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Modern Electroanalytical Methods in the Analysis of Environmental Samples

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Abstract. The principles of flow-through coulometry with porous electrodes are listed in the paper. These electrodes enable a simple determination both of extremely low and high concentrations of electrochemically active species. Low analyte concentrations are measured by making use of stripping coulometry consisting of two principal steps: The analyte species are electrochemically deposited first and the galvanostatically stripped whereas the stripping chronopotentiogram is obtained. Higher analyte concentrations can be measured by making use of in-electrode coulometric titrations.

Key words: flow-through coulometry, trace analysis, coulometric titrations, porous electrodes

Flow-through coulometry has became a useful tool not only for scientific research (Tab. 1) but has been intensely used for routine analysis for various samples as well. The principles and experimental background of this method have been known since long but it was considered as a method for the measurement of main components in the samples which significantly hindered its utilisation for trace analysis. Coulometric measurements possess a very high sensitivity which is due to the measurement of electrical charge consumed during the electrolysis and the high value of the Faraday´s constant:

$$Q = z F n \qquad (1)$$

Q electrical charge
z charge number of the electrode reaction
n amount of the species electrolysed.

Notwithstanding the intrinsic high sensitivity of coulometry, it has rarely been used for trace analysis and in specialised laboratories only.

The measurement of consumed electrical charge during electrolysis can easily and reliably be measured. Moreover, there is no technical problem to measure charges as small as μC and nC corresponding to amounts of *nmol* and *pmol*. Hence, coulometry is in principle suitable also for the measurement of extremely low analyte concentrations. The main limiting factor is, that we cannot measure directly the net Faradayic current corresponding to the electrochemical conversion of the species of interest just the total charge consisting also from the background charges, capacitate charges. In the case that these components would be comparable with the net faradayic charge, the results would become unreliable due to the fact, that the net Faradayic charge is obtained as the difference between the total charge and the sum of all background charges, which may be obtained for example from the blank measurement.

The background signal can be minimised by using suitable electrode materials and optimum measurement parameters. Porous electrode materials based on glassy carbon and reticulated vitreous structure (reticulated vitreous carbon – RVC, Fig. 1) have proven their usefulness for this purpose [1]. The average diameter of the pores in the electrode should correspond to the thickness of the diffusion layer (approximately 5 – 50 μm). Here, if applying a constant current, the concentration of the electrolysed species will be virtually the same in the bulk of the electrode and the potential of the electrode will be governed by the Nernst-Peters equation, at least for reversible systems. Hence, the potential of the porous electrode will be given by the ratio of the activities of the oxidised and reduced forms of the treated species. Actually, the electrochemical changes proceed in the diffusion layer only and therefore these processes will proceed fast and exhaustively. Irregular pores in the electrode facilitate the formation of turbulences in the flowing solutions which enhances the mass transfer and correspondingly the effectiveness of the electrolysis from flowing solutions.

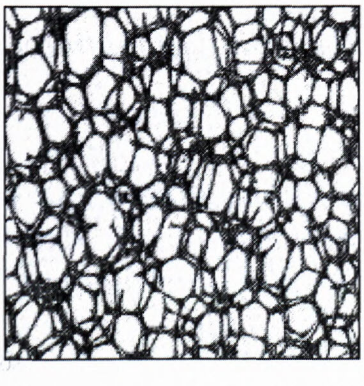

Fig. 1 The reticulated structure of the RVC electrode material

Table 1. Electroanalytical methods based on porous electrodes

Method	Signal	Relationship	Symbols
Hydrodynamic voltammetry	I vs E	$I_{lim} = R\,z\,F\,c\,v_{flow}$	R: recovery v_{flow}: flow rate
Galvanostatic flow-through coulometry	I vs t	$I = R\,z\,F\,c\,v_{flow}$ $Q = \int I dt = R\,z\,F\,c\,V_{sample}$	V_{sample}: Injected sample volume
Potentiostatic stopped-flow coulometry	I vs E	$Q = \frac{1}{e}\int I dE = R\,z\,F\,c\,V_{electr.\ bulk}$	e: potential ramp $V_{electr.\ bulk}$: Effective electrode volume
Galvanostatic stopped-flow coulometry (in-electrode coulometric titration – IECT)	dt/dE vs E	$Q = I\int \frac{dt}{dE} dE = R\,z\,F\,c\,V_{electr.\ bulk}$	I: Current E: Potential Q: Charge
Potentiostatic stripping coulometry	I vs E	$Q = \frac{1}{e}\int I dE = R\,z\,F\,c\,V_{sample}$	z: Charge number F: Faraday´s constant
Galvanostatic stripping coulometry (IECT)	dt/dE vs E	$Q = I\int \frac{dt}{dE} dE = R\,z\,F\,c\,V_{sample}$	c: Concentration

Owing to the above properties of porous electrode materials, they seem to be suitable for the measurement of low as well as high concentrations of electrochemically active species and species which can be converted to an electrochemically active form.

As the measurement mode for porous electrodes, the galvanostatic chronopotentiometry in coulometric mode has been found appropriate [2]. Here, the porous electrode serves as a generator as well as indicator electrode. As mentioned above, the potential change of the electrode corresponds to the change of the oxidised and reduced forms of the treated species during the electrolysis. The total volumes of the pores in the electrode gives the volume of the electrolysed solution, which is in fact the volume of the „titration vessel". The analyte species are titrated by constant current and the end point is indicated by a sudden change of the potential of the porous electrode. The duration of the titration is in fact the chronopotentiometric transition time τ. Knowing the void volume of the porous electrode V_{el} , the analyte concentration c can easily be extracted from the Faraday´s laws of electrolysis:

$$c = I\,\tau/(z\,F\,V_{el}) \qquad (2)$$

I applied current

τ chronopotentiometric transition time

This method – In-Electrode Coulometric Titration – is appropriate for measurement of analyte concentrations from about 10^{-5} – 10^{-7} mol/l, which is given by the lowest electrical charge (about 1 μC) which can be distinguished from the background charges of porous electrodes.

The sensitivity can significantly be enhanced by deposition of the analyte species from the flowing sample solution [3, 4]. Here, the porous electrode will also serve as a preconcentration device. Of course, this approach can only be applied for species which form solid deposits on the electrode surface such as metals, non-soluble compounds. The deposit is then stripped by constant current and the corresponding chronopotentiogram is recorded. Again, a coulometric titration is taking place, for the deposit is in fact titrated with electrical charge until oxidised or reduced quantitatively. The end of the titration (stripping) is indicated by a sudden change of the potential of the porous electrode. The concentration of the analyse can be obtained from the following equation:

$$c = I\,\tau/(z\,F\,V_{vz}) \qquad (3)$$

where V_{vz} denotes the sample volume taken for the deposition. Since this volume is usually 10 to 200 times larger as the void volume of the porous electrode in Eq (2), the lowest attainable concentration will be correspondingly lower as well – down to 10^{-7} – 10^{-9} mol/l.

The typical applications of flow-through coulometry with porous electrodes can be listed as follows:

Acid-base titrations

Determination of acids through reduction of H^+ ions to hydrogen

Determination of bases through oxidation of OH^- ions to oxygen

Redox titrations

Measurement of Cr(VI) through reduction to Cr(III)

Measurement of Fe(II), Fe(III) or total Fe

Measurement of dissolved oxygen

Determination of nitrates through catalysed reduction to ammonia

Determination of phosphates by making use of molybdates

Sulphate measurement through precipitation with barium chromate

Precipitation titrations

Determination of halogenides on silver coated electrodes

Complexometric titrations

Measurement of complexation capacities of waters

Trace and ultratrace analysis

Flow-through stripping coulometry for the determination of metals (As, Pb, Hg, Cd, Ni, etc.)

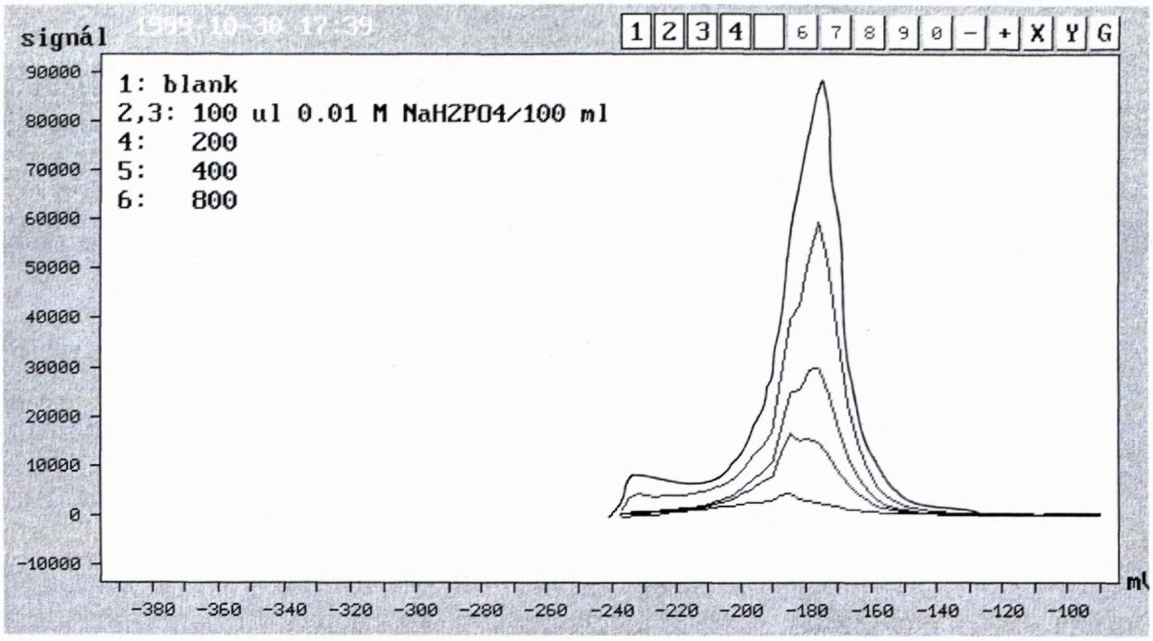

Fig. 2 Chronopotentiogram of phosphate in the presence of molybdate (obtained on EcaFlow Model 150, Istran, s.r.o., Bratislava).

Unattended monitoring

Monitoring of waters for metals

Monitoring of tap water for Fe and Mn

In Fig. 2 there is a chronopotentiogram obtained during the in-electrode coulometric titration of phosphate ions in water after addition of molybdate solution. Here, the formed heteropoly acid is electrochemically reduced to the „molybdenium blue" form giving a typical reduction peak. Owing to the high charge number (up to 12) the measurement exerts a high sensitivity. Since not the colour is measured, turbid and/or coloured sample solutions can be analysed without interferences.

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