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On-line measuring method for the concentration of peroxodisulphate

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Abstract

Although the analytical determination of peroxodisulphate is state of the art, there is no well-established on-line measuring method for this substance. This paper presents an on-line monitoring device for peroxodisulphate concentration that uses a coulometric measuring method. The method is based on the redox potential control in a miniaturised electrochemical reactor. This paper presents the design of the measuring cell and describes the integration of this cell in an on-line measuring device which can be applied in a process environment. Experimental results illustrate its dynamic characteristics and accuracy.

List of symbols

A	cathode surface (cm^2)
c	concentration (g l^{-1})
F	Faraday constant (F=96484 A s mol^{-1})
I	Electric current (A)
i	Current density (A m^{-2})
$\dot{m}_{in}$	incoming mass flow (g h^{-1})
M	molar mass (g mol^{-1})
r	reaction rate (g h^{-1})
R	gas constant (R=8.314 J mol^{-1} K^{-1})
S_2O_8	peroxodisulphate
V_{cat}	volume of the cathodic compartment (cm^{-3})
$\dot{V}_{in}$	incoming volume flow (cm^3 h^{-1})
T	absolute temperature (K)
U_r	redox potential (mV)
U_{00}	standard potential (mV)
ν_e	number of electrons
τ_{cell}	response time (s)

1. Introduction

There is an increasing demand for on-line measuring methods of concentrations of chemical substances in industrial practice in general and especially in electroplating, wet chemical surface finishing and printed circuit board manufacturing. This need is caused by the increase in quality standards and by the higher process dynamics of many modern process technologies. Existing on-line concentration monitoring methods can be divided roughly into two groups. First, there are methods based on relatively simple physical or chemical relations, e.g., concentration dependencies on conductivity, density, light absorption, pH-value or redox potential. These methods are comparatively inexpensive, but the required simple relations exist only for some substances and are seldom applicable to multi-substance solutions. The second group consists of analytical methods from the chemical laboratory, which have been adapted to process requirements. This transformation of laboratory methods to on-line analysers is possible for a wide range of substances. However, these types of devices are problematic due to their sophistication, expense and required maintenance.

Special difficulties arise if no simple measuring method is available for a concentration measuring problem and the application of an on-line analyser is too expensive. This paper presents a measuring method that is intended to address this situation. This method employs a miniaturised electrochemical reactor in which the substance to be determined is converted in a continuous operation mode. The method is used to measure the oxidant peroxodisulphate on-line. A device using this method, which was developed for application in an industrial environment, will be described and the results will be presented.

2. Measuring problem

Some uses of the oxidant peroxodisulphate are for pickling of metal surfaces [1], as a printed circuit board etchant, for the destruction of organic wastes [2] or as polymerisation initiator. In surface technologies, the use of peroxodisulphate prevents pollution and saves chemicals because it can be recycled with an electrochemical cell in direct connection to the etchant bath [1, 3].

While the determination of peroxodisulphate by classical titration is state-of-the-art, there is no well-established on-line measuring method for this substance. In [4] the proposed peroxodisulphate measuring method is the detection of the inflection point during a fixed electric current flow in the solution. Another approach is a voltammetric method which uses an electrode modified with a Prussian Blue film [5]. In [6] the proposed peroxodisulphate measuring method used as amalgamated copper rotating disk electrode. All these constructions are typical laboratory set-ups.

The authors have worked with industrial partners to develop a peroxodisulphate closed cycle copper pickling process. An on-line measuring method for the peroxodisulphate concentration was necessary for the automatic stabilisation of the etchant concentration in the pickling bath and for the monitoring of the peroxodisulphate recycling cell. The first method examined, which has potential industrial application but will not be discussed here, was a calorimetry-based technique where the peroxodisulphate concentration is calculated from the heat of reaction in a continuously operated reaction cell [7, 8]. The second method, which uses a suitable on-line measuring device, is presented in this paper [9].

3. Solution principle

The basic idea of the presented peroxodisulphate concentration measurement is the complete conversion of the peroxodisulphate by means of an electrical current. But in contrast to a classic titration, the peroxodisulphate conversion takes place in a continuous operation mode. For this purpose a volume flow of the process solution is fed to a miniaturised electrochemical reactor. Here the incoming peroxodisulphate is destroyed by electrolysis.

To monitor the degree of conversion a redox potential measurement is used. However, direct measurement from the peroxodisulphate concentration by the redox potential is not possible because the relatively high redox potential in the presence of peroxodisulphate does not have reproducible characteristics. Therefore, a second redox pair must be present in the solution. It can be shown that ferric ions are suitable for this purpose. Figure 1 shows an example of the dependency of the redox potential in a combined peroxodisulphate–ferric solution. If there is peroxodisulphate in the solution the redox potential has a high value. After the total destruction of the peroxodisulphate by electric current, the conversion of ferric to ferrous ions begins. Then a sharp drop in the redox potential occurs. In the ferric region the redox potential has a clear relation to the concentrations of the redox pair Fe^{2+}–Fe^{3+} as expressed by the Nernst equation

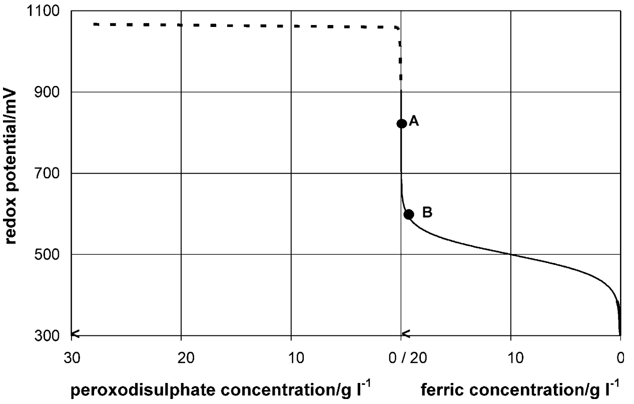

Fig. 1. Combined redox characteristic for S_2O_8 and Fe^{3+}.

$$U_r = U_{00} + \frac{RT}{\nu_e F} \ln\left(\frac{c_{Fe^{3+}}}{c_{Fe^{2+}}}\right) \tag{1}$$

To achieve total conversion of the peroxodisulphate in the continuously operated miniaturised reactor, the current must be at the level that sets a redox potential in the steep part of the redox characteristic (point A in Figure 1). In order to realise a measuring device the necessary electric current will be set by an automatic controller.

If all incoming peroxodisulphate is converted, there is a direct relation between concentration and reaction rate

$$r_{S_2O_8} \overset{!}{=} \dot{m}_{in.S_2O_8} = \dot{V}_{in} c_{S_2O_8} \tag{2}$$

If the current efficiency is unity, the reaction rate is related to the electric current by Faraday's Law

$$r_{S_2O_8} = \frac{M_{S_2O_8}}{\nu_e F} I \tag{3}$$

Consequently, the peroxodisulphate concentration can be calculated from the current

$$c_{S_2O_8} = \frac{M_{S_2O_8}}{\nu_e F \dot{V}_{in}} I \tag{4}$$

This principle can be used for on-line measuring purposes with the device shown in Figure 2. A sample stream containing peroxodisulphate is transported by the dosing pump P1 into the miniaturised electrochemical reactor. If the peroxodisulphate solution does not contain a second redox pair another stream containing ferric ions is added (dosing pump P2). The miniaturised reactor is a divided cell with an overflow. The incoming peroxodisulphate is converted to sulphate at the cathode.

The potential measured by the redox electrode is the input for a controller that sets the electrolysing current so that the redox potential U_r reaches its set point $U_{r.set}$. The current needed for total peroxodisulphate conversion can be measured and shows the peroxodisulphate concentration of the incoming solution – Eq. (4). For

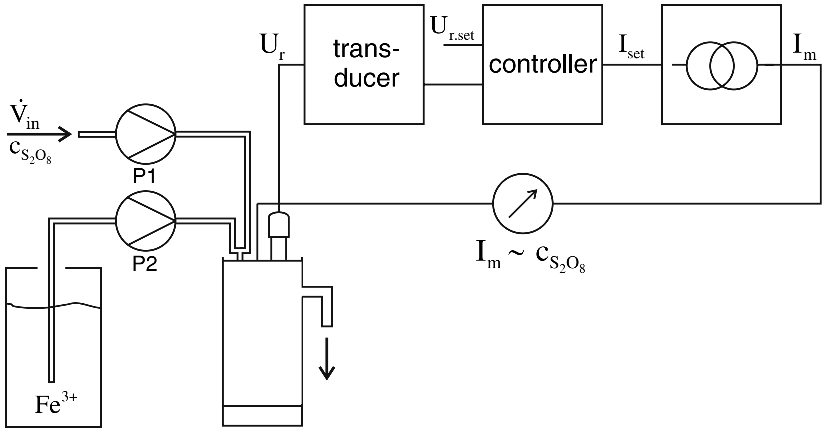

Fig. 2. Principle of the peroxodisulphate measuring device.

Eq. (4) to hold, competitive reactions have to be prevented. Therefore, there has to be sufficient agitation at the cathode.

4. Measuring cell design

The measuring cell consists of an anodic and a cathodic compartment separated by a diaphragm. The cathode and the cathode compartment have to be constructed in a way that ensures sufficient agitation of the measuring solution, a constant current density distribution on the cathode surface and a fast cell response time. With a given maximum current density i_{max} and a given maximum concentration of peroxodisulphate c_{max} the maximum response time of the measuring cell τ_{cell} can be expressed by the following relation

$$\tau_{cell} = \frac{V_{cat}}{\dot{V}_{in}} = \frac{V_{cat}}{A_{cat}} \cdot \frac{c_{max} \cdot \nu_e F}{M \cdot i_{max}} \tag{5}$$

It can be seen from Eq. (5) that in order to meet the demand for rapid response the volume of the cathode space has to be minimised and the cathode surface has to be maximised. The competing demands of sufficient agitation, uniform current density distribution and good cell dynamics are met by a cylindrical design. The construction principle of the cell is shown in Figure 3.

The diameter of the cathodic compartment was minimised to obtain a small volume while guaranteeing sufficient agitation. It can be shown that the response time of the measuring cell decreases with increasing ratio of the cathode height h_{cat} to the cell height h_{cell}, i.e., the cathodic ineffective volume surrounding the magnetic stirrer should be as small as possible.

In experiments with the described measuring cell, a dependence of the measured redox potential on the electrolysis current was found. The dependence is influenced by the placement of the redox electrode. This effect can be minimised by using a type of redox electrode that has a ring diaphragm.

5. On-line measuring device

For application in an industrial environment an on-line measuring device was developed. The wet chemical part of this measuring device was separated from other parts of the device to limit the electrical parts that come in contact with the highly corrosive measuring solution. Figure 4 shows the principle of the device.

The value of concentration is calculated from the noise-filtered current using a linear approximation. The control algorithm for the redox potential control loop is implemented on a Programmable Logic Control (PLC) and uses a PI characteristic. Experiments showed that it is not possible to control the redox potential at the set point A (see Figure 1) due to the steep characteristics of the redox potential. Therefore, a set point in the less steep part but near point A was chosen (point B in

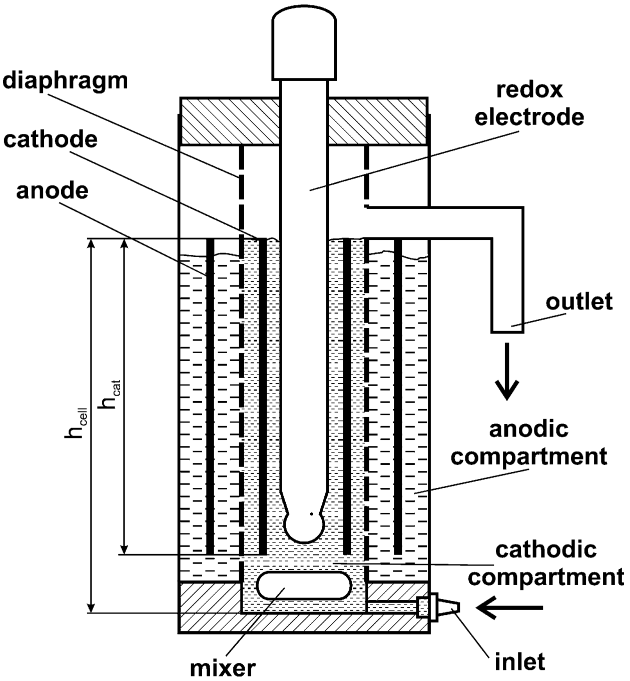

Fig. 3. Principle of the measuring cell.

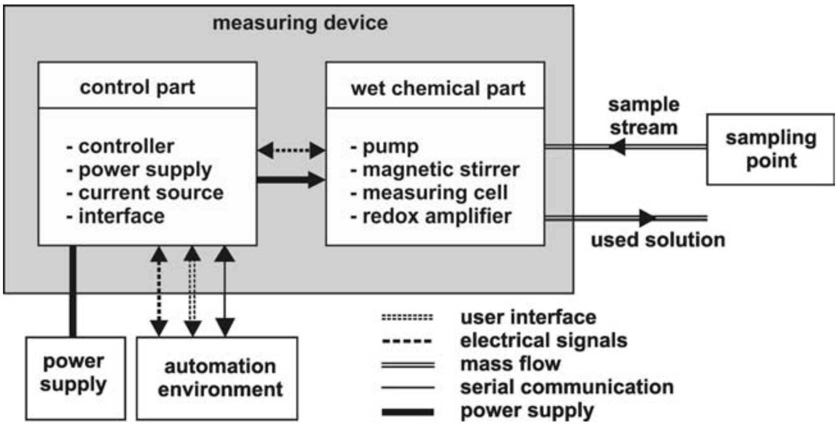

Fig. 4. Principle of the process measuring device.

Figure 1). To facilitate the maintenance of the process measurement device, a semiautomatic calibration was implemented. This enables easy calibration with two test solutions and supports the optimal positioning of the redox electrode (see above).

To enable the measuring device to communicate with its environment three different interfaces were implemented:

- An operator can control, calibrate and parameterise the device using a built-in local control terminal.
- The device can be controlled by external electrical signals.
- A serial interface can be used to control and parameterise the device.

Due to Eq. (4) the exact value of the mass flow, delivered by the pump, strongly influences the measured value of the concentration. Any deviation in the mass flow rate leads to a commensurate deviation in the measured concentration. However, pumps with high accuracy are usually expensive. Alternatively, less expensive peristaltic pumps can be used. Thus, an accuracy of better than 5% is possible, provided that calibrations are performed regularly.

The redox potential is influenced by the solution temperature, ageing effects of the redox electrode and other influences. Nevertheless, the persulphate measuring shows robustness with respect to inaccuracies in the redox potential. This is caused by the low sensitivity of the ferric concentration to redox potential changes in the neighbourhood of set point B in Figure 1. Figure 5 shows the error in the measured persulphate concentration with respect to the redox potential error, as it can be deduced from the theoretical redox potential characteristic.

6. Results

The device performed at a high level of accuracy. Figure 6 shows the electric current that was set by the device for a series of known concentrations. It can be seen that there are only small current errors with respect to Faraday's Law.

It must be pointed out that the use of the redox potential set point B instead of point A (see Figure 1) causes a small current offset because in addition to the total conversion of the peroxodisulphate a small amount of the incoming Fe^{3+} is converted. This offset has to be taken into account to get exact concentration results. This was considered in calculating the current errors in Figure 6.

The dynamics of the peroxodisulphate measurement are of special interest in its application as on-line process

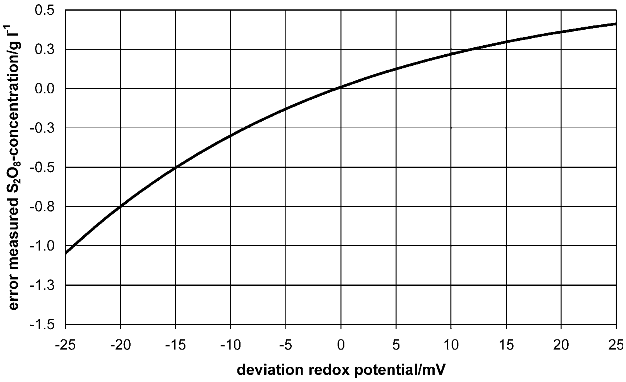

Fig. 5. Concentration error in respect of the redox potential error ($U_{r.set=600}$ mV).

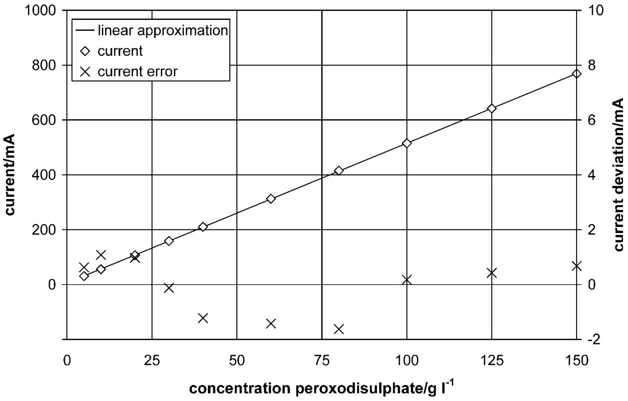

Fig. 6. Concentration current characteristic from experiments and errors due to Faraday's Law.

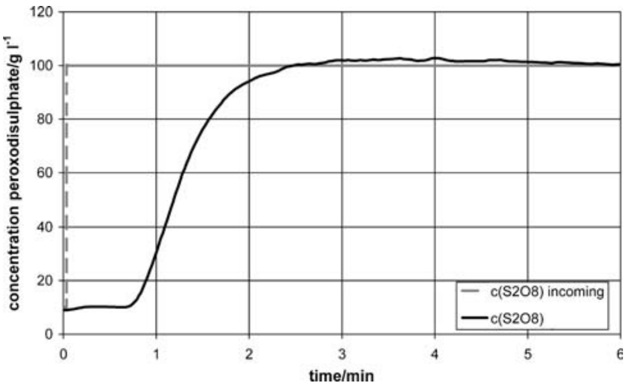

Fig. 7. Step response of the measuring device.

monitor. Figure 7 shows the step response to a concentration change from 10 to 100 g l^{-1}. The dead time at the beginning (approximately 0.7 min) is caused by the transport of the sample solution. It can be minimised if a bypass is used. The following transient of the measured concentration (approximately 2 min) results from the control of the redox potential. The transient of the closed loop control is considerably faster ($\tau = 0.65$ min) than a concentration change would be, in the pure electrochemical reactor with a response time given by Eq. (5) of $\tau_{\text{cell}} = 57$ min

Further experiments demonstrated the robustness of the concentration measurement, e.g., the temperature coefficient was found to be 0.03 g l^{-1} K^{-1}. For application in peroxodisulphate measurement in a copper pickling process, the cross sensitivity to the copper concentration was found to be −0.07 (g l^{-1})/(g l^{-1}).

7. Conclusion

The described technique for the measurement of peroxodisulphate is a viable alternative to expensive analytical methods. Based on this principle an on-line concentration device was developed which provides continuous measurement signal with small delay time. The device measures the peroxodisulphate concentration with an accuracy of about 5%, which is sufficient for industrial application, and with low cross sensitivities to main process factors.

The basic idea is not new and resembles a coulometric endpoint titration. The main difference is that the end point is not approached discontinuously but is set continuously by automatic control. In this form the required current is a measure of the unknown concentration. This method can be characterised as a continuously operated coulometric titration, as described in [10]. However, the method had not been used routinely for on-line monitoring.

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References

1. W. Thiele, *Metalloberfläche* **52** (1998) 846.
2. G.B. Balazs, J.F. Cooper, P.R. Lewis and M.G. Adamson, FY98 Final Report (Lawrence Livermore National Laboratory, 1998).
3. C.W. Walton, H. Uchtmann and H. Matschiner, *Abstracts ISE Meeting* **51** (2000).
4. J. Ogami, *Jap. Patent*, JP55154457 (1980).
5. M.F. Oliveira, R. Mortimer and N.R. Stradiotto, *Microchem. J.* **64** (2000) 155.
6. I.M. Dalrymple, M.L. Hitchman, D. Price and J.P. Millington, *Electroanalysis* **9** (1997) 2, 130.
7. S. Hauser, K.-H. Neumann, E. Giebler and W. Gräfenhan, *Ger. Patent*, DE10042568 (2002).
8. E. Giebler, S. Hauser and K.-H. Neumann, *Tech. Messen* **68** (2001) 12, 544.
9. E. Giebler, *Ger. Patent*, DE10056069 (2002).
10. E.L. Eckfeldt, *US Patent*, US2621671 (1952).