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Coulometric Karl Fischer titration of trace water in diaphragm-free cells

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Abstract

Factors influencing the accuracy and precision for diaphragm-free Karl Fischer coulometric determinations of low μg-amounts of water have been studied using the Metrohm 756 (pulsed current) coulometer and eight different types of commercial coulometric reagents and some modifications of these. As in the case of diaphragm-free coulometric titration of large amounts of water, the positive errors, due to the formation of oxidizable reduction products (of sulfur dioxide) in the cathode reaction (besides hydrogen), were found to be minimized by the use of highest possible pulse current (in the range 100–400 mA) in combination with the fastest possible titration rate. Most accurate (102–103%) and precise results (typical relative standard deviation 1.8%) were obtained for reagents containing very large concentrations of imidazole in combination with the presence of modifiers like hexanol, chloroform and propylene glycol (i.e. the HYDRA-POINT reagents). Similar results were obtained when this type of reagent was mixed 60/40 with xylene according to the ASTM recommendation for water determinations in petroleum products like crude and lubricating oils. Addition of decanol to this type of reagent mixture was found to reduce the influence from the oxidative reduction products significantly. A reduction of the error from 3.6% relative to 1.6% was achieved by addition of 9% (v/v) of decanol to a 60/40 reagent mixture of HYDRA-POINT Coulometric Gen (containing hexanol as modifier) and xylene. For larger concentrations of decanol the pulse current had to be lowered to 100 mA and this might explain why no further improvement was observed. An additional attempt to minimize the interference by lowering the concentration of sulfur dioxide in the reagents gave no significant effect. However, by means of a home-built computer-controlled coulometric instrumentation based on continuous instead of pulsed current (including a large cathodic current density) it was possible to achieve recovery rates close to 100% for the best reagents investigated. The reason for this improvement is discussed.

Keywords: Titration; Trace water; Diaphragm-free cells

1. Introduction

The current trend in coulometric Karl Fischer (KF) titrations is to use cells without a diaphragm between the anode- and cathode compartments. Such cells are known to be easier to operate compared to the conventional type, since they require shorter conditioning times before startup and, of course, that there are no problems due to clogging of the membrane. However, the accuracy of results obtained with diaphragm-free coulometry is not as good as those reported for the conventional method. The reason for this is that sulfur dioxide (one of the components of the KF reagent) is reduced in the cathode reaction and that the species formed (like thiosulfate and sulfide [1]) are oxidized by iodine causing a positive error. Several designs of diaphragm-free coulometric cells have been described in the literature [2–7] with the aim to minimize the influence of the reduction products, for example by achieving delayed mixing of the solution surrounding the cathode and the rest of the reagent [5,6].

There are several prerequisites that have to be fulfilled in order to achieve accurate results in diaphragm-free KF coulometry. Of special importance is the establishment of a high cathode current density (1000–4000 mA cm^{-2})

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throughout the titration [8]. This requirement makes continuous coulometry less suitable because of the small currents (0–1 mA; area of the cathode typically 0.3 cm^2) generated near and at the end-point. For such low current densities [8] a very large fraction of the cathodic current causes the formation of the above-mentioned interferents (hydrogen is the desired reduction product). For this reason, pulsed coulometry is the method of choice [6] since it offers the possibility of using a high cathode current density even during the final part of the titration when the titration rate is low. In order to keep the titration errors at a minimum, pulse lengths above 60% of the total time for the pulse cycle are required (for current pulses of 400 mA this corresponds to titration rates higher than 1440 μg water per min). It has been shown that by minimizing the time during which optimum pulses cannot be used the titration error can be minimized [9]. In the same study it was also found that the error was independent of the pulse frequency. This means that the time at which the current is zero is the same for a fixed current width, independent of the pulse frequency, for a titration of a certain amount of water. It was suggested that a continuous process takes place during the zero-current periods leading to an accumulation of sulfur dioxide at the cathode surface. During the current pulses the situation may be different since it is likely that the methyl sulfite, which is in equilibrium with sulfur dioxide [10], is repelled from the surface by the electric field.

As a consequence of the difference in relative formation of the oxidizable reduction products during the course of the titration and at the base-line (background typically between 1 and 5 μg water min^{-1}) an overcorrection will result when the background is subtracted from the total current-time integral. As was discussed by Nordmark et al. [11] the extent of this effect will be dependent on the size of the background. The formation of oxidizable reduction products has been shown to decrease at higher pH [8], which has been explained by the fact that the free concentration of reducible sulfur dioxide is decreasing at higher pH due to the pH dependence of the equilibrium between this species and methyl sulfite [10].

For titration of relatively large amounts of water (0.3 mg) it has been shown that errors can be kept within a few tenths of a percent when using methanolic reagents having a large quotient (>10) between initial concentrations of imidazole and sulfur dioxide, in combination with the presence of 1–3 M concentrations of modifiers like hexanol, ethylene glycol and chloroform [11].

The accuracy of water determinations using diaphragm-free coulometry has, so far, only been investigated for titrations of relatively large amounts of water. Since coulometric KF titrations are of great importance for trace water determinations in, for example, oil products it seemed to us important to critically investigate the conditions for accurate such determinations. A number of different types of reagents and reagent modifications were selected and their performances were investigated using diaphragm-free coulometry.

2. Experimental

2.1. Chemicals and reagents

Imidazole (pa) and sulfur dioxide were from Fluka, iodine (pa) from Sharlau, and 1-decanol (99%) from Aldrich. Methanol (pa), chloroform (pa), hexanol (pa), and xylene (pa) were from J.T. Baker. HYDRANAL Coulomat A, AG, AG-H, AG Oven, and E from Riedel-deHaën. HYDRA-POINT Coulomeric Gen, Oven, and Ano were from J.T. Baker. Water standard (Eichstandard 5.0) based on a mixture of xylene/butanol was from Riedel-deHaën. An overview of the compositions of all reagents is given in Table 1. The pH values given in the table were based on a pH-scale in methanol, where pH 7.9 corresponds to a 0.05 M salicylic acid/sodium salicylate buffer and 9.7 to a 0.05 M acetic acid/sodium acetate buffer [12]. The catholyte used in the Metrohm diaphragm cell contained 1 M carbon tetrachloride, 2 M imidazole, 0.6 M sulfur dioxide, and 0.1 M iodine in methanol. Before use this solution was nearly decolored with water. The effective concentrations of sulfur dioxide given in Table 1 are the sum of all S(IV) species obtained from the added sulfur dioxide and this was determined by means of coulometrically generated iodine [13] in a water/methanol medium.

2.2. Safety considerations

Methanol is highly flammable and toxic by inhalation, in contact with skin and if swallowed. Chloroform is harmful by inhalation 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.

2.3. Instrumentation

All reagents listed in Table 1 were investigated using Metrohm 756 KF Coulometer (with and without a diaphragm between the anode and cathode) connected to a computer running the Vesuv 3.0 database software. Each determination was manually evaluated and calculated from the titration data recorded every 2 s by Vesuv. The end-point potential (Metrohm 756 uses AC-bipotentiometry) was normally set to 90 mV, the polarization current was 10 μA, and the background was typically 1.0–2.0 μg min^{-1}. In one of the holes in the top of the coulometric cell, an indicating electrode (platinum) system based on zero-current potentiometry was inserted and used to establish the relation between the polarization voltage and the excess iodine concentration. The calibration of this electrode system has recently been described [14]. Determinations using continuous coulometry were performed in a computer-controlled microcell described earlier [15], with the possibility to select between a cathode in the

Table 1
Overview of reagents

Reagent	Imidazole conc.	Diethanol-amine	*N*,*N*-dimethyl dodecylamine	Hexanol	Chloroform	Propylene glycol	Pentanol	[SO_2] (M)	pH
HYDRANAL Coulomat AG-H	Medium	–	X	–	–	–	X	0.73	8.9
HYDRANAL Coulomat E	Medium	X	–	–	–	–	–	0.77	7.8
HYDRANAL Coulomat AG Oven	Medium	–	–	–	–	X	–	0.43	9.2
HYDRANAL Coulomat A	Medium	–	–	–	X	–	–	0.88	8.7
HYDRANAL Coulomat AG	Medium	–	–	–	–	–	–	0.85	9.3
HYDRA-POINT Coulometric Ano	High	–	–	–	X	–	–	0.46	9.8
HYDRA-POINT Coulometric Oven	High	–	–	–	–	X	–	0.47	9.8
HYDRA-POINT Coulometric Gen	High	–	–	X	–	–	–	0.51	9.7

same or in a separate compartment as the anode. The cathode inside the anode compartment was a polymer coated platinum pin, diameter 0.5 mm, sharply cut off at one end to achieve an exposed area of 2×10^{-3} cm^2.

2.4. Standardization of test solution

Methanol solutions were used to introduce μg amounts of water in the titration cells by means of a computer controlled stepper motor driven Hamilton syringe. The Hamilton needle was kept in the titration cell, with the tip under the surface of the reagent, and connected to the syringe via Teflon tubing. The above mentioned computer-controlled microcell [15], containing 4 mL HYDRANAL Coulomat AG as anolyte, was used for standardization of the methanol solutions. The expected error using this instrumentation is in the order of 0.1 μg water. For water amounts larger than 50 μg the diaphragm cell of Metrohm was used (5 mL catholyte, 100 mL HYDRANAL Coulomat AG or AG-H as anolyte).

3. Results and discussion

3.1. Reagents and titration parameters

Depending on purpose of use, the reagents listed in Table 1 contain modifiers such as chloroform, to increase solubility of oils, propylene glycol, to minimize volatility, and diethanol amine, to increase pH. Besides different modifiers, the reagents also show a large variation in pH. The five reagents at the top of the table, those of HYDRANAL, have a pH in the range 7.8–9.3 as compared with range 9.7–9.8 found for the remaining three. It should be pointed out that the value for the ethanol-based regent is not comparable with the others since it is related to buffers using methanol as solvent (see Section 2). The large difference in pH between the groups can be related to the excess concentration of imidazole or, more correctly, to the quotient between the free and protonated imidazole.

As was discussed in the introduction three critical parameters in diaphragm-free coulometry are the cathodic current density, the rate of titration, and the nature of the reagent. An illustration of the importance of these parameters is given in Figs. 1 and 2 for titrations of ~250 μg water (HYDRANAL Eichstandard 5.00) with all reagents included in this study. As can be seen, the smallest errors were obtained for the combination of highest possible pulse current (400 mA) and

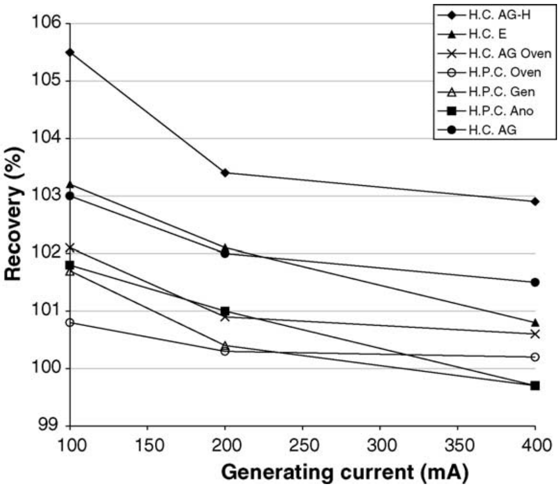

Fig. 1. Recovery as a function of generating current for titration of ~250 μg water. H.C. stands for HYDRANAL Coulomat and H.P.C. for HYDRA-POINT Coulometric. Reagent H.C. A is outside the graph with recoveries between 105 and 118%.

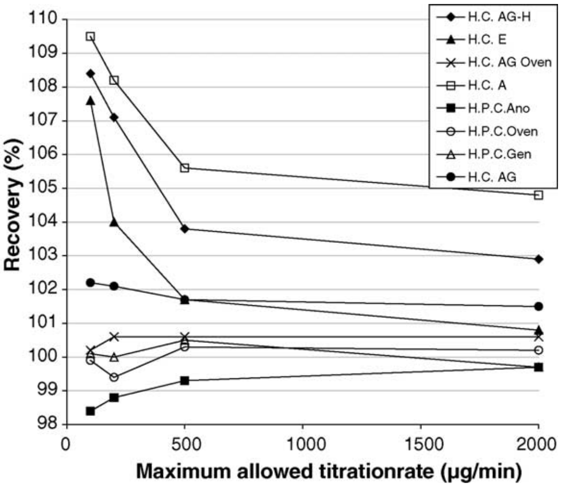

Fig. 2. Recovery as a function of maximum allowed titration rate for titration of ~250 μg water. Pulse current: 400mA.

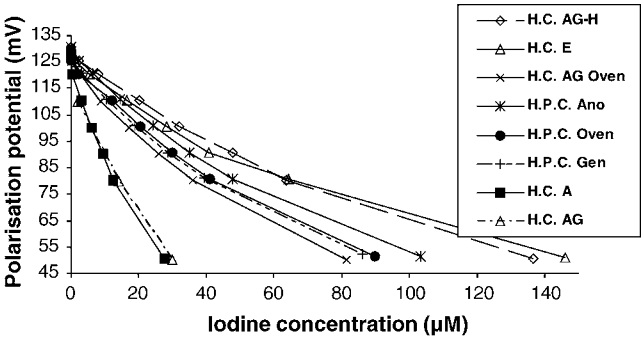

Fig. 3. Polarization voltage and corresponding iodine concentration in the reagents.

maximum titration rate. The HYDRA-POINT reagents containing high concentrations of imidazole, together with HYDRANAL Coulomat AG Oven, gave the lowest error. Even at titration rates as low as 100 μg min^{-1} the relative error is less than 1% for three of the reagents. The somewhat lower than 100% recovery rate observed with HYDRA-POINT Ano is due to change in stoichiometry, which has been shown to take place for this type of reagent when prolonged titration times (3–4 min) are used for titration of relatively large amounts of water [9].

End-point potentials in the range 80–120 mV were investigated to determine the influence of iodine concentration on recovery. As can be seen in Fig. 3 there is a large variation in the response of the bipotentiometric system depending on the type of reagent. Taking all reagents into consideration the mentioned potential range corresponded to iodine excesses (end-point concentrations) in the range 10–70 μM. There were, however, no indications that a variation within the tested interval significantly influenced the results for titration of relatively large amounts of water. However, for titrations of very small amounts of water the choice of end-point potential should correspond to as low iodine excess as possible. This gives a higher response from the indicating electrode and ensures that the time during which the titration rate is very low is minimized. Besides, a low end-point concentration of iodine will reduce the background over compensation due to parasitic side reactions. The iodine concentration is effectively suppressed by the Karl Fischer reaction and therefore the rate of parasitic iodine consumption will be lower during the actual titration than at the end-point where the background is determined. The over compensation will obviously be smaller with a lower end-point iodine concentration.

Table 2
Recovery rates for titrations of μg-amounts of water using pulsed-current coulometry (Metrohm)

Reagent	Amount (μg)	Recovery (%)	R.S.D. (%)	No. of replicates
HYDRANAL Coulomat AG-H	12.2	115	1.50	9
HYDRANAL Coulomat E	10.0	108	5.63	3
HYDRANAL Coulomat AG Oven	12.4	103	1.20	11
HYDRANAL Coulomat A	12.4	116	6.67	3
HYDRA-POINT Coulometric Ano	13.3	103	1.43	5
HYDRA-POINT Coulometric Oven	13.3	103	1.84	3
HYDRA-POINT Coulometric Gen	14.1	102	1.84	4

3.2. Trace determination of water

The reagents were tested with the commercial Metrohm titrator by titration of 10 μL methanol samples containing small amounts of water (<15 μg). The resulting recovery rates, given in Table 2, were in line with what could be expected from Fig. 2, i.e. relatively large errors for all HYDRANAL reagents at low titration rates except for Coulomat AG Oven. It should be mentioned that HYDRANAL Coulomat A is not recommended for diaphragm-free coulometry by the manufacturer.

The low levels of water in the samples allowed for the use of a very small cathode with continuous coulometry, thereby maintaining a high current density of 700 mA cm^{-2} during the main course of the titration, despite a titration rate of less than 8 μg min^{-1}. Table 3 summarizes the results obtained for three selected reagents tested with continuous diaphragm-free coulometry. A remarkable improvement was seen with recoveries close to hundred percent for the two HYDRA-POINT reagents, and about 106% for HYDRANAL Coulomat AG-H. The recoveries resemble those of pulsed coulometry at higher titration rates. It is evident that although a high current density is achieved in pulsed coulometry, the relatively long zero-current periods in between are not favorable. The trade off between high titration rate and high current den-

Table 3
Titrations of μg-amounts of water using continuous diaphragm-free coulometry

Reagent	Added amount[a] (μg)	Found[b] (μg)	Recovery (%)
HYDRANAL Coulomat AG-H	12.61 ± 0.05 (13)	13.39 ± 0.07 (8)	106.2
HYDRA-POINT Coulometric Ano	12.81 ± 0.05 (12)	12.78 ± 0.07 (11)	99.8
HYDRA-POINT Coulometric Gen	12.81 ± 0.04 (12)	12.80 ± 0.04 (12)	99.9

[a] Results obtained with anode and cathode separated.
[b] Results obtained with anode and cathode in the same compartment.

Table 4
Recovery rates for titrations of μg-amounts of water with modified reagents using pulsed-current coulometry

Reagents and modifiers	Result (μg)	Reference (μg)	Error (μg)	I_{pulse} (mA)
100 mL HYDRANAL Coulomat AG-H	14.03 ± 0.07 (10)	12.19 ± 0.04 (8)	1.84 ± 0.11	400
60 mL HYDRANAL Coulomat AG-H 40 mL xylene	15.25 ± 0.09 (10)	13.08 ± 0.04 (12)	2.17 ± 0.13	200[a]
60 mL HYDRANAL Coulomat AG-H 40 mL xylene 10 mL decanol	14.43 ± 0.15 (6) 15.08 ± 0.06 (6)	12.76 ± 0.08 (8)	1.67 ± 0.23 2.32 ± 0.14	200[a]
100 mL HYDRA-POINT Coulometric Gen	14.35 ± 0.26 (4)	14.1[b] (2)	0.25[b]	400
60 mL HYDRA-POINT Coulometric Gen 40 mL xylene	12.98 ± 0.06 (12)	12.51 ± 0.04 (10)	0.47 ± 0.10	200[a]
60 mL HYDRA-POINT Coulometric Gen 40 mL xylene 10 mL decanol	12.69 ± 0.09 (12)	12.53 ± 0.05 (10)	0.16 ± 0.13	200[a]
60 mL HYDRA-POINT Coulometric Gen 40 mL xylene 20 mL decanol	13.04 ± 0.08 (12)	12.60 ± 0.09 (10)	0.44 ± 0.14	100[a]

[a] Highest possible pulse current due to low conductivity.
[b] No confidence interval was calculated due to few determinations.

sity cannot be fully overcome by the pulsed current technique at low titration rates.

3.3. *The effect of further reagent modifications*

According to the ASTM method for determination of water in petroleum products like lubricating and crude oils by coulometric Karl Fischer titration, a modification by adding 4 parts of xylene to 6 parts of anode reagent is recommended [16]. Such a large concentration of xylene ensures that oil samples are fully dissolved in the reagent, and that all water is available for the Karl Fischer reaction. In view of this recommendation it was of importance to study how large concentrations of solubilizers influence the recovery when μg-amounts of water are titrated. Two chloroform-free reagents, HYDRANAL Coulomat AG-H and HYDRA-POINT Coulometric Gen, were selected and modified according to the ASTM method and the results are given in Table 4. As can be seen the errors are about the same with and without dilution with xylene.

Earlier studies on imidazole-buffered reagents for diaphragm-free coulometry showed that the extent of formation of interfering reduction products can be essentially reduced by the addition of hexanol to the reagent [8]. The reason for the favorable effect caused by hexanol is not clear. However, this compound is expected to adsorb more strongly on platinum surfaces than methanol, and because of increased local resistance in the double layer of the cathode surface, 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 methyl sulfite may increase, and because of the equilibrium between the reducible species, sulfur dioxide, and methyl sulfite there will be less sulfur dioxide available for reduction at the cathode surface. Similarly the good result of HYDRANAL Coulomat AG Oven in Table 2 could be explained by adsorption of propylene glycol on the cathode surface. Based on these speculations we decided to test the effect of an even more long-chained alcohol, decanol, which is likely to be more strongly adsorbed than hexanol. In addition, this alcohol serves as an excellent solubilizer for petroleum products.

The effect of decanol addition to the two different xylene-containing reagents can be seen in Table 4. Before each experiment, the results of which are given in the table, the reagent was equilibrated in the titration cell for several hours/days. For the HYDRANAL reagent mixture we found initially a significant reduction in the error, but the effect disappeared directly after titration of a larger sample. The reason for this might be that the adsorption of decanol in this case is very weak. For the HYDRA-POINT reagent mixture a remarkable improvement of the error was observed on addition of 10 mL decanol; from 3.6% relative to 1.6%. The effect in this case was found to be more persistent and remained even after titration of a large water sample. For still larger additions of decanol the pulse current was restricted to 100 mA which means that it is difficult to judge the single effect of decanol in this case.

Of great interest was also to investigate whether a decrease in the concentration of the sulfur dioxide would lead to a decrease in the formation of interfering reduction products. Therefore, an imidazole-buffered reagent containing ten times lower concentration of sulfur dioxide was prepared. Surprisingly, the error decreased only marginally. One explanation for this may be that the cathode surface is effectively saturated with sulfur dioxide during the zero-current periods of the pulse cycle independently of the sulfur dioxide concentration (or possibly any other sulfur compound).

4. Conclusions

More research is needed in order to better understand the function of the cathode reaction in diaphragm-free coulometry with different types of KF media. A detailed knowledge of the mechanisms will give valuable hints on how to chemically modify the cathode surface in order to discriminate the reduction of sulfur species in favor of the desired reduction of protonated base forming inert hydrogen. From the results given in this paper it can be concluded that pulsed current diaphragm-free coulometry always gives results which are biased high for small amounts of water (in the order of 10 μg). However, by using certain reagent compositions the errors can be kept within a few percent which means that for trace water determinations in oils, for example, using sample sizes of 2 g, the errors due to interference from the reduction products can be kept well below 0.5 ppm.

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