reduction in pH=4 buffer, (6) SO₃²⁻ oxidation in pH=8 buffer and (7) SO₃²⁻ oxidation in pH=10 buffer

posed that the bisulfite oxidation is electrocatalysed by the central metal ion of the $[Fe(II)TSPc]^{4-}$.

$$\mathrm{HSO}_{3}^{-} + \mathrm{H}_{2}\mathrm{O} \stackrel{\leftarrow}{\rightarrow} \mathrm{SO}_{4}^{2-} + 3\mathrm{H}^{+} + 2\mathrm{e}^{-} \qquad (4)$$

However, an additional condition, that k_1 in reaction 1 is relatively small, needs to be fulfilled. This is indeed the case and is confirmed by two additional experiments. In a first experiment the pH was varied from 0 to 2 in 5 steps. The peak height of wave III in Fig. 3 increased while the one of wave IV decreased with increasing pH value, due to formation of HSO₃⁻ with increasing pH. In a second experiment, a preconditioning of the electrode at a potential of +0.6 V vs. Ag|AgCl was applied prior to cycling from +0.6 V to +1.3 V vs. Ag|AgCl. With increasing preconditioning time, the peak height of wave IV decreased, indicating that during the preconditioning $SO_2 \cdot xH_2O$ is transformed (however slowly) to HSO₃⁻, which is in turn oxidized at the preconditioning potential. Despite the fact that k_1 in reaction 1 is relatively small, reaction of $SO_2 \cdot xH_2O$ to HSO_3^- still occurs. Indeed, a much higher ratio of $I_{p,III}/I_{p,IV}$ is obtained than was found for the actual concentration ratio of $[HSO_3^{-}]/[SO_2 \cdot xH_2O]$ in solution (Table 1). This shows that during the oxidation of HSO₃⁻, fresh HSO_3^- is produced by reaction 1. This result also suggests that the peak current of waves III and IV in Fig. 3 cannot be attributed to the actual concentrations of bisulfite and sulfur dioxide in solution. However,

the sum of these peak currents is proportional to the analytical concentration of sulfur dioxide and can therefore be used for analytical purposes.

Another possibility is to make use of the reduction wave V. No reduction prewave of HSO_3^- was observed and since k_{-1} in reaction 1 is high, it can be concluded that HSO_3^- is transformed fast into $SO_2 \cdot xH_2O$, during sulfur dioxide reduction. As was pointed out earlier, dithionite is supposed to be the reaction product, therefore wave V is attributed to

$$2SO_2 + 2e^- \overleftrightarrow{\longrightarrow} S_2O_4^{2-} \tag{5}$$

Based on the reduction of SO₂ · xH₂O a detection limit of $8.5 \pm 0.1 \times 10^{-5}$ mol L⁻¹ is obtained, which is lower than the one obtained by using waves III and IV $(1.2 \pm 0.1 \times 10^{-4} \text{ mol L}^{-1})$. The determination of the detection limit was based on the criterion that the detection limit corresponds to an electrode signal of twice the background current. However, an advantage of using the oxidation is that sulfate is formed as reaction product instead of dithionite. The latter species itself is electroactive and relatively unstable. Decomposition occurs easily into sulfite and related products. Therefore dithionite can become an influencing species in continuous measurement or for measurements in small volume cells.

Sulfite and Sulfur Dioxide in pH = 4 Buffer

In Fig. 5 current-potential curves are shown for different sulfur dioxide concentrations, recorded in pH=4 buffer at a $[Fe(II)TSPc]^{4-}$ modified glassy carbon electrode. Two waves can be detected, an oxidation wave centered around 0.05 V vs. Ag|AgCl and a reduction wave with a peak potential of -0.65 V vs. Ag|AgCl. Based on the results obtained above in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, the oxidation wave corresponds to electrocatalytic oxidation of HSO_3^- catalysed by Fe in [Fe(II)TSPc]⁴⁻, which is oxidized at the same potentials. No wave for $\text{SO}_2 \cdot x\text{H}_2\text{O}$ is observed because SO_2 is transformed almost totally into HSO_3^- (Table 1) at this pH. A similar voltammogram as shown in Fig. 5 was obtained with sodium sulfite as starting species. The oxidation wave corresponds to reaction 4 with exchange of two electrons and is proportional to the analytical concentration of sulfur dioxide and sulfite (Fig. 4, curve 4).

The reduction wave cannot be attributed to reduction of $SO_2 \cdot xH_2O$ or HSO_3^- with exchange of two electrons. Its slope is twice as high as the one for the oxidation (Fig. 4, curve 5). Therefore, this wave is assumed to result from the reduction of HSO_3^- (because this is the only compound in solution) to $S_2O_3^{2-}$ (reaction 6) with exchange of four electrons, because $S_2O_3^{2-}$ does not show electroactive properties over the entire potential region and is a relatively stable species.

$$2\text{HSO}_3^- + 4\text{H}^+ + 4\text{e}^- \overleftrightarrow{} S_2\text{O}_3^{2-} + 3\text{H}_2\text{O} \qquad (6)$$

Because of the higher slope obtained for the reduction, a lower detection limit can be obtained. Detection limits of $3.8 \pm 0.1 \times 10^{-5}$ and $7.4 \pm 0.1 \times 10^{-5}$ mol L⁻¹ were obtained respectively for the reduction and oxidation of SO₂ · *x*H₂O, with HSO₃⁻ as electroactive species.



Fig. 5. Current-potential curves recorded in pH=4 buffer solution for increasing SO₂ concentrations at a glassy carbon electrode modified with $[Fe(II)TSPc]^{4-}$. SO₂ concentrations are (1) 0, (2) 3.89×10^{-5} , (3) 6.02×10^{-5} , (4) 8.79×10^{-5} , (5) 1.51×10^{-4} , (6) 2.71×10^{-4} and (7) 4.71×10^{-4} mol L⁻¹. v = 100 mV s⁻¹



Fig. 6. Current-potential curves recorded in pH = 10 buffer solution for increasing SO₂ concentrations at a glassy carbon electrode modified with $[Fe(II)TSPc]^{4-}$. SO₂ concentrations are (1) 0, (2) 7.47 × 10⁻⁵, (3) 2.02 × 10⁻⁴, (4) 3.92 × 10⁻⁴, (5) 6.95 × 10⁻⁴, (6) 1.51 × 10⁻³ and (7) 2.70 × 10⁻³ mol L⁻¹. v = 100 mV s⁻¹

Sulfur Dioxide and Sulfite at pH = 8and pH = 10 Buffer

Completely different results were obtained for sulfur dioxide and sodium sulfite as starting species in a buffer of pH = 8. Starting from sulfite only one oxidation wave is obtained around 0.7 V vs. Ag|AgCl. From Table 1 it can be seen that sulfite itself is the main compound in solution, therefore it is rather clear that this wave can be attributed to reaction 7. Its slope (Fig. 4, curve 6), obtained by plotting the peak current vs. concentration, is situated in the range that allows exchange of 2 electrons.

$$\mathrm{SO_3}^{2-} + \mathrm{H_2O} \xrightarrow{\longleftrightarrow} \mathrm{SO_4}^{2-} + 2\mathrm{H}^+ + 2\mathrm{e}^-$$
 (7)

Starting from sulfur dioxide, only one wave around 0.7 V vs. Ag|AgCl is observed at concentrations smaller than 10^{-4} mol L⁻¹. At concentrations higher than this value, this wave disappears and two new oxidation waves with $E_p = -0.2$ and +1.1 V vs. Ag|AgCl and a reduction wave is observed. It is well known that SO_3^{2-} reacts to form $HS_2O_5^{-}$ if SO_2 is present in excess [4]. This excess is temporarily present during dissolution of SO_2 . It is expected that this indeed occurs, but HS₂O₅⁻ itself decomposes further. However the new waves occurring are not proportional to the SO_2 concentration. Moreover the peak current of the new reduction wave shifts to less negative potentials with increasing sulfur dioxide concentration. Similar results were obtained in buffer solutions of pH 7.5 to 9.0. Since these results are not suitable for analytical purposes, no experimental curves are

shown and they were not further investigated. Therefore, SO₂ cannot be detected in the pH range from 7.5–9.0 due to the instability of SO₂ · xH₂O or its related compounds HSO₃⁻ and SO₃²⁻. However, sulfite can be detected in the absence of SO₂ in pH = 8 buffer.

In Fig. 6 current-potential curves are shown of increasing SO₂ concentration, recorded in a pH = 10 buffer at a glassy carbon electrode modified with $[Fe(II)TSPc]^{4-}$. It can be seen that in alkaline solution only one wave is obtained at 0.75 V vs. Ag|AgCl, which is identical to the one obtained when starting from sodium sulfite. Therefore, it can be proposed that SO₃²⁻ is the main electroactive compound in solution (Table 1). As expected, the slope between peak current and SO₂ or Na₂SO₃ concentrations, corresponds to exchange of 2 electrons (Fig. 4, curve 7) and a detection limit of $7.3 \pm 0.1 \times 10^{-5}$ mol L⁻¹ was obtained.

Conclusion

It can be concluded that the electrocatalytic detection of SO_2 is not based on a simple reaction and is strongly dependent of pH. However, in this study it became clear that the influence of the pH on the curves is not caused by changes in electrode surface condition but purely by transformation and shift of equilibrium conditions in solution. The modified glassy carbon electrode may be an alternative to gold and platinum which may prove to be more stable in the long term. From this study it can also be concluded that weakly acidic or alkaline solutions should be used as electrolyte in SO_2 -gas sensing applications. For an optimal detection limit a buffer of pH = 4 should be used in combination with the reduction reaction of HSO_3^- , the main compound in solution related to SO_2 . In other cases advantage should be given to oxidation of SO_2 (and related compounds) to sulfate because reduction causes formation of possible interfering and poisoning products. Except for the pH range from 7.5–9, SO_2 or its related compounds HSO_3^- and SO_3^{2-} , a detection limit of about $4 \pm 0.1 \times 10^{-5} \text{ mol L}^{-1}$ in pH = 4 buffer (reduction) and $7.5 \pm 0.1 \times 10^{-5} \text{ mol L}^{-1}$ for other pH values are possible.

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References

- H. J. Reich, J. H. Rigby, H. Cerfontein, B. H. Bakker (Eds.) Handbook of Reagents for Organic Synthesis, Acidic and Basic Reagents. John Wiley and Sons, Chichester, UK, 1999.
- [2] E. Potteau, E. Levillain, J. P. Lelieur, J. Electroanal. Chem. 1999, 476, 15.
- [3] C. E. Boyd (Ed.) Water Quality. Kluwer Academic Publishers Group, New York, USA, 1999.
- [4] F. A. Cotton, G. Wilkinson, P. L. Gaus (Eds.) Basic Inorganic Chemistry. John Wiley and Sons, New York, USA, 1987.
- [5] R. C. Weast, CRC Handbook of Chemistry and Physics, 64th Edn. CRC Press, Boca Raton, Canada, 1983.
- [6] T. Sawyer, R. S. George, R. C. Rhodes, Anal. Chem. 1959, 31, 2.
- [7] G. Belanger, Anal. Chem. 1974, 46, 1576.
- [8] R. W. Garber, E. Wilsons, Anal. Chem. 1972, 44, 1357.
- [9] B. Chachulski, Analyst 1998, 123, 1141.
- [10] A. Rios, M. D. Luque de Castro, M. Valcarel, A. Mottola, *Anal. Chem.* **1987**, *59*, 666.
- [11] A. W. Hodgson, P. Jacquinot, P. C. Hauser, Anal. Chem. 1999, 71, 2831.

- [12] J. W. Rios, J. H. Risemann, J. A. Krueger, Pure Appl. Chem. 1973, 36, 473.
- [13] Y. Yang, X. X. Zhang, T. Korenaga, K. Hitguchi, *Talanta* 1997, 45, 445.
- [14] I. Nikolov, K. Petrov, T. Vitanov, J. Appl. Electrochem. 1996, 26, 703.
- [15] T. J. Cardwell, M. J. Christophersen, Anal. Chim. Acta 2000, 416, 105.
- [16] L. M. Carvalho, G. Schwedt, Anal. Chim. Acta 2001, 436, 293.
- [17] E. Gasana, P. Westbroek, E. Temmerman, H. P. Thun, Anal. Commun. 1999, 36, 387.
- [18] E. Gasana, P. Westbroek, E. Temmerman, H. P. Thun, F. Twagiramungu, *Electrochem. Commu.* 2000, 2, 727.
- [19] P. Westbroek, K. Van Uytvangh, J. De Strycker, E. Temmerman, J. Electroanal. Chem. 2001, 516, 83.
- [20] N. Rea, B. Loock, D. Lexa, *Inorg. Chim. Acta* 2001, 312, 53.
- [21] S. M. Chen, J. Electroanal. Chem. 1996, 407, 123.
- [22] S. M. Chen, S. W. Chiu, *Electrochim. Acta* **2000**, *45*, 4399.
- [23] S. M. Chen, J. Electroanal. Chem. 1997, 432, 101.
- [24] S. M. Chen, J. Electroanal. Chem. 1996, 417, 145.
- [25] C. M. N. Azevedo, K. Araki, L. Angnes, H. E. Toma, *Electroanalysis* **1998**, *10*, 467.
- [26] C. M. N. Azevedo, K. Araki, H. E. Toma, L. Angnes, Anal. Chim. Acta 1999, 387, 175.
- [27] T. H. Weber, D. H. Busch, Inorg. Chem. 1965, 4, 469.
- [28] A. I. Vogel (Ed.) A Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis, 4th Edn. Longman Group Limited, London, 1978.
- [29] W. A. Nevin, W. Liu, M. Melnik, A. B. P. Lever, J. Electroanal. Chem. 1986, 213, 217.
- [30] A. Hadasch, A. Sorokin, A. Rabion, B. Meunier, New J. Chem. 1998, 22, 45.
- [31] S. Zecevic, B. Simic-Glavaski, E. Yeager, A. B. P. Lever, P. C. Minor, J. Electroanal. Chem. 1985, 196, 339.
- [32] M. Sanchez, N. Chap, J. B. Cazaux, B. Meunier, *Eur. J. Inorg. Chem.* 2001, 7, 1775.
- [33] G. Mc Lendon, A. E. Martell, *Inorg. Chem.* **1977**, *16*, 1812.
- [34] B. Simic-Glavaski, S. Zecevic, I. Yeager, J. Phys. Chem. 1983, 87, 4555.