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Conditions for Accurate Karl Fischer Coulometry Using Diaphragm-Free Cells

Ulrika Nordmark and Anders Cedergren*

Department of Chemistry, Analytical Chemistry, Umeå University, S-901 87 Umeå, Sweden

Factors influencing the extent of formation of oxidizable reduction products in coulometric cells used for Karl Fischer (KF) determination of water were investigated. For methanolic KF reagents buffered with imidazole (Im) or diethanolamine (DEA) (separately or in combination), three parameters were found to be of outmost importance: the cathodic current density, the pH, and the concentration of protonated base (ImH^+ or $DEAH^+$). For reagents buffered with only Im, the relative formation of oxidizable reduction products varied in the range 2−40%; i.e., 51−70 μg of water was found for a 50 μg water sample, depending on the above-mentioned parameters. The lowest values were observed for reagents having a pH around 10 in combination with cathodic current densities in the range 2000−5000 mA cm^{-2}. For all the Im-buffered reagents investigated, the addition of modifiers such as chloroform, hexanol, and carbon tetrachloride was found to decrease the formation of oxidizable reduction products significantly. For example, a reagent buffered at pH 10 containing 1 M hexanol gave less than 0.3% formation in the current density interval from 200 to 4000 mA cm^{-2}. The best reagents based on the above-mentioned modifiers were tested in the continuous coulometric mode with errors typically in the interval 0−0.5% using optimum conditions. One prerequisite for obtaining such small errors with diaphragm-free continuous coulometry is to use a cathode area no larger than 0.002 cm^2. For some of the reagents based on both Im and DEA, the formation of oxidizable reduction products was close to zero at certain current densities, although the analytical performance was not as good as for the reagents buffered solely by Im due to longer conditioning and titration times.

The Karl Fischer (KF) coulometric titration method is currently used extensively (500 000 determinations/day) and is considered to be of special importance for the determination of low concentrations of water. A conventional coulometric cell is equipped with a cathodic compartment that is in electrolytic contact with the anode via a diaphragm. In this way, the iodine formed in the anode reaction is hindered from reaching the cathode where it can be reduced. In addition, the diaphragm makes it possible to use a separate solution in the cathode compartment in order to eliminate the influence of the reduction products formed in the cathodic reaction. When spent KF reagent is used both as catholyte and anolyte, problems arise because sulfur dioxide/methyl sulfite are reduced and the reduction products of these sulfur compounds, e.g., hydrogen sulfide, sulfide, and thiosulfate,[1] can diffuse/migrate into the anodic chamber where they are oxidized by iodine. Nowadays, it is recommended that a catholyte without sulfur dioxide, normally a soluble ammonium salt,[2] be used. With such an electrolyte, inert hydrogen is believed to be formed quantitatively at the cathode.[2]

Except for the need to use two different electrolytes in coulometric cells containing a diaphragm, there are additional problems associated with this concept, e.g., the relatively long conditioning times needed before starting up. Clogging of the diaphragm is also known to be problematic since the resulting increase in cell resistance may cause electronic problems. These drawbacks explain the development toward the use of cells without a diaphragm, which has been described in the literature during recent years.[3−8] In principle, three different designs of such cells have been proposed. (i) the cathode is placed together with the anode in a single compartment;[3−6] (ii) the cathode is held inside a tubelike cathodic compartment[8] having an open cylindrical hole at the bottom (diameter 1.2 mm, height 8 mm) and the liquid inside this compartment can be drained by pushing a Teflon plunger down and up (the accumulated oxidizable reduction products are thus eliminated in a simple way); (iii) the cathode is situated in a semiopen cathodic compartment,[7] which means that there will be delayed mixing of the electrolytes in contact with the anode and the cathode.

Irrespective of the type of diaphragm-free coulometric cell used, the fundamental requirement for obtaining results with high accuracy is that a negligible fraction of the generating current causes the formation of oxidizable reduction products at the cathode. This is known to be a problem in both pulsed and continuous electrolysis when diaphragm-free cells are used. For currents larger than 400 mA (pulse electrolysis) in combination with a cathode area of less than 1 cm^2, it has been shown that the positive errors obtained when milligram amounts of water are titrated can be kept in the interval 0−3% (relative).[3,4,7] The results reported are difficult to interpret since different reagents as well as different types of cells were used. For the commercially

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* Corresponding author: (e-mail) anders.cedergren@chem.umu.se.

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available Hydranal Coulomat AD, which has been designed for diaphragm-free cells, Scholz[7] reported +0.2 ± 1.5% (1 mg water sample) while Dahms[3] found +2%. For continuous coulometry, i.e., the technique in which the generating current varies from a high value at the beginning of the titration to a low value at the end, Katoh[4] reported positive errors between 20 and 40% for a 50 μg water sample, depending on the type of reagent used. These results are consistent with those reported by Cedergren,[8] who determined the amounts of oxidizable reduction products accumulated inside the cathode compartment at low current densities for different types of KF reagents.

The aim of the work presented in this paper was to systematically investigate important factors for achieving a minimal formation of oxidizable reduction products in the cathode reaction even when small electrolysis currents are used. Imidazole-buffered KF reagents are the most commonly usd, and since these systems have unique advantages due to their fast kinetics,[9,10] all reagents investigated were based on the use of this substance. In addition, we chose to investigate the influence of diethanolamine (DEA) in some reagents because this base is one component of the commercial product Hydranal Coulomat AD mentioned above. The study also included modified KF reagents containing large concentrations of hexanol and chloroform because of their great importance for water determinations in hydrocarbons.

EXPERIMENTAL SECTION

Chemicals. Diethanolamine (>98% for synthesis), sodium salicylate (pa), carbon tetrachloride (pa), and chloroform (pa) were from Merck. Imidazole (pa) and sulfur dioxide (>99.9%) were from Fluka. Trichloracetic acid (pa), iodine (pa), hexanol (99%), acetic acid (pa), sodium acetate (pa), and Hydranal Coulomat AD were from Riedel-deHaën. Methanol (pa) was from KeboLab. Salicylic acid was from Analar (99.9%).

Safety Considerations. *Methanol* is highly flammable and is toxic by inhalation, in contact with skin, and if swallowed. *Chloroform* is harmful by inhalation and ingestion and may be fatal. Inhalation of vapor may cause headache, nausea, vomiting, and dizziness. Prolonged skin contact may result in dermatitis. The liquid is readily absorbed through the skin. *Imidazole* is harmful by inhalation, in contact with skin, and if swallowed. *Sulfur dioxide* is intensely irritating to eyes and the respiratory tract. *Iodine* is a poison and may be fatal if swallowed; avoid contact with eyes, skin, or clothing, do not breathe the vapor, and use with adequate ventilation. *Trichloroacetic acid* is a poison and causes severe burns; avoid contact with skin and eyes. *Carbon tetrachloride* is a potential carcinogen; inhalation and ingestion are harmful and may be fatal. Eye/skin protection with safety goggles and face shield, uniform, protective suit, and poly(vinyl alcohol) gloves are recommended. *Asbestos* is carcinogenic. Avoid the buildup of pressure, especially when mixing large amounts of imidazole/diethanolamine and trichloroacetic acid with methanol when preparing the regents.

Reagents. The compositions of reagents under investigation are given in Table 1. pH measurements were made for some reagents using a Metrohm pH meter with saturated lithium chloride in methanol as internal electrolyte. Buffer solutions (0.05 M) were prepared in methanol from salicylic acid/sodium salicylate (pH 7.9) and acetic acid/sodium acetate (pH 9.7).[11] The effective sulfur dioxide concentration $[\mathrm{SO_2}]_{\mathrm{eff}}$ (i.e., the sum of all S(IV) species obtained from the added sulfur dioxide) was determined coulometrically according to the method described by Cedergren et al.[12]

Table 1. Compositions and pH of the Investigated Reagents

	concentration[a] (M)						
reagents	$[\mathrm{Im}]_0$	[TCA][b]	$[\mathrm{DEA}]_0$	$[\mathrm{CCl_4}]_0$	$[\mathrm{CHCl_3}]_0$	$[\mathrm{hexanol}]_0$	pH
A	0.8	0	0	0	0	0	7
B	2.4	1.6	0	0	0	0	7
C	1.3	0	0	0	0	0	9
D	6.6	0	0	0	0	0	10
E	1.3	0.5	0.5	0	0	0	9.2
F	3	0.5	1.18	0	0	0	10.6
G	2.3	1.5	1	0	0	0	9.5
H	5	1	1	0	0	0	10.1
I	1.3	0	0	0.5	0	0	9[c]
J	6.6	0	0	0.5	0	0	10[c]
K	6.6	0	0	1	0	0	10[c]
L	1.3	0	0	1	0	0	9[c]
M	0.8	0	0	0	1	0	7[c]
N	1.3	0	0	0	1	0	9[c]
O	6.6	0	0	0	1	0	10[c]
P	6.6	0	0	0	3	0	10[c]
Q	0.8	0	0	0	0	1	7[c]
R	1.3	0	0	0	0	1	9[c]
S	6.6	0	0	0	0	1	10[c]
T	6.6	0	0	0	0	3	10[c]

[a] Subscript zero denotes initial concentrations before decoloring with water, $[\mathrm{SO_2}]_{\mathrm{eff}} = 0.5$ M, and $\mathrm{I_2} = 0.1$ M for every reagent given above. [b] Trichloroacetic acid. [c] Estimated values.

Instrumentation. Two different cells were used for coulometric KF titrations, a three-compartment cell[9] and a diaphragm-free cell.[8] The former consisted of three chambers: the reference electrode (Pt) in the left chamber, the working (Pt) and the indicating electrode (Pt) where the sample is injected through a silicone rubber septum in the middle, and finally the right chamber for the auxiliary electrode (Pt). A plug containing a small channel was placed in the chamber where the reduction of protonated base to hydrogen gas takes place in order to avoid pressure buildup in the KF apparatus. One additional platinum wire electrode was placed in the middle chamber near the working electrode and was used as a cathode in the investigation of the formation of oxidizable reduction products. This electrode was coated with a thin layer of fluorinated ethylene propylene (FEP) with an uncoated area of 0.002 cm^2. The maximum current that can be used in the generating electrode system, when using this small cathode surface, was about 10 mA for a 10 V output voltage from the titrator. For the normally used 28 V, the maximum current should be 28 mA, which corresponds to a maximum titration rate of 156.8 μg of water/min. In some separate experiments, this electrode was replaced by the same type of electrode having a free platinum surface area of 0.02 cm^2. No cleaning of electrodes was necessary under normal operating conditions. Electrolytic contact between the chambers was made by asbestos-filled liquid junctions.

The diaphragm-free cell was equipped with a platinum cathode (0.002 cm^2) inside a tubelike cathodic compartment with a draining

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function.[8] By pushing down a Teflon plunger, this cathode could be brought in direct contact with the anolyte. Samples were injected through a silicone rubber septum. Both cells were connected to the computer-controlled coulometric titrator (zero-current potentiometric end-point indication) recently described[13] or to a Fluke dual-display multimeter which in turn was connected to a computer in which the data collection program Fluke QS 45 was available.

Procedure. Procedures for preparation of the three-compartment cell (5 mL) and the diaphragm-free cell (13 mL) have been described in detail in refs 14 and 18, respectively. For calibration, i.e., the establishment of the relation between the redox potential of the indicating electrode and the excess iodine, the same procedure as that outlined in ref 13 was used. To bring about a certain constant current level during electrolysis, a variable resistor was placed in series with the generating electrode system. By selecting a suitable amplification factor (generating current/deviation in potential between the actual redox potential and a preset value) and end-point concentration of iodine (normally 5×10^{-6} M), the shape of the titration curve looked like a rectangle. This means that the height of this rectangle, with good approximation, represents the current–time profile used for the entire experiment. Normally 10 μL (Hamilton syringe) of a Hydranal water standard (5.0 mg of H_2O/mL of xylene/butanol) was injected into the cell in which the cathode was either separated from the anode compartment or in direct contact (see above).

Calculations. The baseline drift (corresponding to the moisture diffusing into the coulometric cell) was typically in the range 0.1–1.0 μg of H_2O/min, and this value was obtained with the cathode placed in the cathodic compartment of the respective cell. The difference between this value and that obtained when the cathode was operated in direct contact with the anolyte, i.e., at the background level, was used in the calculations of the relative formation (%) of oxidizable reduction products at a certain current. This was done by multiplying this drift difference (Δdrift (μg of H_2O)^1 min^{-1}) with the time (t/min) for the titration, and the product was then added to the integrated value (corrected for the background) ($m_{\text{diaphragm-free cell}}/\mu$g) and compared to that obtained for the standard (obtained with the cathode in the cathodic compartment) ($m_{\text{diaphragm cell}}/\mu$g) according to the following equation:

$$\text{relative formation (\%)} = \frac{((m_{\text{diaphragm - free cell}} + \Delta\text{drift} \times t) \times 100)}{m_{\text{diaphragm cell}}} - 100 \quad (1)$$

Irrespective of what type of reagent was used (Table 1), the values obtained for this standard (50 μg of water) did not vary by more than 0.5% (relative) during a 9 month period.

RESULTS AND DISCUSSION

Current Density. The effect of the cathodic current density on the formation of oxidizable reduction products is illustrated in Figure 1 for the commercially available reagent Hydranal Coulomat AD discussed in the introduction. As can be seen in the figure, there is a pronounced decrease in the formation of oxidizable species in the interval where the current density is increased from 50 to 400 mA cm^{-2}. It is also evident that a further increase in the current density by a factor of 10 does not further improve the situation. The dashed line in the figure marks the value being used in the commercial coulometric instrumentation of Metrohm (400 mA and a cathode area of 0.28 cm^2). For this current density we obtained about 2% formation, which is in line with results reported by Scholz and Dahms for the same reagent. It should be pointed out that our results are based on constant continuous current while Scholz and Dahms used constant current pulses. Also inserted in the figure are values for Coulomat AD, reported previously by Cedergren,[8] using the diaphragm-free cell. As can be seen, these data fit relatively well into the curve although they were obtained under different experimental conditions. Because of the good agreement between the results obtained with pulse and continuous electrolysis, it can be concluded that no significant advantages are to be gained by the use of the pulse technique at high current densities. It should be pointed out that the commercial reagent discussed in this paragraph is a relatively slowly reacting one, which means that a relatively high (and sometimes unfavorable) end-point concentration of iodine is required for the KF reaction to take place in a reasonably short time. By means of the kinetic method described earlier,[9] the rate constant corresponding to an iodine excess concentration of 10^{-6} M was determined to be 2.0×10^4 M^{-2} s^{-1}. This means that the time for a complete reaction at this iodine level will be more than 5 min ([SO_2] assumed to be 1 M). As has been shown before,[15] much more rapid reactions at low iodine concentrations can be attained by selecting a very high concentration of nonprotonated imidazole,

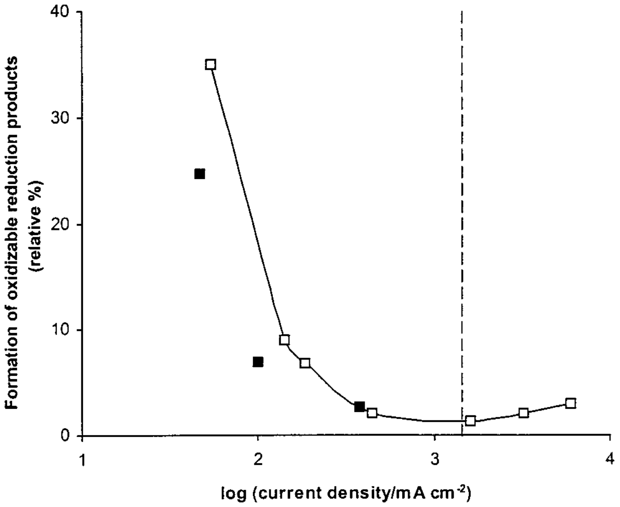

Figure 1. Influence of the current density on the formation of oxidizable reduction products using Hydranal Coulomat AD. Open squares represent results obtained with a three-compartment cell in which an additional cathode was placed in direct contact with the anolyte in the middle chamber. Cathode areas of 0.02 and 0.002 cm^2 were used for the lower and higher current densities, respectively. The filled squares represent results reported earlier[8] obtained with a diaphragm-free cell. The dashed line corresponds to the conditions used in a commercially available instrumentation.

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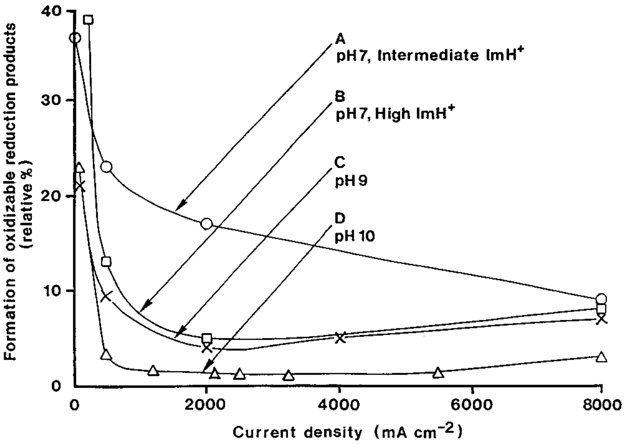

Figure 2. Formation of oxidizable reduction products as a function of current density for different types of Im-buffered reagents. The concentration of ImH$^+$ was 0.7 M for all reagents, except for reagent B (2.4 M).

especially in combination with the use of a modifier like chloroform.

Imidazole-Buffered Reagents. The main components of a methanolic imidazole-buffered KF reagent, which were assumed to be of greatest importance for the problem at hand, are free imidazole (Im_{free}), protonated imidazole (ImH^+), free sulfur dioxide ($SO_{2,free}$), and methyl sulfite ($CH_3SO_3^-$). A large number of reagents were prepared in which the composition of these species was varied considerably. By increasing pH, i.e., the quotient $[Im]_{free}/[ImH^+]$, the following equilibrium ($K = 10^{-5}$) is displaced to the right:

$$SO_2 + 2CH_3OH \leftrightarrow CH_3SO_3^- + CH_3OH_2^+ \qquad (2)$$

Since pK_a for ImH$^+$ in these media is around 9, the concentration of this species could be varied by adding trichloroacetic acid (pK_a 4.9 in methanol[11]) to the reagent solution with excess imidazole. In the cathodic reaction, protonated Im produces hydrogen as indicated by the formation of gas bubbles.

The most important results are represented in Figure 2, where it can be seen that the most favorable conditions are obtained at high pH. It is also clear that the effect of increasing the concentration of ImH$^+$ (2.4 M) is very large for reagent at pH 7. The combination of a high concentration of ImH$^+$ and pH was not studied. For a reagent containing 1.3 M ImH$^+$ at pH 9, however, no significant differences in the results were observed as compared with those (0.7 M ImH$^+$) for the same pH in the figure. It should be pointed out that the values given in Figure 2 may be somewhat underestimated in view of the results reported by Nichugovskii[6] for a pyridine-buffered reagent. He reported that continuous addition of oxygen during the titration significantly reduced the influence of the reaction products formed at the cathode.

The results given in the figure clearly indicate that sulfur dioxide is the sulfur species being reduced at the cathode and not (or too much lesser extent) methyl sulfite because of the strong pH dependence of the equilibrium reaction 2. It can also be concluded that ImH$^+$, although present in a large excess over sulfur dioxide, cannot completely hinder the reduction of this species although the concentration of free sulfur dioxide should be as low as 5 μM at pH 10 (calculation based on equilibrium reaction 2). The free imidazole concentration does not seem to influence the formation of oxidizable reduction products, as was indicated by experiments with an acetate-buffered reagent at pH 9.7. This reagent did not contain any imidazole, and the results were between the curves for reagents C and D in Figure 2. The relation between the formation of oxidizable reduction products and the total concentration of sulfur dioxide (effective) was investigated for some Im-buffered reagents and found to be linear. This means that the extent of formation can be reduced compared to that shown in Figure 2, by lowering the concentration of sulfur dioxide in the reagents. However, an increase of the iodine end-point concentration is then required in order to compensate for the decrease in reaction rate.

The possible reduction of iodine when the cathode was placed in direct contact with the anolyte was studied for a Im-buffered reagent at pH 10 by measuring the background drift at different end-point concentrations of iodine. Since no significant increase in the baseline level was noted in the interval 10^{-6}–5×10^{-4} M iodine, we concluded that this species is not reduced under the experimental conditions used in this work.

The reaction rate between iodine and some of the oxidizable sulfur species formed at the cathode was found to be slow, and this was discussed earlier by Schöffski.[16] In some cases the original baseline level was never reached again after the sample was injected, and in some cases a continuous increase in the background was observed. For such a case, the original background was immediately regained when the cathode was placed in the catholyte instead of remaining in direct contact with the anolyte. This behavior might be explained by an accumulation of reduced species such as elemental sulfur (reduction product of sulfur dioxide or thiosulfate) because when this species is reduced to sulfide, iodine will immediately oxidize it back to elemental sulfur.

The slow reaction between iodine and an interfering sulfur species may give rise to an error in the coulometric determination irrespective of whether this is carried out by means of pulsed or continuous coulometry. Assume that a slow-reacting sulfur species is present in the end point and that a certain part of the current is used to oxidize this substance. In a real situation, this looks like a small gradual decrease in the background value. During the titration, water will be in large excess and the KF reaction will dominate completely. However, when the end point is reached and the value of the background is subtracted from the total integral, this will result in an overcorrection because the true drift during the titration is less than that at the end point.

Reagents Buffered with Imidazole and Diethanolamine. To study the conditions at even higher pH, we included DEA in the Im-buffered reagents discussed in the preceding paragraph. This base has a pK_a around 11.6 in such media and is used in the commercial reagent Hydranal Coulomat AD (see Figure 1). Results obtained for four different types of reagents are given in Figure 3. To facilitate the interpretation of these results, we estimated the actual concentrations of protonated Im and DEA

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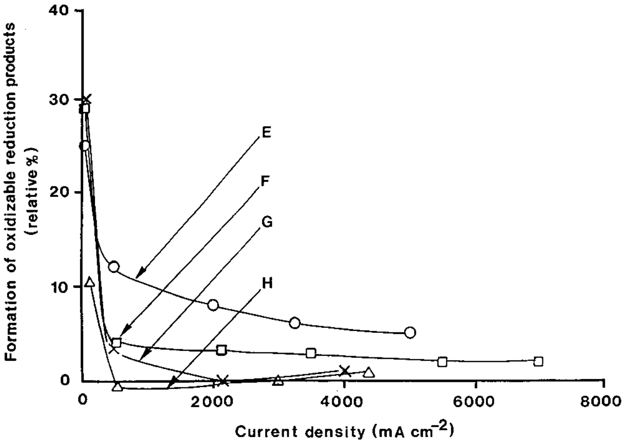

Figure 3. Formation of oxidizable reduction products as a function of current density for reagents buffered with both Im and DEA. The concentrations of the most important components of these reagents are given in Table 2.

Table 2. Estimated Concentrations of the Most Important Components of Reagents E–H[a]

reagent	$[Im]_{free}$ (M)	$[ImH^+]$ (M)	$[DEAH^+]$ (M)	pH	$[SO_2]_{free}$ (μM)
E	0.7	0.7	0.5	9.2	32
F	3	0	1.2	10.6	1
G	1.2	1.2	1.0	9.5	16
H	4.4	0.7	1.0	10.1	4

[a] For pH <9, 1 mol of iodine is assumed to produce 2 mol of protons, while for higher pH (due to side reactions that do not result in the formation of protons), only half as much formation is assumed in the calculations.

and the free concentrations of Im and sulfur dioxide; these values can be seen in Table 2. The concentation of sulfur dioxide was calculated from the equilibrium reaction 2.

Figure 3 shows that the best results are obtained for reagent H. If we compare the composition of this reagent with that of reagent E (see Table 2), we can see that the former reagent has a high pH as well as a higher concentration of $DEAH^+$ ($[ImH^+]$ equal). By taking into consideration the results for reagent D, which has about the same pH as well as concentration of ImH^+ (in Figure 1), it can be concluded that the better performance of reagent H, as compared to reagent D, is caused by the presence of $DEAH^+$.

The importance of the presence of ImH^+ becomes clear when we compare the results for reagent H with those for reagent F. These reagents have the same concentration of $DEAH^+$, and although the pH is higher for reagent F, the performance of reagent H is much better. The obvious explanation for this is that the concentration of ImH^+ in reagent F is close to zero. The same conclusion with respect to the importance of ImH^+ can be drawn by comparing the results obtained with reagents G and F. These have about the same concentration of $DEAH^+$, but the pH is much higher for reagent F. Nevertheless, much less formation of oxidizable reduction products takes place, which can be explained by the absence of ImH^+ in reagent F. Finally, if we compare reagent H with reagent G, the analysis is not straightforward. The concentration of ImH^+ is higher in reagent G, but this fact does not counterbalance the higher pH (and consequently lower $[SO_2]_{free}$) of reagent H. As can be seen in Figure 3, small negative values were obtained within the current density interval 500–2 000 mA cm^{-2}. One possible explanation for this is that small amounts of peroxide are formed in the cathode reaction, since both oxygen and water are present. Peroxides are known to be able to oxidize iodide to iodine[17] although the main reaction in KF media is considered to be oxidation of sulfur dioxide to sulfate.

Surprisingly, for a reagent containing 1 M $DEAH^+$ at pH 5.6, the formation of oxidizable reduction products was found to be lower as compared with reagent A (0.7 M ImH^+, pH 7) although its concentration of free sulfur dioxide should be 20 times higher. Since voltammetric studies (0.5 M $DEAH^+$ or ImH^+ in methanol) showed that $DEAH^+$ requires about 0.35 V more negative potential (for a current density of 120 mA cm^{-2}) compared to ImH^+; one explanation for this difference in behavior might be the strong ion-pairing ability of $DEAH^+$ toward the methyl sulfite ion. As a consequence of such an interaction, the equilibrium reaction 2 will be displaced to the right, resulting in a lowering of the free concentration of sulfur dioxide. It should be mentioned that still higher concentrations of $DEAH^+$ and ImH^+ could not be studied because the system became more and more noisy when the concentration of trichloroacetic acid (used to deliver protons) exceeded 1.5 M.

Reagent H seems promising since less than 1% formation was obtained over a large range of current densities. However, the analytical performance was found not to be as good as for those reagents buffered solely with Im. A typical response curve for iodine, after addition of water, showed a knee at approximately 3×10^{-6} M end-point iodine concentration. It is therefore evident that at least two different iodine species are present. To illustrate how this influences the shape of the titration curve, two water samples, 1 and 50 μg, respectively, were titrated using the two different iodine end-point concentrations shown in Figure 4. When the 50 μg water sample (upper diagram) was titrated at higher end-point iodine concentration, the main peak was followed by a smaller secondary peak. This secondary peak was, however, absent when the lower end-point iodine concentration was used. For both titrations with the 50 μg water sample, the same concentration of water was found but the time for the titration was 2 min longer when the higher iodine concentration was used. No secondary peak was observed for the 1 μg sample (lower diagram), either at the low iodine end-point concentration or at the higher one. At iodine end-point concentrations higher than 3×10^{-6} M, the following slow equilibrium reaction might explain the knee shape of the response curve:

$$DEAH^+\cdot I_3^- \leftrightarrow DEAH^+ + I_3^- \tag{3}$$

The KF reaction involving $DEAH^+\cdot I_3^-$ is probably slow, as compared to I_3^-, which means that the rate-determining step will be the dissociation rate of $DEAH^+\cdot I_3^-$. At low iodine concentrations, reactants such as Im_2I^+ and $Im_2I^+\cdot I_3^-$ have been proposed to explain the dramatic increase in the rate constant of the KF reaction[10] for reagents containing large concentrations of free Im. Since these species do not form any ion pairs with $DEAH^+$, this

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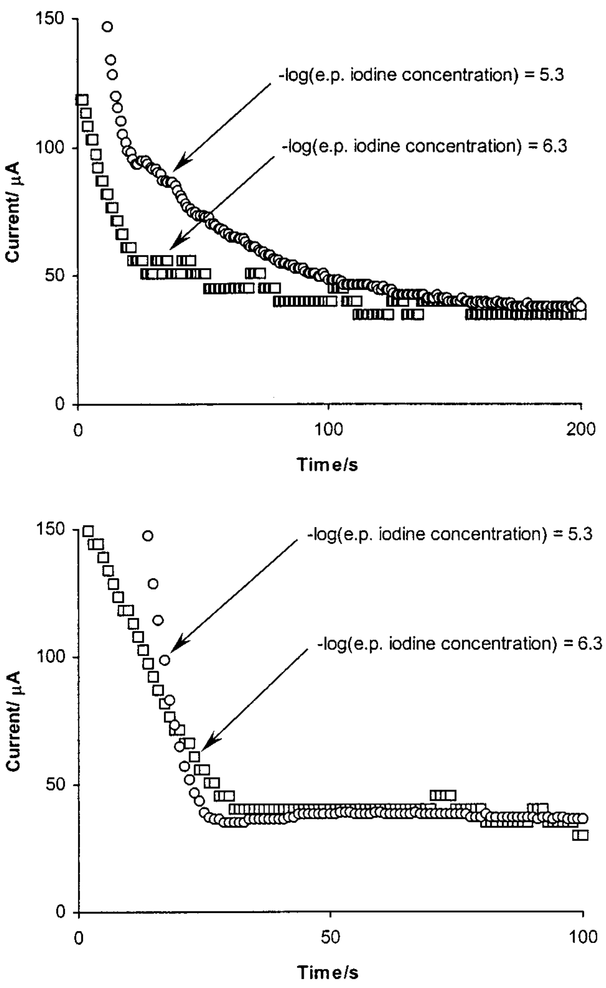

Figure 4. Titration curves when using different end-point concentrations of iodine for a large amount (50 µg) of water (upper part) and a small amount (1 µg) of water (lower part).

may explain the absence of any secondary peak when 50 µg of water is titrated to a very low end-point concentration. The titration of 1 µg is carried out in a much shorter time, which means that the I_3^- is rapidly consumed and regenerated without disturbing the slow equilibrium reaction 3 too much. As a consequence of this, no secondary peak is observed even at higher end-point concentrations of iodine.

An additional drawback with reagent H is the very long equilibrium time needed to obtain a stable baseline (at least 8 h). After this time, the baseline was stable all day and did not increase by more than 0.05 µg/min, even when the cathode was working in direct contact with the anolyte.

Modified Reagents. The influence of carbon tetrachloride, chloroform, and hexanol was investigated for the three different types of Im-buffered reagents A, C, and D, and the results for a reagent containing hexanol are given in Figure 5. The curves for reagents containing carbon tetrachloride or chloroform looked quite similar to those shown in Figure 5, at respective pH. By comparison with the results obtained without modifier, it can be seen that there is a significant decrease in the formation of oxidizable reduction products for all types of reagents when any of these modifiers is present. By inspecting the results obtained for the different modified reagents at pH 9 ($[SO_2]_{free} = 50$ µM), it was observed that an increase in the concentration of carbon tetrachloride from 0.5 to 1 M results in a nearly negligible formation of oxidizable reduction products. At this pH, chloroform causes only a small improvement, while the presence of hexanol has practically no effect. The difference in the results obtained for carbon tetrachloride and chloroform can be explained by the fact that both compounds are able to compete with the reduction of sulfur dioxide and that the former is reduced at less reducing potentials. The following reactions have been shown to take place:[2]

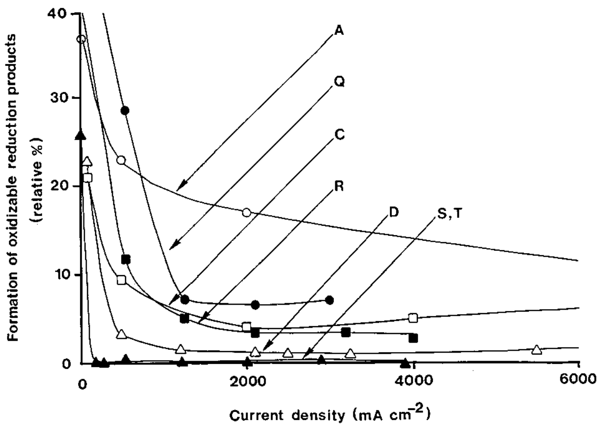

Figure 5. Formation of oxidizable reduction products as a function of current density for Im-buffered reagents modified with hexanol. For comparison, the results obtained with reagents without modifier are inserted in the figure (see curves A, C, and D).

$$CCl_4 + ImH^+ + 2e^- \Leftrightarrow CHCl_3 + Cl^- + Im \qquad (4)$$

$$CHCl_3 + ImH^+ + 2e^- \Leftrightarrow CH_2Cl_2 + Cl^- + Im \qquad (5)$$

Schöffski[16] reported positive errors in the range 5−15% using a DEA-buffered reagent containing 1 M carbon tetrachloride at low pH both as anolyte and catholyte (separated by a glass filter). At low pH, we experienced experimental difficulties due to a negative background, which seems to be caused by the following reaction:

$$2I^- + CCl_4 + ImH^+ \Leftrightarrow I_2 + CHCl_3 + Cl^- + Im \qquad (6)$$

Our results for a similar reagent at pH 7 containing 1 M carbon tetrachloride were in line with those given by Schöffski[16] and close to those represented by curve C in Figure 5. Scholz[2] used a catholyte containing 1.1 M DEA, 1 M SO_2. and 1 M carbon tetrachloride and found recovery rates close to 100% when he titrated 18 mg water samples. The reason for the better recoveries obtained by Scholz can be explained by the higher pH used, and this is in line with our results.

For all modified reagents at pH 10 ($[SO_2]_{free} = 5$ µM), a very favorable situation prevails, since the relative formation is well below 1% over a large range of current densities. It can be concluded that, for very low current densities, carbon tetrachloride is the most effective modifier while hexanol is more efficient at higher current densities. Although it is advantageous to use a modifier like carbon tetrachloride to reduce the formation of oxidizable products, hexanol should be preferred in view of the potential health risk as well as environmental aspects.

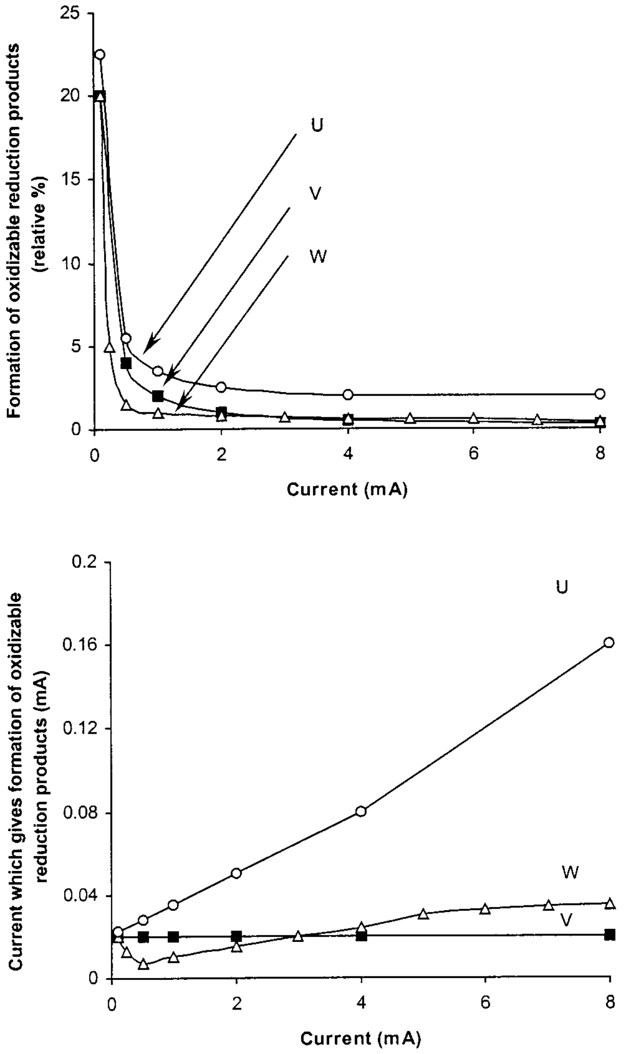

Figure 6. Formation of oxidizable reduction products as a function of current (for a given cathode surface area) for three hypothetical reagents, upper part of the figure. The lower part shows the absolute value of the current, which leads to the formation of oxidizable reduction products, versus the electrolysis current density.

The reason for the favorable effect caused by hexanol is not clear. However, hexanol is expected to adsorb more strongly on platinum surfaces than methanol, and because of increased local resistance in the double layer, an increase in the strength of the electric field will be required for the reduction process. As a consequence of this, the repulsion of anions such as $CH_3SO_3^-$ may increase, and because of the equilibrium between the reducible species SO_2 and $CH_3SO_3^-$ (see equilibrium reaction 2), there will then be less SO_2 available for the reduction to take place at the cathode surface.

Analytical Results Obtained with Continuous Coulometry. By taking into consideration the shape of the titration curve in combination with knowledge about the extent of formation of oxidizable reduction products as a function of current, the error arising in continuous coulometric titrations carried out in cells in which the cathode is in direct contact with the anolyte can be estimated. To make this clear, consider the three hypothetical curves given in the upper part of Figure 6 and which have the same meaning as those shown above, i.e., Figures 2, 3, and 5. In the lower part of Figure 6 the values have been transformed to yield absolute current values, and these were then used to calculate the maximum errors (background corrected) expected for two idealized (rectangular) titration curves. The results are given in Table 3, where it can be seen that the errors can vary from negative to positive values depending on the conditions for the titration and the properties of the reagent. For slow-reacting reagents, especially in combination with low end-point concentrations of iodine, the titration curve will deviate from the rectangular shape and in such cases it will more resemble a parallel trapezoid. This will of course make the error estimations somewhat more complicated.

Table 3. Maximum Errors (Relative %) Calculated for the Hypothetical Reagents Described in Figure 6 Considering a Slow and a Rapid Titration

reagent	slow titration[a]	rapid titration[b]
U	+1.5	+1.8
V	0	0
W	−1.0	+0.2

[a] Electrolysis current 1mA during the titration (4 min). [b] Electrolysis current 8mA during the titration (0.5 min).

Experimental results obtained with reagent S and a similar one containing twice as much sulfur dioxide are summerized in Table 4. Different gains and two different water samples, 8 and 50 μg, were used to investigate the accuracy for the reagents given in the table. For the highest gain, the error is within ± 0.5% compared to the water standard for both reagents. Lower gain leads to lower currents during the titration, and this increases the amount of formation of oxidizable reduction products as previously shown in Figures 1−3 and 5. To understand the low values obtained with the 50 μg sample at low gain, consider the calculations made for the hypothetical reagents shown in Table 3. Negative errors can be obtained if the fraction of current that results in the formation of oxidizable reduction products is lower during the titration than at the end point; an excessively high value will be subtracted from the integrated value, resulting in a too low water concentration (compare the theoretical results for the best reagent in Table 3).

As can be concluded from the experimental results given in Table 4, the smallest errors are obtained for rapid titrations (i.e., high gains). The possibility of using such conditions without causing instability or overshoot is illustrated by the titration shown in Figure 7, which were carried out using a low end-point concentration of iodine, 5 × 10^{-6} M.

CONCLUSIONS

Interferences generated in the cathode reaction in coulometric KF cells can be almost eliminated by means of a very high current density in combination with suitable reagents buffered at about pH 10. The best analytical performance was obtained for Im-buffered reagents containing a high concentration of free imidazole and modifiers such as carbon tetrachloride, chloroform, and hexanol. For certain types of reagents, such as those with low pH or those based on nonalcoholic solvent (high $[SO_2]_{free}$), unacceptably large errors will be obtained if the cathode is operating in direct contact with the anolyte. In such cases, the

Table 4. Results Obtained with Continuous Coulometry Using a Cell in Which the Cathode (0.002 cm^2) Is in Direct Contact with the Anolyte[a]

		8 μg water sample			50 μg water sample		
reagent	gain[b]	I_{max} (mA)	recovery[c] (%)	std dev (rel %)	I_{max} (mA)	recovery[c] (%)	std dev (rel %)
S + 0.5 M SO_2	0	1.3	103.1	0.5	1.7	98.3	0.2
	1	2.2	101.6	0.5	3.2	99.1	0.1
	2	3.8	100.3	0.6	6.0	99.9	0.2
S	0	1.1	101.0	0.3	1.7	99.5	0.1
	1	1.8	99.9	0.3	3.1	100.2	0.1
	2	3.2	100.0	0.4	6.0	100.4	0.1

[a] Reagent S (pH 10, $[SO_2]_{eff} = 0.5$ M) is compared with one of the same type containing 1 M $[SO_2]_{eff}$ (pH 9.7). [b] Gain 0 = 10 μA/mV; gain 1 = 19 μA/mV; gain 2 = 46 μA/mV. [c] This value is related to that obtained when the three-compartment cell with diaphragm was used. Each recovery value represents the mean of four determinations.

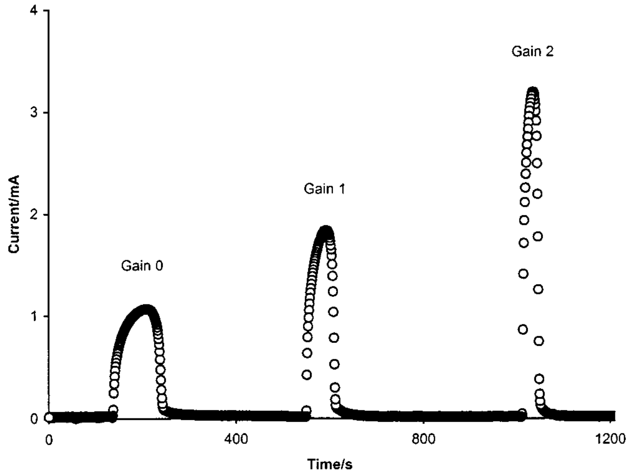

Figure 7. Titration curves for reagent S using different amplification factors when titrating 8 μg of water. (The same shape is obtained with a reagent containing 6.6 M Im, 1 M hexanol, 1 M SO_2, and 0.1 M I_2).

diaphragm-free cell construction, recently described by Cedergren and Jonsson[8] (see introduction) can be recommended, since it offers the possibility of placing the cathode in the anode compartment or allowing it operate from inside a drainable cathodic compartment.

Pulsed coulometry will, in principle, give a higher degree of accuracy as compared to continuous electrolysis because a significant amount of interference will always be formed at the low current densities prevailing near the end point when the latter technique is used. However, the errors could be kept below 1% in general and very near zero when optimum conditions are used, which means that the results obtained with the continuous coulometric method are accurate enough for most applications.

In our opinion, it is likely that diaphragm-free coulometric cells will increase in importance in the future, not least in view of the investigation reported earlier by Scholz.[7] He showed, in a study including 70 different types of organic liquids representing hydrocarbons, halogenated hydrocarbons, alcohols, phenols, ketones, carboxylic acids, and nitrogen bases, that the diaphragm-free cell of Metrohm could be used with acceptable accuracy for water determinations in the same way as the standard coulometric cell.

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