

Coulometric titration



A. De Agostini

The technique of coulometric titration was originally developed by Szabellédy and Somogy [1] in 1938. The method differs from volumetric titration in that the titrant is generated in situ by electrolysis and then reacts stoichiometrically with the substance being determined. The amount of substance reacted is calculated from the total electrical charge passed, Q , in coulombs, and not, as in volumetric titration, from the volume of the titrant consumed.

According to Faraday's Law, the amount of substance converted, m [g], is given by the equation

$$m = \frac{M \cdot Q}{z \cdot F}$$

where M is the molar mass [g/mol], F is Faraday's constant (96485 C/mol) and z is the ionic valence.

The initial ideas behind coulometric titration can be traced back to the beginnings of electroanalytical chemistry. As early as 1917, Grower [2] described a method for determining the thickness of tin plate on iron by electrolysis. Coulometric analyses [3] can in fact be carried out according to two different techniques: controlled-current coulometry (galvanostatic coulometry), in which the electrolysis is performed while the current is held constant, or controlled-potential coulometry (potentiostatic coulometry), in which the potential is kept constant.

In practice, relatively few titrations are used in which both the reagent and the analyte (e.g. acids) react at the electrodes of the electrolysis cell. A fundamental and essential requirement for a coulometric titration is 100 percent current efficiency at the electrodes of the electrolysis cell. The reagent generated (titrant) must react stoichiometrically and preferably rapidly and irreversibly with the substance being determined (analyte). The reagent can be gener-

ated in situ, i.e. in the analysis solution, or in an external vessel with continuous flow. In practice, most commonly used coulometric titrations allow the direct determination of substances that are not reduced or oxidized at the generator electrodes. This has the advantage that the generation of titrant takes place with 100 percent current efficiency. With electrolytically generated reagents, neutralization titrations, redox titrations, precipitation titrations and complexometric titrations can be performed. An overview of possible titrations is given in table 1 [4].

The equivalence point or end point of a coulometric titration can be determined as in any other titration, for example by color indication, potentiometry, amperometry or with polarized electrodes [5].

Advantages of coulometric titration

- Coulometric titration has the advantage that constant current sources for the generation of titrants are relatively easy to make.
- The electrochemical generation of a titrant is much more sensitive and can be much more accurately controlled than the mechanical addition of titrant using a burette drive. For example, a constant current flow of 10 μA for 100ms is easily generated and corresponds

to about 10^{-8} mol or just a few micrograms of titrant.

- The preparation of standard solutions and titer determination is of course no longer necessary.
- Chemical substances that are unstable or difficult to handle because of their high volatility or reactivity in solution can also very easily be used as titrants. Examples are bromine, chlorine, Ti^{3+} , Sn^{2+} , Cr^{2+} and Karl Fischer reagents (iodine).
- Coulometric titrations are easier to automate because a source of current is appreciably easier to control than a burette drive.
- Coulometric titrations can also be performed under inert atmosphere or be remotely controlled, e.g. with radioactive substances.
- Dilution effects due to the addition of the titrant are of no importance, which makes it easier to determine the end point.

Experimental requirements

Several important experimental factors have to be taken into consideration in order to benefit from the advantages of coulometric titration. As mentioned before, 100 percent conversion or current efficiency at the generator electrodes is a fundamental requirement. But, how can 100 percent efficiency be ensured? The main condition is that the potential of the generator electrode (anode or cathode) toward its surroundings (the electrolyte) is in a range in which no other reactions can take place. This is achieved by controlling the applied voltage or through a suitable choice of the electrolyte. The electrolyte solution must be inert and have a sufficiently high concentration so that changes in potential due to undesired reactions are of no importance. Most coulometric titrations therefore use buffer solutions as electrolytes. Besides this, the geometry of the measuring cell and the stirrer speed (rapid homogeneity

of the analysis solution) also play a very important role. The reagent generated must be dispersed as rapidly as possible throughout the measuring cell. Efficient and rapid mixing of the analysis solution with the titrant leads to steady state conditions at the electrodes (sensors) being attained more quickly. This in turn allows the titration to be more easily controlled and improves the evaluation.

Another important factor is the electrode substrate (material) of the generator electrodes and their arrangement in the measuring cell. The hydrogen overvoltage is also an important quantity to consider when choosing the electrode substrate. Typical electrode substrates with high hydrogen overvoltages are mercury and platinum. The polarization range at these metals is by far the greatest. Sometimes, gold and synthetic materials such as glassy carbon are used. Platinum is also suitable as an electrode substrate because it is chemically stable and corrosion-resistant in most electrolyte solutions.

Electrolysis cells with and without diaphragms

Usually the anode and cathode of an electrolysis cell are physically separated. The ion transport necessary for current flow is maintained by a membrane or diaphragm. Separation of cathode and anode is usually necessary to avoid undesired side reactions such as the oxidation or reduction of the substance being determined. Coulometric titration cells with non-isolated generator electrodes are however possible and are being increasingly used [6]. Such electrolysis cells are above all used in the Karl Fischer titration technique and are referred to as “diaphragm-less cells”. What has to be taken into account when using such cells? Since 100 percent current efficiency is the prime target in all these cells, the geomet-

Electrogenerated titrant	Generator electrode and electrolyte	Typical substances determined
		Oxidants
Bromine	Pt/NaBr	As(III), U(IV), NH ₃ , olefines, phenols, SO ₂ , H ₂ S, Fe(II)
Iodine	Pt/KI	H ₂ S, SO ₂ , As(III), water (Karl Fischer) Sb(III)
Chlorine	Pt/NaCl	As(III), Fe(II), various organic substances
Cerium (IV)	Pt/Ce ₂ (SO ₄) ₃	U(IV), Fe(II), Ti(III), I ⁻
Manganese (III)	Pt/MnSO ₄	Fe(II), H ₂ O ₂ , Sb(III)
Silver (II)	Pt/AgNO ₃	Ce(III), V(IV), H ₂ C ₂ O ₄
		Reductants
Iron (II)	Pt/Fe ₂ (SO ₄) ₃	Mn(III), Cr(VI), V(V), Ce(IV), U(VI), Mo(VI)
Titanium (III)	Pt/TiCl ₄	Fe(III), V(V,VI), U(VI), Re(VIII), Ru(IV), Mo(VI)
Tin (II)	Au/SnBr ₄ (NaBr)	I ₂ , Br ₂ , Pt(IV), Se(IV)
Copper (I)	Pt/Cu(II)(HCl)	Fe(III), Ir(IV), Au(III), Cr(VI), IO ₃
Uranium (V), (IV)	Pt/UO ₂ SO ₄	Cr(VI), Fe(III)
Chromium (II)	Hg/CrCl ₃ (CaCl ₂)	O ₂ , Cu(II)
		Complexing agents
Silver(I)	Ag/HClO ₄	Halide ions, S ²⁻ , mercaptans
Mercury (I)	Hg/NaClO ₄	Halide ions
EDTA	Hg/HgNH ₃ EDTA ²⁻	Metal ions
Cyanide	Pt/Ag(CN)	Ni(II), Au(II,I), Ag(I)
		Acids and bases
Hydroxide ions	Pt(-)/Na ₂ SO ₄	Acids, CO ₂
Hydrogen ions	Pt(+)/Na ₂ SO ₄	Bases, CO ₃ , NH ₃

Table 1: Overview of possible titrations [4]

ric design is important. The simplest rule is to separate anode and cathode as far as possible from each other in order to avoid side reactions at the cathode (assuming the titrant is generated at the anode e.g. in Karl Fischer titrations). This is, however, only possible if the conductivity of the solution is sufficiently high and the capacity of the voltage source adequate, or with very small measuring cells. In commercially available Karl Fischer coulometers, this is achieved by optimizing the ratio of surface areas of the electrodes (anode to cathode). The cathode surface area is made as small as possible. This results in high current densities at the cathode so that only hydrogen ions can be reduced.

The cathode should be positioned so that a homogeneous current density distribution is obtained at the anode. This ensures a current efficiency of almost 100 percent. If these conditions are satisfied, coulometric titrations with non-isolated electrolysis cells can be performed without any difficulty.

The advantages of non-isolated (diaphragmless) electrolysis cells are:

- Only one electrolyte solution is required. This simplifies the cleaning and maintenance of the analysis cell.
- The electrolysis current is not reduced or interrupted by blocked membranes (diaphragms).

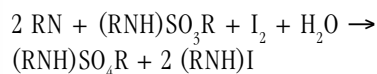


DL39
coulometer

- The conductivity of the analysis solution remains constant over a longer period of time, depending on the sample.
- Diaphragmless cells are therefore suitable for oily and poorly conducting substances.

Coulometric Karl Fischer titration with the METTLER TOLEDO DL32 and DL39 coulometers

By far the most widely used coulometric titration is the Karl Fischer titration (KF titration) for the determination of water content. In the Karl Fischer reaction, iodine is generated in situ from iodide ions. The iodine then reacts stoichiometrically with water in the presence of chemically bound sulfur dioxide according to the following reaction scheme [7]:



The coulometric Karl Fischer titration can be used to measure a large variety of samples. They are prepared in different ways depending on the type of sample involved. Liquid and soluble samples are simply injected into the titration cell. With solid samples, the water content can be determined either by (external) extraction or by heating the samples in an oven and passing the moisture evolved into the titration cell using a carrier gas and a transfer tube.

Due to its extremely high sensitivity, the coulometric Karl Fischer titration is an excellent method for the determination of very low quantities of water (a few ppm). It can however also be used to measure samples with water contents of up to five percent. In this respect, it is therefore an alternative to the volumetric Karl Fischer titration.

At the beginning of the year 2002, METTLER TOLEDO announced two new instruments for coulometric Karl Fischer titration, the DL32 and DL39 coulometers. Both coulometers can be used with cells with or without diaphragm. In comparison with the DL32 instrument, which is ideal for routine determinations, the DL39 coulometer offers a number of additional features. These include the Autostart function, a method for performing external extractions (METTLER method 913) and enhanced possibilities for the evaluation of results (statistical functions, calculations). Besides the Karl Fischer standard methods, the DL39 coulometer provides four additional

METTLER methods that can be used as templates to prepare and store fifty user methods.

Methods are also supplied with the DL39 coulometer for another special application, the Bromine Index determination (METTLER methods No. 914, 915). These methods are used for the determination of double bonds in organic compounds, for example in gasoline. The Bromine Index indicates the amount of bromine that reacts with an olefinic substance [mg/100g], and is therefore a measure of the double bond content, or degree of saturation.

In the development of both the DL32 and DL39 coulometers, particular attention was of course paid to customer requirements such as GLP-conforming printouts, user-friendliness, etc. All in all, the new DL32 and DL39 coulometers are excellent additions to the already comprehensive range of METTLER TOLEDO titration instruments.

References:

- [1] L. Szebelledy and Z. Somogyi, *Z. anal. Chem.*, 112, 313, 323, 332, 385, 391, 395, 400 (1938)
- [2] G. G. Grower, *Am. Soc. Testing Materials, Proc.*, II, 17, 129 (1917)
- [3] James J. Lingane, *Electroanalytical Chemistry*, Second Edition, Interscience Publishers (1958)
- [4] A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, Second Edition, Wiley (2001)
- [5] Paul Delahay, *New Instrumental Methods in Electrochemistry*, Interscience Publishers (1954), p.304
- [6] E. Eisner et al., *Analytica Chimica Acta* 359 (1998), 115-123
- [7] E. Scholz, *Karl Fischer Titration*, Springer-Verlag Berlin (1984)