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Coulometric Karl Fischer titration with a diaphragm-free cell: Cell design and applications

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Abstract

Coulometric Karl Fischer titration is a useful technique for wide-range water determination, from the percentage level down to trace amounts at the ppm level. Coulometric Karl Fischer titration cells having a current generator with a ceramic diaphragm, separating the anodic and the cathodic compartment, as well as diaphragm-free cells, are commercially available. From an applicative point of view, a diaphragm-free cell for Karl Fischer coulometry is favourable because of its ease-of-use.

We have found that improving the design of the diaphragm-free cell may contribute towards its application down to low water amounts. In this contribution, we will illustrate our recent work on optimising a diaphragm-free Karl Fischer cell for application over a wide water determination range, from the percentage level down to trace amounts at the ppm level.

Keywords: Karl Fischer titration; Water determination; Traces; Diaphragm-free cell; Coulometry

1. Electrochemical cell and current generator for diaphragm-free Karl Fischer coulometry

The use of diaphragm-free generating cells in Karl Fischer coulometric instruments has brought relevant advantages. A diaphragm-free generating cell is easier to clean and to refill than a cell having a diaphragm. Further, there are no problems such as contamination and clogging of the ceramic porous diaphragm, e.g. with oil products, or unwanted standby drift values due to impurities or moisture leaking out of the diaphragm. Therefore, optimisation of the diaphragm-free coulometric KF titration, in such a way that it can reliably be used down to the trace water determination level, would be an advantage to the users.

Various kinds of geometrical designs have been conceived for diaphragm-free Karl Fischer cells, as illustrated, e.g. in Cedergren (1998); Dahms (1994); Richter and Hürlimann (1995); Scholz (1992). In particular, optimisation of the iodine generating cell geometry in diaphragm-free systems is necessary to decrease a partial chemical or electrochemical reduction of the anodically generated iodine through the counter-cathode. Such reduction of the anodically generated iodine is an unwanted side-reaction. When it occurs, the measured water recoveries are too high. Chemical reduction of the anodically generated iodine may occur through oxidizable reaction products, which are produced at the cathode when the cathodic current density is not sufficiently high (Cedergren & Jonsson, 2001; Nordmark, Rosvall, & Cedergren, 2000). At high cathodic current densities, hydrogen gas is the only relevant product at the cathode in most coulometric Karl Fischer electrolytes. Furthermore, we assume that direct electrochemical reduction of the anodically generated iodine at the counter-cathode may also contribute towards too high recoveries. In this case, strong hydrogen gas bubbling at the cathode will prevent dissolved iodine from being

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reduced electrochemically at the cathode (Aichert, 2002).

The principle of an electrochemical cell for diaphragm-free Karl Fischer coulometry is shown in Fig. 1. The vessel for the coulometric analysis contains a generating cell (“current generator”) for electrochemical production of iodine, and a double pin platinum electrode as the indicating system (“measuring electrode”). In the case of the METTLER TOLEDO DL32/DL39 coulometer, two-electrode potentiometry (Bard & Faulkner, 2001) is applied as an indicating system. The generator cell consists of a suitable Pt anode and a Pt counter-cathode. Iodine is produced at the anode of the current generator by oxidation of iodide, whereas hydrogen gas is the main electrochemical reaction product at the counter-cathode.

In the case where a coulometric Karl Fischer cell does not have a diaphragm separating the anodic sample compartment from the counter-cathode compartment, it must be designed in a way to minimise electrochemical reduction of anodically generated iodine at the cathode. In fact, reduction of iodine directly at the cathode would diminish the coulometric conversion efficiency. An optimum geometrical shape of the current generator and its arrangement within the Karl Fischer titration cell are necessary to achieve this goal. The iodine generated at the anode must be rapidly distributed in the Karl Fischer electrolyte to enable a fast reaction with the moisture to be detected. Therefore, the anode of the generator cell must have a sufficiently large iodine-producing surface exposed to the Karl Fischer electrolyte, with a homogeneous current distribution to improve fast diffusion of iodine. Further, the convective flow provided by stirring the Karl Fischer electrolyte must be strong enough to provide a fast mixing of the anodically generated iodine with the electrolyte.

On the other hand, when considering the cathode of the current generator, it should expose just a small electrode surface area to the Karl Fischer electrolyte to minimise the electrochemically reactive contact area with the electrolyte. It has to be noticed that the size of the cathode may be considerably smaller than that of the anode. The minimum size of the cathode is determined by the electrolyte conductivity and the maximum available generator voltage. A smaller electrode surface area at a given generator current means a higher current density, which requires a higher generator voltage at a given electrolyte conductivity. For example, the maximum generator voltage of the METTLER TOLEDO DL32/DL39 coulometer is 28 V. In combination with the diaphragm-free generating cell available with this instrument, this voltage is sufficient for measuring water contents in Karl Fischer electrolytes with conductivities down to ca. 5 mS/cm (Lanz et al., 2001).

Based on these considerations, a generating cell with a cylindrical grid Pt anode arranged concentrically around a small Pt wire cathode has been constructed for the DL32/DL39 coulometer, as shown in Fig. 2. This specific geometry fulfills all of the requirements for the anode and the cathode geometry as described above.

Further to optimising the cell geometry, improvement of the diaphragm-free Karl Fischer titration involves also an optimisation of the electrochemical control of

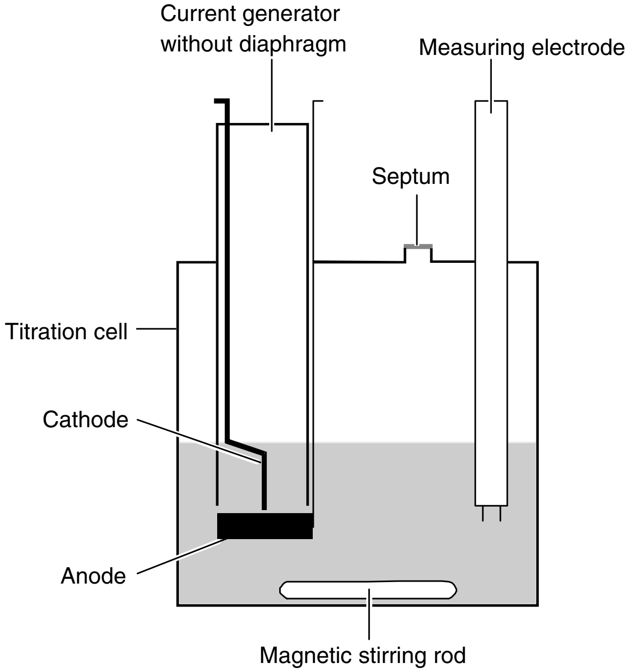

Fig. 1. Electrochemical cell for diaphragm-free Karl Fischer coulometry.

Fig. 2. Diaphragm-free current generator for the METTLER TOLEDO DL32/DL39 coulometer.

the titration. Current generation for diaphragm-free coulometric Karl Fischer titration has thoroughly been studied by Cedergren and co-workers (Cedergren & Jonsson, 2001; Nordmark & Cedergren, 2000a, 2000b). The most relevant findings of such studies have been implemented in commercial coulometric Karl Fischer titrators. For example, the METTLER TOLEDO DL32/DL39 coulometer applies a mixture of current pulses in the range from 60 to 400 mA for iodine generation. At the trace-water determination level, the coulometer applies short but relatively high current density pulses. Such high current density favours hydrogen formation and prevents the formation of oxidizable reaction products or direct electrochemical iodine reduction at the cathode.

2. Recovery tests with water standards

First of all, recovery tests have been performed with certified water standards. Fig. 3 shows a series of trace water determinations with the METTLER TOLEDO DL39 coulometer equipped with the diaphragm-free generator cell illustrated in Fig. 2. As a sample, small amounts of Riedel-de Haën HYDRANAL® 100 ppm standard solution were injected into the Karl Fischer cell by means of a syringe. As an electrolyte, HYDRANAL® Coulomat AD was used as a one-component reagent for coulometric analysis. Standard instrument parameter settings were used at the DL39 Coulometer, i.e., a polarization current of 2 μA, an endpoint setting at 100 mV, and a normal current generation rate. The graph shows that recoveries were close to 100% within the experimental error,[1] down to trace water amounts as low as 10 μg. For even lower water amounts, recoveries started to exceed 100%. This is due to the previously described processes, i.e., for low water amounts, a partial chemical or electrochemical reduction of the anodically generated iodine occurs through oxidizable reaction products or direct electrochemical iodine reduction at the counter-cathode.

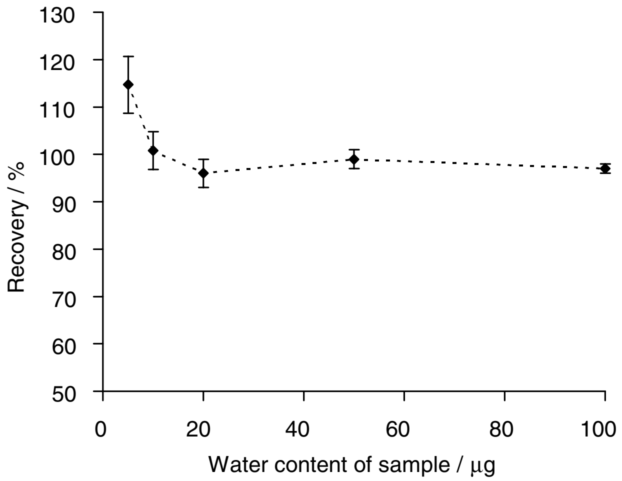

Fig. 3. Trace water recoveries measured with a diaphragm-free KF cell on a DL39 coulometer, displayed versus the injected water content of the samples. An average result for five sample injections is displayed for each data point. Sample: Riedel-de Haën HYDRANAL® 100 ppm standard solution; KF electrolyte: HYDRANAL® Coulomat AD.

3. Low water content determination in foodstuffs

With respect to foodstuffs, trace water determinations at the ppm level may occur for foods such as, e.g. salt or sugar, or, in particular, for edible oils. Water in salt is determined by heating the sample in a Karl Fischer drying oven, and transferring the evaporated moisture to the Karl Fischer cell by means of a purge gas (Aichert, 2002). Water in sugar can, e.g. be determined by external extraction (surface water), or by dissolution of the sugar crystals in a suitable solvent (total water content), and subsequent injection of the solvent into the Karl Fischer cell. Thus, depending on the selected solvent or solvent mixture used for sample preparation of sugar prior to KF analysis, it is possible to distinguish between the water adsorbed on the surface of sugar crystals, and the total water content of sugar crystals (Aichert, 2002).

Low water content foodstuffs such as edible oils can be easily injected into the Karl Fischer cell by means of a syringe. Table 1 gives some examples on edible oils. The sample amount was about 0.2 g for each sample injection, which corresponds to approximately 100 μg of water at the expected water content. HYDRANAL® Coulomat AG-H/CG was used as an electrolyte for the cell with diaphragm, and Coulomat AD + 20% octanol for the diaphragm-free cell. The addition of a long chain alcohol such as octanol improves the dissolution of oils. The table shows that the diaphragm-free coulometric KF titrations and results obtained by titration with a diaphragm show a good agreement within the experimental precision. The result difference in sunflower's oil may be due to slower and incomplete dissolution of the sample in the coulometric electrolyte mixture. Note that, for sunflower oil, turbidity occurred in the Coulomat AD + octanol electrolyte mixture after a few sample injections, which disappeared after a few hours stirring time.

Coulometric Karl Fischer analysis can also be performed on samples with a higher water content. In Table 1, the results for samples having a water content at the

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[1] Experimental errors may, e.g., occur through inadequate instrument parameter settings, such as too high or too low endpoint, wrong drift correction, or wrong titration speed. Experimental errors may also occur during sample preparation, or through use of exhausted KF electrolyte, or inadequate KF electrolyte selection.

Table 1
Examples of water determination in foodstuffs with coulometric KF titration with or without diaphragm. An average result for five sample injections is given in each case

Sample	Sample preparation			Result for cell with diaphragm	Result for cell without diaphragm
Olive oil	Direct injection with syringe			507 ± 7 ppm	504 ± 13 ppm
Corn seed oil	Direct injection with syringe			378 ± 4 ppm	376 ± 6 ppm
Sunflower oil	Direct injection with syringe			698 ± 22 ppm	657 ± 2 ppm
Dried spice (marjoram)		Ext. extraction with methanol		8.33 ± 0.14%	8.33 ± 0.15%
			Oven 180 °C, 15 min	8.58 ± 0.17%	8.94 ± 0.18%
Black tea		Ext. extraction with methanol		6.10 ± 0.16%	6.10 ± 0.15%
			Oven 180 °C, 15 min	6.35 ± 0.18%	6.19 ± 0.17%
				6.14 ± 0.12%	6.26 ± 0.09%

percentage level are given (dried spice and tea). Their water content was first determined by external extraction in methanol as it follows: 5 g of marjoram was extracted for two hours in 50 mL of methanol, or 2 g of black tea was extracted over night in 50 ml of methanol in an ultrasonic bath. To perform the analysis, aliquots of approximately 0.2 ml of the extraction solvent were then injected into the KF cell for water determination, which corresponds to approximately 1000–2000 μg of water at the expected water content. HYDRANAL® Coulomat AG/CG was used as an electrolyte for the cell with diaphragm, and Coulomat AG for the diaphragm-free cell. As an alternative to the external extraction procedure, water determination was performed by extracting the water of the samples with an automated Karl Fischer oven (METTLER TOLEDO Stromboli KF sample changer), and transferring the moisture into the coulometric cell with dry air as a carrier gas. The sample weight was ca. 0.05 g in this procedure, and Baker HYDRA-POINT® Coulometric Ano/Cat (cell with diaphragm) or Coulometric Oven (diaphragm-free cell) was used as an electrolyte. The results given in Table 1 show a very good agreement between the values obtained using a generating cell with and without ceramic diaphragm. However, water recoveries were somewhat higher with the Karl Fischer oven than with the external extraction method. We assume that the temperature applied in the oven could lead to the formation of additional water during the heating process, due to chemical reaction of other sample components having water as a reaction product.

4. Conclusions

We have illustrated our optimisation of diaphragm-free coulometric Karl Fischer titration. This optimisation involves both optimising the cell geometry and optimising the electrochemical control of the titration, i.e., the current generation at the iodine-generating anode and its cathodic counter-electrode. Precise water recoveries can be obtained with a commercially available, diaphragm-free Karl Fischer cell, down to trace water amounts below 10–20 μg. The suitability of this technique was demonstrated by performing determinations of water in low water content foodstuff samples such as edible oils. Determinations in diaphragm-free Karl Fischer cells showed good agreement with determinations in Karl Fischer cells that contained a diaphragm.

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