Electrochemical titrations of thiosulfate, sulfite, dichromate and permanganate using dual microband electrodes

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Applications of titration using dual gold microband electrodes in generator–collector mode are presented. The main advantage is that the method dispenses with the need for accurate volume measurements and reagent preparation: rather than balancing of molar amounts, the fluxes of analyte and titrant are balanced instead. The titrant is generated electrochemically and the end-point is detected amperometrically by the apppearance of a current due to the presence of the titrant at the other band. The aim is to show the versatility and capability of the method that employs disposable mass-produced electrodes and uses pulsed motion of the electrode before a measurement to renew the boundary conditions. The titration of ascorbic acid (vitamin C) with ferricyanide, which has been a model system, was extended to the determination of thiosulfate and sulfite with iodine and the determination of dichromate and permanganate with iron(II). The accuracy, limited by the present fabrication reproducibility of the disposable electrodes, is ±10%. The results demonstrate that the method is effective even with a very simple set-up, and the actual time needed for common titrations is significantly decreased. These examples demonstrate a comprehensive basis for further development and applications, including standard titrations in industry.

Introduction

In this paper, we show the usability of a simple, inexpensive and rapid titration method that employs dual microband electrodes in generator–collector mode. We continue the development presented in previous papers[1–4] and demonstrate new applications. The main advantage is the lack of separate titrant solutions, *i.e.*, the method dispenses with the need for accurate volume measurement and reagent preparation. Instead, the titrant is electrogenerated and the flux of reactive material is balanced instead of balancing the molar quantities of the titrant. The microband electrodes are disposable and user-friendly because there is no need for electrode polishing or prior calibration if the electrode geometry is known. On the basis of these examples the method can be easily applied to other analytical systems.

Method

In this titration method a current is applied at the generator electrode in order to generate the titrant electrochemically, and the collector potential is kept constant. The potential is chosen to drive a certain collector electrode reaction, namely the reversed reaction to the generator electrode reaction. The end-point of the titration is detected amperometrically. The presence of an analyte is observed as a decreased current and as a lower collection efficiency:

$$\Phi = \frac{I_{\text{coll}}}{I_{\text{gen}}} \qquad (1)$$

The concentration of the analyte can be determined by using both the decrease in collection efficiency and the change in shape of the collector current transient following the application of the generator current.[4] In this paper we concentrate on the first method.

The principle of the titration and the microband electrode construction are presented in Scheme 1.

It is required that the titration reaction itself is fast. The simplest case is that both the analyte C and the species D [Scheme 1(a)] produced in the titration reaction are electrochemically inactive in the potential range of interest but, as we show here, the method can be applied even if C and D are electrochemically active. A pulsed movement (vibration) of the microband electrode before each experiment is employed in order to stir the solution, to renew the surface conditions at the electrodes and to improve the reproducibility of the measurements. The pulsed motion of the electrode when the generator electrode is still off and the electrochemical measurement when the electrode is stationary leads to reliable mass transport. The
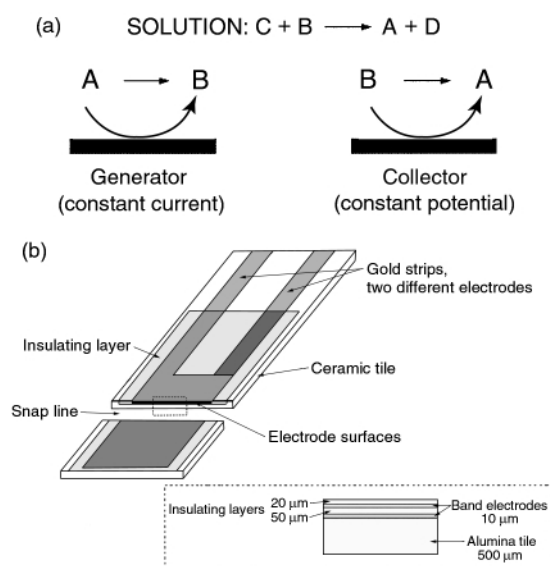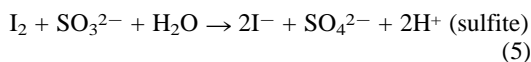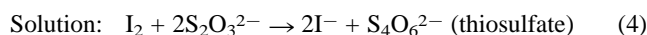

Scheme 1 (a) Electrochemical titration using dual microband electrodes. B, titrant; C, analyte. (b) Printed double microband electrode.[4] Au electrodes nominally 10 μm × 0.5 cm.

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measurements can be carried out on a short enough time-scale, during which convection does not disturb the signal. The determination of ascorbic acid (vitamin C) with ferricyanide has been used as an example earlier[4] and the same method was applied here to the determination of thiosulfate and sulfite with iodine and the determination of dichromate and permanganate with iron(II).

Titrations with electrogenerated I_2

Titrations of thiosulfate ($S_2O_3^{2-}$) and sulfite (SO_3^{2-}) with iodine (I_2) are analogous to vitamin C determination [Scheme 1(a)]. [4] Titration of thiosulfate with iodine is a very common titration reaction in analytical chemistry,[5–7] the stoichiometry of which is well established. It can be applied to back-titrations. The determination of sulfite is important, e.g., in food analysis, and can be applied to sulfur dioxide determination.[8–10] The overall reactions for these systems are as follows:[6,11–15]
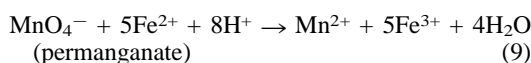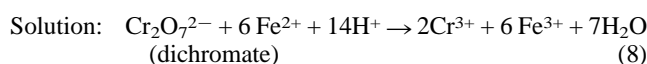
Generator: $2I^- \rightarrow I_2 + 2e^-$ $E° = +0.294$ V vs. SCE (2)

Collector: $I_2 + 2e^- \rightarrow 2I^-$ (3)

Solution: $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ (thiosulfate)   (4)

$I_2 + SO_3^{2-} + H_2O \rightarrow 2I^- + SO_4^{2-} + 2H^+$ (sulfite) (5)

In practice, when an excess of iodide is present in the solution, the triiodide ion (I_3^-) is the reactive species instead of iodine (I_2)[5,11,16] and the generator–collector reactions and the actual titration reactions, respectively, change. The pH of the solution in the range 1–7 has not been observed to affect the redox behaviour of I^-–I_3^-–I_2 systems.[11,17]

Margerum et al.[6,12] studied the reaction mechanisms and kinetics of the reactions (4) and (5) in acidic solution. They reported very fast multi-step mechanisms for both cases that include short-lived intermediates $I_2S_2O_3^{2-}$ and $IS_2O_3^-$ for thiosulfate titration and ISO_3^- for sulfite titration. The kinetic parameters of I^-–I_3^-–I_2 –systems have proved to be dependent on the experimental conditions used.[11]

Both I^- and I_2 adsorb on gold electrodes, but the phenomenon is not expected to affect the reversibility of a I^-–I_2 couple,[11,17,18] especially when disposable electrodes are employed. There are also several references[19,20,21] reporting the solubility of gold in iodide solutions, but again this is not expected to cause problems with disposable electrodes.

## Titrations with electrogenerated Fe(II)

Both dichromate and permanganate titrations are widely used in analytical chemistry.[7,10,22] Titration of dichromate ($Cr_2O_7^{2-}$) with iron (Fe^{2+}) is similar to the titrations above. Determination of permanganate (MnO_4^-) differs from them because the analyte itself is electroactive in the potential range of interest. The reactions are as follows:[13,22]

Generator: $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E° = +0.437$ V vs. SCE (6)

Collector: $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (7)

Solution: $Cr_2O_7^{2-} + 6\,Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6\,Fe^{3+} + 7H_2O$
        (dichromate)   (8)

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
        (permanganate)   (9)

The experimental conditions are important because both chromium and manganese can be present in several oxidation

states. For example, the formation of MnO_2 is prevented by choosing a low pH value.[23]

The cyclic voltammograms of Fe(III), $Cr_2O_7^{2-}$ and MnO_4^- solutions are presented in Fig. 1. It can be seen that permanganate is reduced in the potential range where iron is also active, and therefore a more complex approach is needed. When a constant current is applied at the generator, both reaction (6) and reduction of permanganate:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E° = +1.249$ V,
    $E_{1/2} = +0.943$ V vs. SCE   (10)
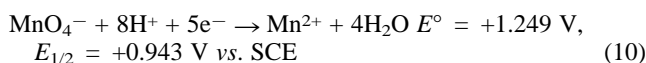
take place.[13,23] Similarly, the current at the collector is the sum of reactions (7) and (10). The reduction potential of dichromate is more negative than that of permanganate ($E° = +1.088$ V vs. SCE,[13] in practice $E_{1/2} \approx +0.500$ V vs. SCE). When a collector potential that is positive enough is chosen an analogous reaction to reaction (10) is not observed. Therefore, the dichromate titration can be carried out in the same way as the ascorbic acid titration. Both the dichromate titration and the permanganate titration can be extended to applications where a back-titration is needed.

Experimental

The screen-printed microband electrodes have been described in detail in previous papers and are presented in Scheme 1(b).[2,4] A new microband was employed and the fresh electrode surface was exposed before each set of measurements with a certain analyte concentration. The generator electrode was the microband next to the alumina tile and the collector electrode was that adjacent to the outer insulating layer. The reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinum sheet. The experiments were carried out in an open cell at room temperature. All the solutions were prepared using water purified using a Millipore Milli-Q system (18.2 MΩ cm) and all the chemicals were of analytical-reagent grade ($Na_2S_2O_3$, Fisons, Loughborough, UK; Na_2SO_3, Fisher Scientific, Loughborough, UK; $Na_2Cr_2O_7$, Fisons; $KMnO_4$, BDH, Poole, Dorset, UK). The electrolyte was either KI or $NH_4Fe(SO_4)_2$ (both from Sigma-Aldrich, Gillingham, Dorset, UK), depending on the species to be determined. The supporting electrolyte in all the measurements was 0.1 M H_2SO_4 (pH 1.5) (BDH). The solutions were prepared immediately prior to the measurements and degassed with argon. In previous work,[4] a hydrophobic spray coating over the electrodes was used to prevent solution creep up to the contacts. In this work, it was omitted because of the low pH of the solution, without causing difficulty. A summary of the experimental conditions and reagents is presented in Table 1.
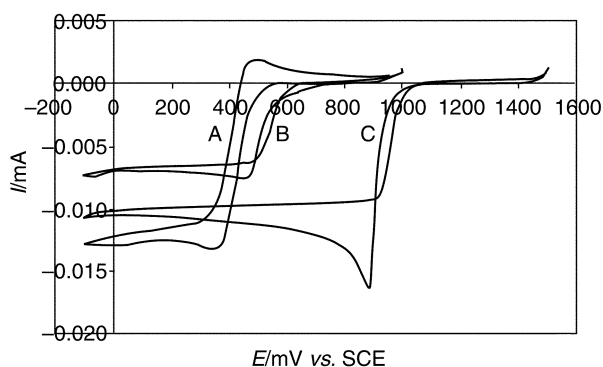

Fig. 1 Cyclic voltammograms at freshly snapped gold microband electrodes for iron(III) [A, 50 mM $NH_4Fe(SO_4)_2$], dichromate (B, 2 mM $Na_2Cr_2O_7$) and permanganate (C, 5 mM $KMnO_4$). Scan rate, 25 mV s^{-1}; supporting electrolyte, 0.1 M H_2SO_4.

For electrochemical measurements, a purpose-built dual potentiostat–galvanostat (Sycopel Scientific, Washington, Tyne and Wear, UK) was employed: the assembly drove a constant current to the generator while the collector potential was kept constant. For each analyte concentration nine generator currents $|I_{gen}|$ of 1–9 µA were applied, starting from the lowest current. For electrode vibrations a toothed wheel fitted to a stepper motor was used. The electrode was moved by a push rod between the disc and the electrode holder. The collector potential was applied just before a movement pulse of the electrode, and the generator current was applied 1 s after the movement and removed shortly before the next movement. The collector current I_{coll} was measured as a function of time.

Results and discussion

The data were analysed by plotting I_{coll} after a particular time (3 s after the generator current pulse) against I_{gen}. The value of I_{gen} that is needed to reach a certain threshold value of I_{coll} determines the concentration.

Titrations with electrogenerated I$_2$

The experimental collector current transients for thiosulfate titration as a function of t at fixed I_{gen} are presented in Fig. 2, and the collector currents for the same analyte as a function of I_{gen} at fixed t are shown in Fig. 3. The results are in a good agreement with the reaction layer model:[4] at sufficiently high generator currents, the curve of the collector current as a function of the generator current lies parallel to that in the absence of analyte. The displacement, ΔI_{gen}, of the curve is the additional flux from the generator that is required to compensate the flux of the analyte:

$$\Delta I_{gen} = zv\Delta c_C^b F l D_C / \Gamma_{D,C} \quad (11)$$

where z is the charge number for generation of titrant, v is the number of moles of titrant to react with 1 mol of analyte, c_C^b is the analyte bulk concentration (species C in Scheme 1), F is the Faraday constant, l is the length of the band electrode, D_C is the diffusion coefficient of species C and $\Gamma_{D,C}$ is the diffusion layer thickness for the analyte, which may be determined by numerical simulations.[4] In Fig. 4, the generator current required to reach a particular value of collector current is presented for thiosulfate and sulfite titration. As eqn. (11) predicts, the results are straight lines. The displacement of the generator current is proportional to the number of moles of titrant that is needed to react with 1 mol of analyte, and therefore the displacements of the curves in the sulfite titration are twice as high as those in the thiosulfate titration with the same analyte concentrations. This is due to the different stoichiometries of reactions (4) and (5): 1 mol of iodine reacts with 2 mol of thiosulfate [reaction (4)] but 1 mol of sulfite [reaction (5)]. This leads to a higher possible analyte concentration to be detected in the thiosulfate titration and a lower detection limit in sulfite titration. The rates of both reactions can be assumed to be very fast, and the kinetic differences can be neglected.

Both systems give reliable results with approximately the same relative standard deviation (typically 10%) as reached in the ascorbic acid titration.[4] The variation in the results is caused by the geometry of the microband electrodes: the electrodes are not ideally flat and the snapping line near the electrode can distort the diffusion field. The effect varies from electrode to electrode, and might be reduced by improvements in manu-
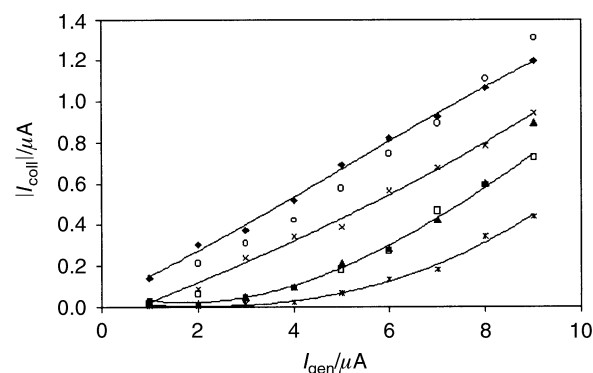
Fig. 3 Collector current *vs.* generator current in thiosulfate titration. Values determined 3 s after generator current was applied. $E_{coll} = 0$ V *vs.* SCE; 50 mM KI; 0.1 M H$_2$SO$_4$; $c_{thiosulfate} = $ (◆) 0, (○) 0.25, (×) 0.5, (▲) 0.75, (□) 1.0 and (*) 2.0 mM. Mean values from four measurements with different electrodes for each concentration.

Table 1 Experimental conditions and reagents for different analytical systems. Supporting electrolyte, 0.1 M H$_2$SO$_4$, pH 1.5

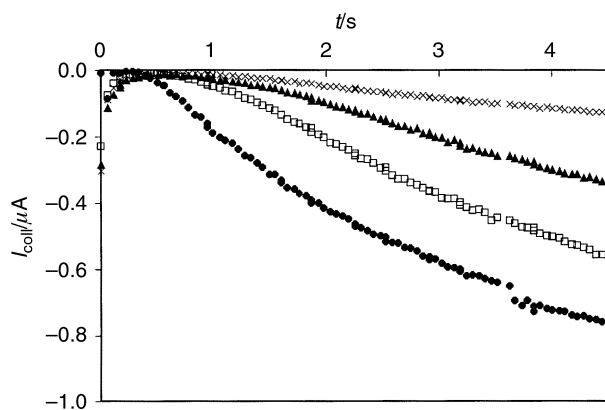| Analyte	Titrant	Electrolyte	E_{coll}/V *vs.* SCE
Sulfite (SO$_3^{2-}$)	I$_2$	50 mM KI	0
Thiosulfate (S$_2$O$_3^{2-}$)	I$_2$	50 mM KI	0
Permanganate (MnO$_4^-$)	Fe^{2+}	50 mM NH$_4$Fe(SO$_4$)$_2$	+0.600
Dichromate (Cr$_2$O$_7^{2-}$)	Fe^{2+}	50 mM NH$_4$Fe(SO$_4$)$_2$	+0.850

Fig. 2 Experimental collector current transients with different thiosulfate concentrations. Generator current applied at $t = 0$ s, *i.e.*, 1 s after the movement pulse of the electrode. $I_{gen} = 6$ µA; $E_{coll} = 0$ V *vs.* SCE; 50 mM KI; 0.1 M H$_2$SO$_4$: $c_{thiosulfate} = $ (●) 0, (□) 0.5, (▲) 1.0 and (×) 2.0 mM.

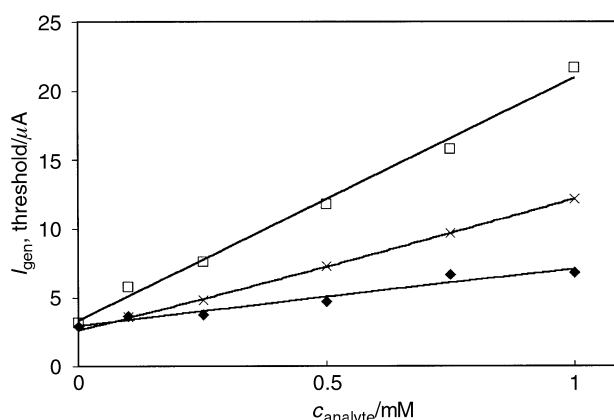**Fig. 4** Generator current that is required to produce a collector current, $|I_{coll}|$, of 0.4 µA after a particular time (3 s after the generator current pulse was applied) in thiosulfate (◆), sulfite (×) and dichromate (□) titration. Experimental conditions are presented in Table 1. Mean values from four measurements with different electrodes for each concentration. In the case of Cr$_2$O$_7^{2-}$, I_{gen} was negative; for higher analyte concentrations (0.75 and 1.0 mM) it was in the range −10 to −20 µA.

facturing tolerance. The accuracy could also be improved by establishing more reproducible experimental conditions, *i.e.*, identical chemical environments and careful temperature control, but that would affect the user-friendliness of the method.

Titration with electrogenerated Fe(II)

Dichromate titration. The calibration curve, *i.e.*, the absolute value of the generator current required to reach a particular value of collector current, for the dichromate titration is presented in Fig. 4. The threshold values are relatively high because of the stoichiometry of reaction (8): 1 mol of dichromate reacts with 6 mole of Fe(II). This was also seen as a delay of the collector current after the generator was switched on at $t = 1$ s, and the delay increased with the increasing analyte concentration. Owing to the stoichiometry, the detection limit is very low.

Permanganate titration. The collector currents with different analyte concentrations in permanganate titration are given in Fig. 5. Two different detection methods are compared. In the direct detection method, no iron is present in the solution and the generator electrode is completely disconnected. The collector potential is stepped to a value on the diffusion limit for reaction (10) at $t = 0$, and only one value (diffusion limited current) is detected for each concentration. In the indirect method, the Fe(III) concentration is 50 mM, *i.e.*, the same as in $Cr_2O_7{}^{2-}$ titration, and Fe(II) (titrant) is generated electrochemically at the generator electrode. The total current detected at the collector represents the sum of the oxidation of Fe(II) back to Fe(III) and reaction (10). In the experimental data the transients at times $0 \leqslant t \leqslant 1$ s, *i.e.*, before the generator is switched on, are consistent with the transients of the direct detection method [reaction (10)]. In Fig. 5, the collector current value for the indirect method is the difference between the current at the point when I_{gen} is switched on ($t = 1$ s) and 3 s after that. Analogous values are also recorded for the direct method. The dual microband has the advantage over a simple determination of permanganate concentration through the limiting current for reaction (10) by providing an additional, complementary route to check the measurement. The permanganate system demonstrates the capability of the dual microband system to be used to measure concentrations of electroactive species accurately and reproducibly. The method can be applied to other comparable systems.
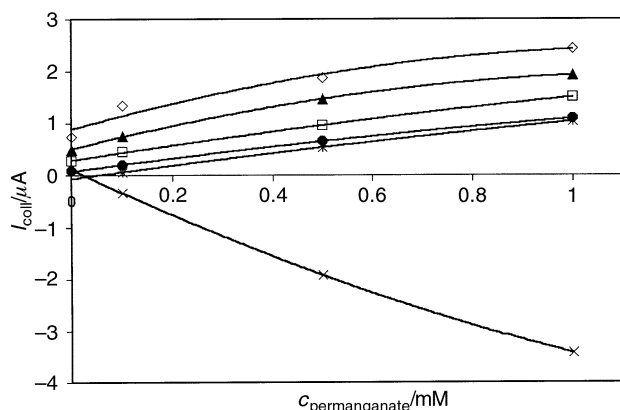
Electrode poisoning

Minor deviations in the results can be caused by electrode poisoning. The same microband electrode was used for the entire set of measurements with a given analyte concentration (nine scans, currents from 1 to 9 μA). The actual effect of poisoning was studied by performing sets of measurements where the same solution (iodine present), the same generator current and the same microband electrode were used for nine scans in a row. We observed that the currents became smaller when the scans were repeated but variation in the currents occurred also due to other effects (*e.g.*, convective effects, noise). The electrode poisoning is most probably due to adsorbed species, especially I_2,[16] at the electrode surface. In addition, the surface structure of a just snapped (fractured) electrode differs from that of a used or polished electrode.[24] Reliable results are achieved when disposable electrodes are used immediately after snapping to expose the gold, for a single measurement only, and the results from the same scans are compared with each other. The reactivity of the insulating material and its effect on the behaviour of the gold electrodes could be investigated. After repeated measurements on a given electrode, darkening of the electrodes or a dark precipitate at the electrode surface was observed by an optical microscope. This effect originated particularly at the boundary of electrode material and insulator and may have been due to an electro-oxidation of lead leached out from the insulator (a commercial dielectric preparation comprising PbO–SiO_2 glass containing barium titanate).

Conclusions

We have presented new applications of titrations with dual microband electrodes. The titration of thiosulfate and sulfite with iodine and the determination of dichromate and permanganate with iron(II) have been demonstrated to work reliably within error bars similar to those observed in previous ascorbic acid measurements. The results showed the usability of the method in various titration systems, including determination of an electroactive analyte. The titration can be further extended to several applications, where at present complicated and time-consuming analyses are carried out. The errors in the measurements might be reduced by new electrode fabrication, and electrode poisoning can be avoided when disposable electrodes are employed.

Fig. 5 Calibration curves for permanganate titration. Direct detection method ($\times$), *i.e.*, no iron present in the solution and the generator disconnected. Values recorded 4 s after the movement pulse of the electrode. Indirect method where Fe(II) electrogenerated: I_{gen} = ($\bullet$) -1, ($\bigcirc$) -3, ($\blacktriangle$) -6 and ($\Diamond$) -9 μA. The current value is the difference between the current at $t = 1$ s (when the generator current switched on) and $t = 4$ s. The current difference in direct detection, $I(t = 4$ s$) - I(t = 1$ s$)$ for I_{gen} = 0 (*). E_{coll} = +0.6 V *vs.* SCE. Mean values from four measurements with different electrodes for each concentration.

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