

Flow-Through Chronopotentiometry in Waste Water Analysis

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1. Introduction

Waste water analysis is still a challenging task for analytical chemistry due to extremely different and complex composition of most of the samples as well due to difficulties in fulfilling the demanded low concentration limits for the analyte species.

For the determination of inorganic species such as metal and semi-metal ions, non-metals and simple compounds titrimetric and spectrophotometric methods are commonly in use. The employment of electrochemical methods is usually limited to potentiometric determinations either as direct potentiometry or potentiometric titration. Voltammetric methods are rarely used though exhibit superior sensitivity, in many instances a satisfactory selectivity and their simple and low cost instrumentation is undisputable. Yet, tedious sample preparation and working procedures, frequent electrode fouling and sample matrix influences have significantly limited the use of voltammetric methods in waste water analysis especially in routine laboratories.

Chronopotentiometric methods, especially in galvanostatic mode seem to be a reasonable alternative to voltammetric ones. By making use of the fast sampling of potential values combined with the memory mapping technique (Hu et al., 1983; Thomsen et al., 1994) their sensitivity equals or even overruns that of voltammetric pulse techniques. The intrinsic disadvantage of chronopotentiometry is the nonlinear (quadratic) concentration dependence of the actual analytical signal – chronopotentiometric transition time, τ – in accordance with the Sand's equation (Bard & Faulkner, 2001). This is of course valid only for conditions the equation was derived for: homogeneous bulk concentration of the analyte at the beginning of the experiment, planar electrode facilitating linear diffusion only, infinite solution thickness, and no movement of the solution relative to the electrode.

If the solution thickness is limited to the value of the diffusion layer and the current density nears to zero, the analyte concentration in the solution decreases virtually equally in the whole bulk and there is virtually no difference between the analyte concentration at the electrode surface and that in the bulk. Hence, the electrode potential corresponds also to the composition of the bulk. In such a case the τ -value is directly proportional to the initial bulk concentration. Thin-layer cells with planar electrodes and solution thickness of 10 – 100 μm can do this. A technically simpler but equally effective way is the use of porous electrodes with pore sizes of the same value.

Linearity at chronopotentiometry can also be achieved by making use of the deposition-stripping approach well known in stripping voltammetry. The analyte species are deposited

first at the electrode surface and then stripped by constant current whereas the potential of the working electrode is monitored. The chronopotentiometric transition time is a linear function of the amount of the deposited species, in accordance with the Faraday's laws of electrolysis. In such a way extremely low concentrations can be addressed at least for species which can be reversely deposited at the electrode surface.

By introducing this measurement principle into flow systems, simple but versatile and full automatic analytical systems can be constructed. The heart of the system is the flow-through cell which, especially for routine use and process applications, should comply with strict requirements: long-life, maintenance-free working electrode, robust construction and simple maintenance. Porous electrodes in flow systems offer some unique features making them suitable also for routine applications (Blaedel & Wang, 1980; a Beinrohr et al., 1992). Owing to the porous character and large electrode surface, high electrochemical recoveries, up to 100 % can be achieved. The flow system adds an additional advantage, namely the easy exchange of the electrolyte after electrodeposition enabling to strip the deposit to an ideal electrolyte, which minimises the adverse influence of the sample matrix.

1.1 In-Electrode coulometric titrations

Porous electrodes facilitate a special kind of electrochemical measurements, namely thin-layer electrochemistry and coulometry (Bard & Faulkner, 2001). In this type of measurements the average thickness of the solution is beneath the diffusion layer thickness, usually below 100 μm . This can be experimentally achieved by forming a thin solution layer at a planar electrode or by making use of porous electrodes with an average pore size corresponding to the diffusion layer thickness. The former arrangement demands a well-defined geometry of the cell, especially a thoroughly planar electrode. The maintenance of this type of cells and the cleaning and activation of the working electrode are cumbersome. Porous electrodes, on the other hand, can be handled much easier and there are fewer problems with electrode fouling and activation, for this material is cheap and can simply be exchanged if fouled. The electrochemical performance of the porous electrodes, as regards thin-layer properties are virtually the same as those of thin-layer cells with planar electrodes (Bard & Faulkner, 2001).

Thin-layer cells with porous electrodes exhibit some special features:

- i. Anodic and cathodic peaks in the cyclic voltammograms of reversible systems appear virtually at the same potentials, especially at lower scan rates. At higher scan rates some shift is observed corresponding to an IR-drop within the cell.
- ii. Since the solution forms a thin layer, the electrochemical processes are no more diffusion controlled but the rate is governed by the electron transfer rate, chemical reaction rate and adsorption/desorption phenomena.
- iii. The electrochemical changes, especially for reversible systems are extremely rapid and a complete electrochemical change of the whole solution volume can be achieved within a short period of time.
- iv. The products of the electrode reaction and consecutive chemical reactions remain within the thin-layer inside the cell and can undergo subsequent electrochemical and chemical changes, such as back-reduction or oxidation.
- v. The electrode potential during the electrochemical changes reflects the changes in the chemical composition of the solution and vice versa.
- vi. The solution flowing through the porous electrode is intensively mixed facilitating high mass transfer rates which ensure high electrochemical yields.

The above thin-layer properties of cells with porous working electrodes enable to provide some peculiar measurements not available with cells with normal geometry, namely the so called in-electrode coulometric titrations (IECT). The porous electrode alone can be used as a coulometric titration vessel: The virtual sample volume is given by the electrode void volume and the porous electrode serves as the generation as well as the indicator electrode. Hence, there is no need for a separate indication system as in the classical coulometric titrations. The change of the potential of the porous electrode during the coulometric titration with constant current reflects the change of the solution and gives information about the end of the titration.

All in-electrode coulometric titrations are in fact oxidation-reduction titrations and can be applied for species undergoing electrochemical changes at the electrode material and solutions used in the time-scale of the measurement. IECT can be used for species which can directly be oxidized or reduced in the porous electrode. In some instances, the analyte species can be determined by a chemical reaction with electrochemically generated species as known in classical coulometric titrations. The only condition is the appropriate shift of the potential of the porous electrode in the presence or absence of the analyte species in the sample. Hence, the method can hardly be used for species reacting too slowly with the electrogenerated reagent. The material of the porous electrode plays a decisive role in IECT. The electrochemical change of the solvent and the electrolyte should proceed at high overpotentials to ensure low background signals.

The analyte concentration in the sample can be extracted from the electrical charge consumed for the corresponding electrochemical change by making use of the Faraday's laws of electrolysis (Beinrohr, 2001):

$$c = Q / (z F V) \quad (1)$$

c is the analyte concentration, mol/L

Q is the electrical charge, C

z is the effective charge number

F is the Faraday constant, 96 485.4 C/mol

V is the effective void volume of the porous electrode, L

The consumed charge is given by the product of the applied constant current and the chronopotentiometric transition time, resulting from the potential - time dependence recorded in the course of the titration:

$$Q = I \tau \quad (2)$$

I is the applied current, A

τ is the chronopotentiometric transition time, s.

Obviously, the applied current is not consumed for the electrochemical conversion of the analyte species completely but also for the so called background processes, notably for double layer charging, electrode surface and sample matrix reactions. The measurement of a proper blank may compensate for this influence significantly.

The effective void volume of the electrode can approximately be calculated from the geometry and porosity of the electrode. Its exact determination demands analyses of standard solutions at the same experimental parameters, especially at the same currents as those for the samples. Once calibrated, the electrode can be used until it fouls.

A problem in IECT with porous electrodes arises from the fact that the solution inside the pores of the electrode is connected with the solution bulk and some diffusion could occur during the electrolysis. Hence, the time scale of the measurement influences the effective volume of the sample, the slower the electrochemical process the larger is the effective volume treated.

In principle, the following types of determinations can be done by IECT listed with some possible examples:

i. Acid-base titrations

Titration of acids: $2 \text{H}_3\text{O}^+ + 2 \text{e}^- = \text{H}_2 + 2 \text{H}_2\text{O}$

Titration of bases: $4 \text{OH}^- - 4 \text{e}^- = \text{O}_2 + 2 \text{H}_2\text{O}$

ii. Precipitation titrations

Argentometry: $\text{X}^- + \text{Ag}^0 - \text{e}^- = \text{AgX}_{(\text{s})}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)

Mercurimetry: $2 \text{X}^- + 2 \text{Hg}^0 - 2 \text{e}^- = \text{Hg}_2\text{X}_{2(\text{s})}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)

iii. Oxidation-reduction titrations

Determination of iron: $\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$

Determination of chromium: $\text{Cr}^{3+} + 8 \text{OH}^- - 3 \text{e}^- = \text{CrO}_4^{2-} + 4 \text{H}_2\text{O}$

iv. Complexation titrations

Complexation capacity measurements: $\text{Cu}^0 + \text{Y} - 2 \text{e}^- = [\text{CuY}]$ (Cu: copper from the electrode material, Y: complexing species in the sample)

1.2 Stripping chronopotentiometry

For lower analyte concentrations the analyte species can be pre-concentrated at the electrode surface and then "titrated" with constant current: the method is known as stripping chronopotentiometry or constant current potentiometric stripping analysis - PSA (Jagner & Graneli, 1976). All species which can be deposited at the electrode surface and consecutively stripped are available to this method. Electrochemically active metal ions, such as heavy metals and some anions forming negligibly soluble precipitates with the Ag or Hg electrodes can be collected and determined.

Stripping chronopotentiometry with porous electrodes can be employed for the following groups of species:

- Metal ions deposited as elements and then stripped as soluble ions (Zn, Cd, Pb, Hg, Ni, etc.)
- Metal ions depositing as negligibly soluble metal oxides (Mn, Pb, Tl)
- Anions depositing at Ag and Hg electrodes as low-soluble precipitates such as chlorides, sulfides, etc.

The utilization of adsorption phenomena as known from adsorptive stripping voltammetry, has not yet been demonstrated for porous electrodes. This is mainly due to the fact, that adsorbed species tend to remain on the large surface of the porous electrodes and there are problems with the electrode cleaning and regeneration.

An additional feature of the porous electrode is the potential drop inside the electrode bulk arising from the ohmic resistance of the solution and the current flowing through the cell. The higher is the current the larger is the potential drop. In the case of extremely large potential drops some regions of the porous electrode remain virtually inactive and the effective sample volume decreases. Nevertheless, this ohmic drop can successfully be used for the removal of some interference caused by intermetal formation during deposition such as during the determination of Zn in the presence of copper ions (Lazar et al., 1981). Here, the ohmic drop

along the electrode bulk may facilitate some sort of electrolytic separation (Nakata et al., 1983) of Zn from Cu and prohibit the formation of the Zn-Cu intermetallic species.

There are several applications of flow-through chronopotentiometry in waste water analysis both in direct chronopotentiometric and stripping chronopotentiometric modes. Some examples for both measurement modes are listed below.

2. Experimental

2.1 Instrumentation

Flow-through chronopotentiometric measurements were carried out by an electrochemical analyser EcaFlow model 150 (Istran, Ltd., Bratislava, Slovakia, www.istran.sk) equipped with two solenoid inert valves, a peristaltic pump, 1 mm inner diameter PTFE tubing and a microprocessor controlled potentiostat/galvanostat. The system is controlled by a PC by making use of a software developed and delivered by the producer. The block diagram of the system is depicted in Fig. 1. The signals were recorded and evaluated by the memory-mapping technique (Hu et al., 1983; Thomsen et al., 1994). The measurement consists of two main steps: i) the background signal is measured first by means of a blank sample, ii) followed by the sample or standard solution giving the signal of the sample or standard: In the stripping mode the sample or standard is pre-concentrated and the cell is rinsed with the carrier electrolyte into which the deposit is stripped. The cell is then rinsed again to remove the stripped analyte species enabling the next run. In the IECT mode the cell is just filled with the sample or standard solution, the flow is stopped and the solution inside the pores of the electrode is titrated by constant current. The background signal is then subtracted from the signal of the standard or sample yielding the corresponding background corrected net signal.

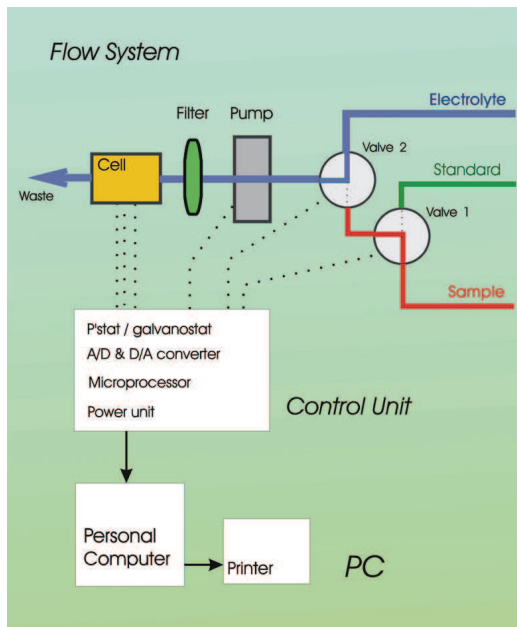


Fig. 1. The block diagram of the flow-through chronopotentiometric analyser

For the sulphide measurement a compact flow-through electrochemical cell of type 104 with Pt auxiliary and Ag/AgCl reference electrodes was used (Istran, Ltd., Bratislava, Slovakia, Fig. 2). The working electrode was a reticulated vitreous carbon plug of 100 ppi (pores per inch) porosity (Electrosynthesis Co. Inc., Lancaster, New York, USA) of 10 mm and 4 mm in diameter and length, respectively.

For Pb and Cr(VI) measurement the cell of type 353c with Pt auxiliary, Ag/AgCl reference and E-53C (for Pb) or E-56C (for Cr(VI)) compact porous carbon working electrodes were used (Istran, Ltd., Bratislava, Slovakia). These electrodes were made of crushed reticulated vitreous carbon material with an effective inner volume of about 20 and 40 μL , respectively.

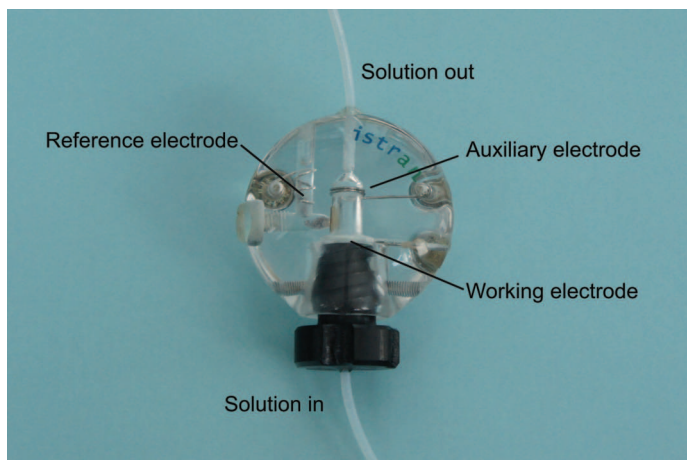


Fig. 2. The 3-electrode flow-through cell

The operation parameters are listed in Tab. 1. All potentials are expressed versus the silver/silver chloride reference electrode built in the cell.

Parameter	Dimension	Sulphide	Lead	Chromium(VI)
Deposition potential	mV	-300	-1400	700
Quiescence potential I	mV	-600	-900	700
Quiescence time I	s	10	10	5
Quiescence potential II	mV	0	-900	700
Quiescence time II	s	30	10	0
Terminal potential	mV	-700	-200	200
Regeneration potential	mV	-1000	0	700
Standby potential	mV	-600	-100	700
Stripping current	μA	-500	100	-50
Sample volume	mL	1	0.5 - 5	4
Blank volume	mL	1	0.5 - 5	4
Rinsing volume	mL	4	3	0
Flow rate	mL/min	6	3	6

Table 1. Operation parameters of the flow-through electrochemical analyser for sulphide, lead and chromium determination

The accuracy of the results of Pb and Cr(VI) measurements was checked by GF AAS on the atomic absorption spectrometer Perkin Elmer 5000 equipped with Zeeman background correction. The experimental parameters used were those recommended by the manufacturer.

Analytical-reagent grade chemicals were used in all experiments. Deionised and degassed water was used for the preparation of all solutions.

2.2 Reagents and procedures for sulphide measurement

Carrier electrolyte: 0.1 mol/L Na_2SO_4 , 0.01 mol/L CH_3COONa , 0.01 mol/L CH_3COOH .

Electrolyte for sample preparation: 0.1 mol/L NaOH

Hg coating solution: 1.0 mg/L Hg(II) in 0.1 mol/L KSCN.

The bulk standard solution of about 10 g/L S^{2-} was prepared from sodium sulphide ($\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$, containing approx. 60 % Na_2S) in water. Its concentration was determined by iodometric titration. The solution was stable one week if stored in a refrigerator. The calibration solutions were prepared fresh before the measurement by diluting the bulk standard solution in 0.1 mol/L NaOH. The concentration of the standards was in the range of 0.1 to 0.5 mg/L. The calibration solutions should be used immediately after preparation.

The Nafion® solution was prepared by diluting a Nafion® 117 solution (Fluka) in ethanol.

The porous electrode was moistened with 0.1 % (V/V) solution of Nafion® in ethanol. On drying the electrode was coated at -500 mV with 50 ml of Hg coating solution at a flow rate of 6 ml/min. After coating the electrode was rinsed with 10 ml of the carrier electrolyte solution at a potential of -200 mV. During pauses, the cell was switched to a standby potential (Tab. 1). The electrode was used until fouling then it was replaced by a new one.

The samples were taken into amber glass bottles and stored in a refrigerator. The control measurements were performed at the same time as the chronopotentiometric measurements. Prior to analysis, the sample in the bottle was shaken and then let to sediment for few minutes. For analysis the supernatant was pipetted.

20 to 500 μL of the sample was added to 50 mL of 0.1 mol/L NaOH and on mixing the solution was immediately analysed. The waste water samples were analysed with the elaborated method independently in two laboratories by two different operators.

The accuracy of the results for waste water samples was checked independently in an accredited laboratory by the iodometric titration method according to the Slovak Standard STN 830530, part No. 31b (STN 83 0530-31, 1999). The method is based on the precipitation of sulphides as cadmium sulphides during a 24 h period, then cadmium sulphide is filtered off and the sulphide content was determined iodometrically.

2.3 Reagents and procedures for lead measurement

Nitric acid and hydrochloric acid were purified by subboiling and isopiestic distillation, respectively. Deionised and degassed water was used for preparing all solutions. All reagent solutions were checked for Pb by GF AAS before use.

Carrier electrolyte: 0.1 mol/L HCl.

Hg coating solution: 1 mg/L Hg(II) in 0.1 mol/L KSCN.

The bulk standard solution of 10 mg/L Pb^{2+} was prepared in the carrier electrolyte from a Certified Reference Material (1.000 g/L Pb, Merck® Darmstadt, Germany).

Coating of the porous electrode: The surface of the porous electrode E-53C (effective diameter 5 mm, length 3 mm, approximate void volume and surface 20 μL and 25 cm^2 ,

respectively) was moistened with 20 μL of 0.1 % (V/V) solution of Nafion® in ethanol. On drying the electrode was coated at -500 mV with 50 mL of Hg coating solution at a flow rate of 3 mL/min. After coating the electrode was rinsed with 10 mL of the carrier electrolyte solution at a potential of -200 mV. The electrode was used until fouling thereafter it was replaced by a new one. To minimise electrode blocking with solid or colloidal particles, an in-line filter (0.45 μm pore size, material nylon) was used downstream of the cell.

Sampling and sample pre-treatment: The waste water samples were obtained from the sewage water treatment plant of an electroplating factory in North Slovakia. Complexing agents (not specified) and residual sulphides from the waste water treatment technology at various concentration levels were to be expected in the samples. The samples were collected into plastic bottles and immediately analysed. The samples were filtered before analysis and hydrochloric acid was added to a final concentration of 0.1 mol/L.

For the GF AAS measurements the filtered samples were diluted with water if appropriate and acidified with nitric acid so that its final concentration was about 0.01 mol/L.

2.4 Reagents and procedures for chromium measurement

Nitric acid and hydrochloric acid were purified by subboiling and isopiestic distillation, respectively. Deionised and degassed water was used for the preparation of all solutions.

Carrier electrolyte: 0.2 mol/L HCl and 0.001 mol/L EDTA. The bulk standard solution of 10 mg/L Cr(VI) was prepared in the carrier electrolyte from K_2CrO_4 .

The bulk standard solution of 10 mg/L Cr(III) was prepared in the carrier electrolyte from a Certified Reference Material (1.000 g/L Cr(III), SMU Bratislava, Slovakia).

The porous electrode E-56, made of crushed glassy carbon particles (effective diameter of the electrode 5 mm, length 6 mm, approximate void volume and surface 40 μL and 50 cm^2 , respectively) was activated by flushing with a 500 $\mu\text{g/L}$ Cr(VI) solution in the carrier electrolyte at 800 mV for 5 min. After activating the electrode was rinsed with 10 mL of the carrier electrolyte solution at a potential of 700 mV. The electrode was used until fouling then it was replaced by a new one. To minimise electrode blocking with solid or colloidal particles, an in-line filter (0.45 μm pore size, material nylon) was used downstream of the cell.

The water samples were analysed immediately after sampling.

Cr(VI): To 10 mL of 1 mol/L HCl add 5 mL of 0.01 mol/L ethylenediamine tetraacetic acid (EDTA) solution. Adjust the volume to 50 mL with the sample and on mixing analyse the resulting solution.

Total Cr: To 50 mL of the sample add 1 mL of 1 mol/L HCl and 0.5 mL of 0.01 mol/L KMnO_4 . Boil the solution gently until its volume reduces to about the half. On cooling transfer the solution to a 50 mL volumetric flask, add 10 mL of 1 mol/L HCl and 5 mL of 0.01 mol/L EDTA and adjust the volume to 50 mL with water.

The blank samples were prepared in the same way just pure water was used instead of the sample.

3. Sulphides in waste waters

Hydrogen sulphide is often present in waste waters especially in tanning processes. Oxidation of sulphide to sulphate must therefore be carried out prior to standard waste treatment processes. Various methods have been used for monitoring of sulphide concentrations such as titration, spectrometric, electrochemical and chromatographic

techniques (Crompton, 1996). Mercury and mercury film electrodes have frequently been used for sulphide determination. Mercury coated platinum microelectrode was employed for in-situ determination of sulphides in water and sediment samples (Daniele et al., 2002). Most of the above methods require the removal of sulphides from the interfering matrix prior to the measurement either through precipitation or evaporation which makes the procedures laborious and time consuming.

The presented procedure makes use of the formation of the negligibly soluble mercury sulphide on the electrode surface from the alkaline sample during the deposition step. In the next step the deposit is stripped into a slightly acidic electrolyte solution by applying a constant negative current, whereas the potential of the porous electrode is measured and evaluated. The main goal was to elaborate a simple, fast and reliable procedure not demanding a pre-separation step.

The low solubility of some sulphides facilitates the electrochemical determination of sulphides through stripping analysis by making use of an electrode material forming such a sulphide. Mercury and silver electrodes offer the best performance. However, silver electrodes, especially porous ones, have high background currents deteriorating their applications for low sulphide contents. Mercury and mercury coated electrodes are more suitable in this context, but are vulnerable to matrix interferences. It was found that the mercury coated bare porous electrode operated properly with waste water samples few hours only. Covering the surface with Nafion® prior to coating with mercury improved significantly its performance. The same electrode could be used for several days virtually without loss of the sensitivity. On deposition the cell is flushed with the carrier electrolyte consisting of sodium sulphate and acetate buffer at a pH of about 4.8 and the deposit is stripped through reducing the mercury sulphide to elemental mercury and hydrogen sulphide, the latter is washed from the electrode during the rinsing step. Porous electrodes possess a unique feature, absent in non-porous structures, namely there is a possibility to strip and deposit the analyte many times in a stopped flow regime. This can be used for signal accumulation in order to increase the signal to noise ratio (Beinrohr et al., 1994), or to shift the signal to a potential range with lower background level. In the case of sulphides it was found, that the background level is lower and signal reproducibility is higher if the stripping is made in the so called deposition-stripping-deposition-stripping sequence. Here, after deposition and rinsing with the carrier electrolyte the flow is stopped, the potential is shifted to a negative value (-600 mV for 10 s) causing the stripping (reduction) of HgS to Hg and HS⁻, as well as the complete reduction of dissolved oxygen in the solution in the pores of the electrode. In the next step the potential is shifted again to a more positive value (0 mV for 30 s) where the HgS deposit is formed repeatedly from the HS⁻ ions in the electrode bulk. In the last step, this deposit is stripped again into the same but now the oxygen-free electrolyte by constant negative current and the stripping chronopotentiogram is measured. Owing to such in-situ reduction of oxygen there is no need for its preliminary removal, which makes the procedure simple and straightforward (a Manova et al., 2007).

The deposition potential influences significantly the signal response. Below -500 mV and above 100 mV no stripping signal was observed, the highest sensitivity was observed in the potential window of -350 mV to -50 mV. At potentials more negative than -500 mV no mercury sulphides is formed, at potentials above -50 mV sulphide is probably oxidised to sulphur, hence, no mercury sulphide is formed again.

For a sample volume of 1 mL taken for preconcentration the response is linear up to about 400-500 µg/L (regression data: slope 0.0095, intercept 0.017, correlation coefficient 0.9994)

with a limit of detection and quantification (Mocak et al., 1997) of 1.6 $\mu\text{g/L}$ and 5 $\mu\text{g/L}$, respectively. At a sample volume of 5 mL the detection limit was found to be about 0.5 $\mu\text{g/L}$.

The repeatability and reproducibility were evaluated from data obtained in a short measurement sequence of 15 analyses, and by repeating the measurement daily with a fresh sulphide solution of the same concentration (200 $\mu\text{g/L}$) during ten days, respectively. Hence, the repeatability and reproducibility were found to be 2.6 % and 4.8 %, respectively. Owing to the large electrode surface, stripping current larger than -200 μA should be used. The measurement time at lower currents is longer than 5 min. The current of -500 μA ensured the best signal to noise ratio and fast measurement.

The waste water samples from a tannery contained dispersed colloidal substances and solids, so the key question was whether the sample preparation procedure (see Experimental) would ensure repeatable results. Sample volumes of 50 μL and 100 μL from the sedimented sample were pipetted to the 0.1 mol/L NaOH solution and analysed. The relative standard deviation of the results for these volumes was found to be 5.8 % and 2.4 %, respectively. Hence, the repeatability did not differ significantly from that for homogenous sulphide solutions. A typical signal of a diluted waste water sample is depicted in Fig. 3.

A possible interferent commonly present in waste waters from tanneries is sulphite. It was found that a 1000-fold excess of sulphites do not influence the signal of sulphide at all, and a 5000-fold excess causes a 8 % drop of the signal only.

The elaborated procedure was used for analyses of waste water samples taken from different locations of a tannery (Tab. 2). In most cases satisfactory agreement was found between the results obtained by the proposed procedure and the control method. However, in samples No 3 and No 6 the chronopotentiometric method provided much lower sulphide content than the control method. These samples spiked with known amounts of sulphides gave recoveries of the spikes near 100 %. Hence, the sample matrix virtually did not interfere. These samples, diluted with NaOH, were then heated in a microwave oven to a temperature of 80-95 °C and on cooling analysed again. The results obtained in such a way were significantly higher and correlated well with the control measurement (Tab. 2).

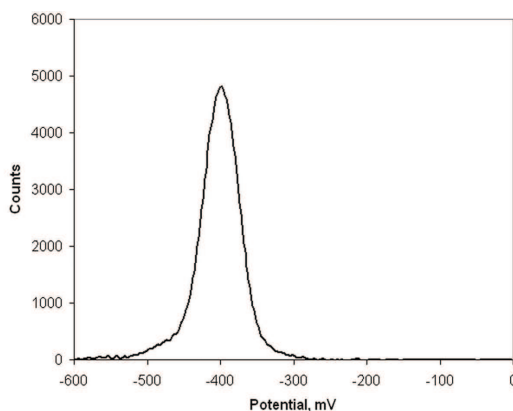


Fig. 3. Stripping signal of a real sample from a tannery containing 85 mg/L sulphide (50 μL of the sample diluted to 50 mL) (a Manova et al., 2007)

<i>Sample</i>	<i>Laboratory A mg/L</i>	<i>Laboratory B mg/L</i>	<i>Control analysis mg/L</i>
1	107.6 ± 4.6	95.1 ± 6.1 99.1 ± 7.2 ^a	97.3 ± 7.8
2	84.8 ± 10.8	89.3 ± 13.3 81.8 ± 9.2 ^a	76.1 ± 6.3
3	1.5 ± 0.3	3.5 ± 1.3 28.2 ± 1.8 ^a	27.5 ± 2.7
4	25.8 ± 3.2	21.1 ± 3.5 20.9 ± 2.9 ^a	28.5 ± 2.8
5	3.5 ± 0.4	3.9 ± 0.5 4.1 ± 0.6 ^a	4.7 ± 0.6
6	3.0 ± 0.5	2.9 ± 0.3 17.5 ± 1.5 ^a	16.5 ± 1.7
7	15.8 ± 2.4	17.8 ± 2.5 18.9 ± 3.5 ^a	18.5 ± 1.9
8	86.0 ± 1.7	85.6 ± 2.0 88.2 ± 2.5 ^a	91.3 ± 7.4
9	4.3 ± 1.8	3.0 ± 0.7 3.3 ± 1.1 ^a	3.15 ± 0.42

Table 2. Analyses of waste water samples from a tannery. ^a Sample heated prior to analysis (a Manova et al., 2007)

For the other samples, a heating did not influenced significantly the result. A plausible explanation is that the reference method evaluates also such sulphide species in some samples, which are not dissolved in the sodium hydroxide solution at laboratory temperatures.

4. Trace lead in waste waters

Electrochemical stripping techniques have been proved to be the most sensitive methods for some electroactive elements such as lead, cadmium, mercury and some others. In these techniques, the trace elements are deposited on a suitable electrode and then are stripped either potentiostatically, galvanostatically or chemically. The galvanostatic stripping (galvanostatic stripping chronopotentiometry) exerts some special features making this technique more suitable for routine use. The electronic control is simpler compared to voltammetric systems and the signal resolution is better due to smaller peak widths. However, the overlapping chronopotentiometric signals are not additive making signal deconvolution known in voltammetry virtually impossible.

Stripping analysis with matrix exchange can easily be performed by making use of a flow-through electrochemical cell (Bard & Faulkner, 2001; Stulik & Pacakova, 1987). Moreover, porous flow-through working electrodes may open the way to achieve complete electrochemical conversions both during the deposition and the stripping steps and hence to provide calibrationless analysis just by making use of the combined Faraday's laws for signal evaluation (Blaedel & Wang, 1979; Curran & Tougas, 1984). An alternative way to provide calibrationless determination in stripping analysis is to deposit completely the

analyte from a small sample volume to a vibrating working electrode (Jagner & Wang, 1995; Jagner et al., 1996).

Flow-through porous electrodes with pore size comparable to diffusion layer thickness possess some special advantages: high electrochemical yields, virtually up to 100 %, fast electrolysis in the electrode bulk, signal accumulation through repeated deposition-stripping cycles inside the electrode (Beinrohr et al., 1994), and direct coulometric titration in the pores of the electrode. However, owing to the large electrode surface, capacitive currents would deteriorate the measurement of low Faradayic currents. To compensate for this, electrode materials with low inherent background currents should be used and the background signal should be subtracted from the total signal.

Assuming an exhaustive deposition of the analyte at the working electrode during the deposition step, the transition time τ corresponding to the dissolution of the deposit during the stripping step is given by the Faraday's laws of electrolysis. Provided that the dissolution is done completely by the applied current, Eq. 1 and Eq. 2 can serve to calculate the analyte concentration directly from the analytical signal τ , i.e. the method is in principle calibrationless.

Trace concentrations of lead have usually been determined by AAS preferably making use of electrothermal atomisation. Lead can also be determined by electrochemical methods such as stripping voltammetry (Wang, 1985) and stripping chronopotentiometry. These methods exert excellent sensitivity, even better than GF AAS, robustness at low costs.

Lead can easily and virtually completely be deposited on mercury coated porous glassy carbon electrode (Beinrohr et al., 1992). The lifetime of the mercury coating enhances significantly by pre-coating of the carbon surface by a thin layer of Nafion, which, additionally, makes the electrode surface more resistive against interfering organics. The lifetime of an electrode surface coated in such a way is at least one day and up to 100 measurements could be performed with the same coating.

The deposition of lead can be done either at a constant deposition potential or by using a constant deposition current. The former offers more selectivity the latter enhances robustness especially when analysing samples with significantly different matrices. Since the treated samples were similar in matrices, the potentiostatic pre-concentration mode was used in these experiments.

The sensitivity of the measurement is governed by two principal parameters: i) sample volume taken for analysis, and ii) stripping current. Obviously, the sensitivity increases by enhancing the sample volume and/or by decreasing the stripping current. The lowest sample volume taken for deposition is limited by an accepted precision of the sample injection with the applied instrument and is usually 0.3 – 0.5 mL. The largest sample volume is given by a reasonable duration of an analysis (5-10 min), hence being 5 – 15 mL. The stripping should be in the range of 50 to 400 μA , 100 μA was used in further experiments.

In diluted nitric acid media, the deposition efficiency was significantly lower than 100 %. Hence, the samples were acidified with hydrochloric acid, which ensures complete depositions.

The flow system enables a simple adjustment of the sample volume taken to the analysis and there is a possibility to match the parameters to samples with low and high lead contents simply by setting an adequate sample volume. The linearity of the method was evaluated by analysing a series of Pb solutions prepared in concentration range of 0.1 to 2000 $\mu\text{g/L}$. Obviously, the sample volume taken for pre-concentration should be matched to the expected concentration range.

The limit of detection (LOD) and limit of quantification (LOQ) values were calculated from the concentration dependence for the low concentration range (Fig. 4) and sample volume of 5 mL. The concentration dependence was evaluated by linear regression according to IUPAC recommendations (Mocak et al., 1997). The LOD and LOQ values were found to be 0.07 µg/L and 0.22 µg/L, respectively.

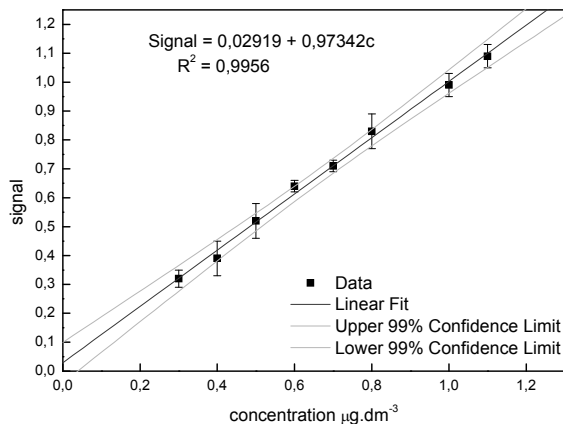


Fig. 4. Assessment of LOD and LOQ values. Sample volume 5 mL. Other parameters are listed in Tab. 1 (Strelec et al., 2007)

The repeatability and reproducibility were tested on the same standard solutions prepared once and stored in a 1000 mL volumetric flask at laboratory temperature, dark. The repeatability test was done with the same instrument by the same operator in a short sequence. The reproducibility test was carried out by different operators and in a daily pace. The repeatability and reproducibility for 11 measurements was found to be 1.1% and 3.7 %, respectively.

The accuracy of the method was checked by analysis of a certified reference material CRM 12-3-10 (SMU Bratislava, Slovakia; certified value for Pb and uncertainty: 0.029 mg/L and 0.006 mg/L, resp.). The elaborated method gave a value of (0.030 ± 0.001) mg/L.

Real water samples may contain various heavy metal ions, which could interfere. As Fig. 5 implies, only Cd affects the signal of lead, and that at concentration ratios higher than 1:50 (Pb:Cd), presumably owing to a coalescence of their signals (Fig. 6). The other tested species, Cu, As, Zn, Hg, Bi virtually do not interfere. Sn can only interfere in more concentrated hydrochloric acid solutions (over 0.5 mol/L), in the 0.1 mol/L HCl solutions used here its deposition is negligible.

The elaborated procedure was used for analyses of water samples from a water treatment plant of a galvaniser. The results are collected in Tab. 3 together with control data obtained by GF AAS. Notwithstanding the complex character of the sample matrix (salts, organics, sulphides, etc.), a reasonable correlation between the chronopotentiometric and AAS data was observed. The lower value found by chronopotentiometry in the sample No 3 may be attributed to the high concentration of complexing agents in this sample. This can partially be assigned to the high Pb contents in the samples enabling a higher dilution of the sample, which, favourably, minimises possible matrix interferences owing to the dilution of the matrix.

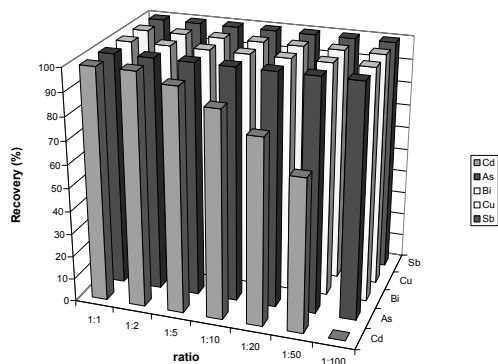


Fig. 5. Influence of some metal ions on the found values of Pb. Sample volume 5 mL, lead concentration 5 $\mu\text{g/L}$ (Strelec et al., 2007)

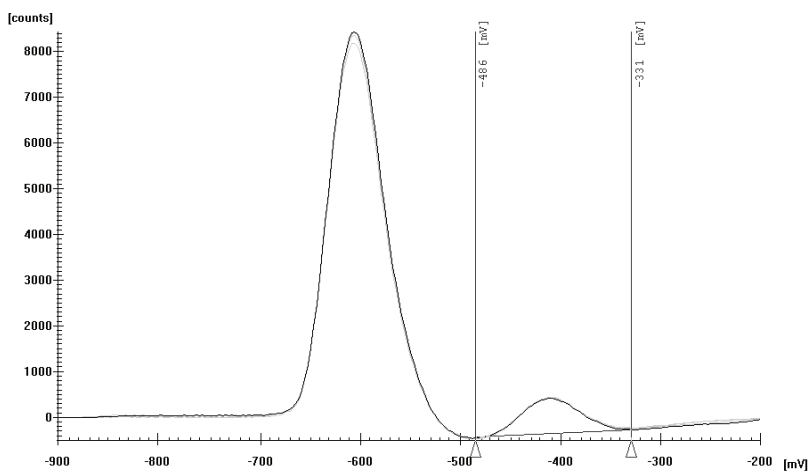


Fig. 6. Stripping chronopotentiogram of Pb (lower peak on the right) in the presence of an excess of Cd (left). Sample volume 5 mL, Pb and Cd concentrations 5 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$, resp. (Strelec et al., 2007)

Sample No	Chronopotentiometry mg/L	GF AAS mg/L
1	1.79 ± 0.03	1.75 ± 0.06
2	0.991 ± 0.011	0.989 ± 0.021
3	0.099 ± 0.005	0.118 ± 0.012
4	0.767 ± 0.012	0.794 ± 0.030
5	0.656 ± 0.025	0.661 ± 0.030
6	14.9 ± 0.2	14.7 ± 0.3

Table 3. Analysis of the waste water samples by flow-through chronopotentiometry and GF AAS. Results obtained from 5 repeated measurements (Strelec et al., 2007)

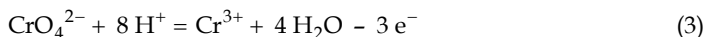
5. Chromium in water samples

Chromium is one of the most abundant elements on Earth. The amount of chromium in the environment has gradually been increased predominantly by industrial activities especially from tanneries, mines and incinerators. The toxicity of Cr(VI) to living organisms is well known and therefore a considerable interest has developed in its determination in environmental and industrial sites.

Chromium(VI) is usually determined by UV-VIS spectrophotometry by means of diphenylcarbazide in acidic solutions (Rudel & Terytze, 1999). Atomic absorption spectrometry with electrothermal atomisation (GF AAS) is one of the most sensitive methods for chromium determination in aquatic samples. Unfortunately, a direct measurement of Cr(VI) is not feasible with this and other atomic spectroscopic techniques. A separation of Cr species prior to the measurement is therefore inevitable either by means of a minicolumn (Cespon-Romero et al., 1996; Rao et al., 1998) or HPLC (Allen & Koropchak, 1993; Lintschinger et al., 1995; Andrieu et al., 1997; Luo & Berndt, 1998). The procedure can be simplified by making use of a flow cell coupled in-line to a flame AAS instrument (Beinrohr et al., 1996), consisting of a porous electrode for oxidising Cr(III) to Cr(VI) and a sorbent for trapping Cr(VI). Cr(VI) is collected without electrolysis and on elution measured by AAS. Total Cr is measured after oxidising Cr(III) electrochemically to Cr(VI) which is collected together with the original Cr(VI) in the sorbent and then measured.

Electrochemical methods provide a simple tool for direct speciation of chromium. The most commonly used technique is based on adsorptive accumulation of the product of the reaction between Cr(VI) and diethyltriaminepentaacetic acid (DTPA) on the hanging mercury drop electrode. The adsorbed deposit is then cathodically stripped, mostly in the presence of nitrate giving rise to an intense catalytic current (Golimowski et al., 1985). Only Cr(VI) species give this product which enables the selective determination of chromate also in the presence of Cr(III). To bypass the use of the toxic mercury electrode, bismuth-film electrodes have recently been used (Chatzitheodorou et al., 2004; Lin et al., 2005).

In-electrode coulometric titrations facilitate the direct determination of Cr(VI) in water samples. The method makes use of a direct electrochemical reduction of chromate ions to Cr(III) in a porous glassy carbon electrode by constant current according to the electrode reaction given below:



The potential of the electrode is monitored during the reduction indicating the end of the coulometric titration. The influences of experimental parameters, metrological figures and possible interferences will be investigated.

A new porous electrode exhibited low sensitivity which enhanced and stabilised gradually after few measurements of Cr(VI) samples. To avoid this initialisation period, the electrode was flushed with a Cr(VI) solution first and then the electrode was used for analyses. The lifetime of the electrode was limited by clogging the pores with solids and/or by a gradual and irreversible increase of the background signal due to a slow oxidation of the electrode surface. When an in-line filter was used to minimise electrode clogging, an average lifetime of an electrode was found to be at least three days, or several hundreds of measurements.

The value of the current forced to the electrode during a chronopotentiometric experiment affects significantly the sensitivity of the signal. In general, the lower the current the higher

is the sensitivity, but the signal to background ratio is virtually not influenced. Theoretically, in a porous electrode with pore diameters near to the diffusion layer thickness an exhaustive electrolysis proceeds, the electrical charge consumed for the electrochemical change is given by the amount of the electrolysed species inside the pores of the electrode. The electrical charge consumed for the reduction of chromate is virtually independent on the value of the current used in the range of -10 to -1000 μA , being at the level of 40 μC and the function can be described by $y = 0.0004x + 39.454$ ($R^2 = 0.081$). However, the noise level enhances significantly at currents larger than -200 μA . Owing to the ohmic resistance of the solutions, the reduction peak is shifted to more negative potentials when enhancing the reduction current. At currents smaller than -10 μA the duration of a single measurement may exceed 5 – 10 min. Hence, reduction currents of -50 to -100 μA were used in further experiment ensuring low noise level and short measurement times.

The electrochemical reduction of chromate proceeds in acidic solutions. Nitric acid interferes (see below), in sulphuric acid media the reduction of frequently present Fe(III) totally coalesces with that for Cr(VI). Hence, hydrochloric acid was chosen as electrolyte for the reduction. Its content influences the peak position and especially the peak area. However, the sensitivity of the signal is not significantly improved at HCl concentrations above 0.2 mol/L, so such a concentration was used in further work.

The concentration range was tested up to several mg/L of Cr(VI) (Fig. 7). The response was found linear up to 500 $\mu\text{g/L}$. The lower concentration range was used for estimation of limits of detection and quantification (Table 4). The repeatability of the measurement was calculated from 10 measurements of Cr(VI) solutions with different concentrations in a short sequence. For reproducibility assessment, solutions the same concentrations were analysed in an interval of ten days.

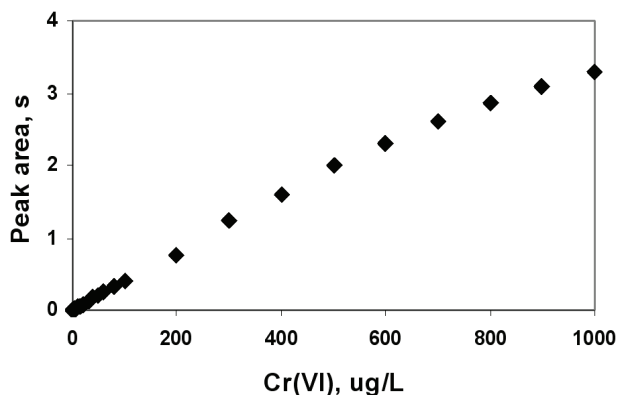


Fig. 7. Concentration dependence of the chromium signal. Reduction current -50 μA (b Manova et al., 2007)

Numerous substances may interfere in the reduction of chromate including species, which can be reduced at similar potentials, species adsorbing at the electrode surface or substances which would reduce chromate chemically prior to the measurement.

The influence of humic acids proved to be significant at contents higher than 0.5 – 1 mg/L (Fig. 8). The Cr(VI) signal decreases with increasing humic acid concentration which can be accounted for by chemical reduction of chromate to Cr(III) by humic substances in the acidic

Parameter	Value
Detection limit	1.9 µg/L
Limit of determination	6.0 µg/L
Linear range	(5 – 500) µg/L
Repeatability at 10 µg/L	5.9 %
100 µg/L	1.2 %
500 µg/L	0.6 %
Reproducibility at 10 µg/L	8.8 %
100 µg/L	1.8, %
500 µg/L	0.8, %
Measurement duration	3 min

Table 4. Analytical figures of merit for chromium determination (^bManova et al., 2007)

solution. As a proof of it, measurement of total Cr in the same sample solution gave the added content of Cr in the sample.

Iron(III), a common species in water samples interferes owing to its reduction at similar potentials as Cr(VI). This interference can partially be suppressed by addition of EDTA to the sample which forms a more stable complex with Fe(III) than that with Fe(II), shifting the reduction peak of Fe(III) to more negative potentials. The reduction peak of Cr(VI) is virtually not influenced by EDTA. The higher the EDTA concentration the larger is the shift of the Fe peak.

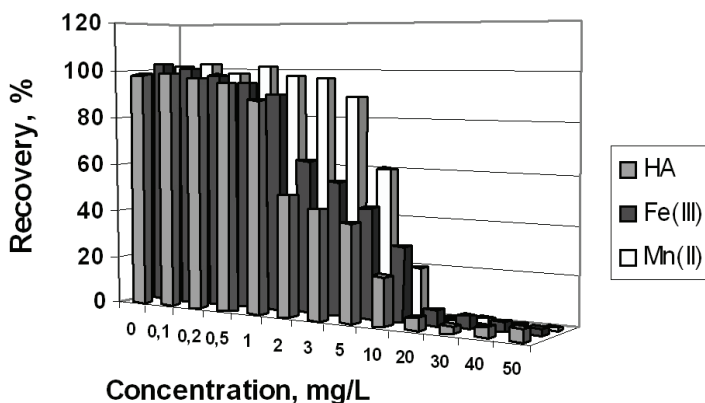


Fig. 8. Influence of humic acids (HA), Fe(III) and Mn(II) on the recovery of Cr(VI). Cr(VI) concentration 100 $\mu\text{g/L}$ (^bManova et al., 2007)

Unfortunately, the concentration of EDTA is limited by its solubility in acidic solutions, here at concentrations above 0.001 mol/L, a white precipitate of EDTA was formed in the solutions after several hours. Nevertheless, in this way, Fe(III) concentrations up to 500 – 1000 $\mu\text{g/L}$ can be tolerated. The interfering effect of higher Fe(III) concentrations can only be minimised by removing Fe(III) from the original sample, e.g. by making use of cation exchanger. Calcium and magnesium ions do not interfere.

Sulphate ions do not interfere. On the contrary, the signal of Cr(VI) decreased significantly with increasing concentration of nitrate ions or nitric acid above 0.1 mol/L. This can be

assigned to a partial electrochemical reduction of nitric acid being in large excess which coalesces with the reduction peak of Cr(VI).

The influence of the tested surfactants is totally different. The neutral Triton X-100 virtually exerts no influence on the signal. Moreover, its addition to the solutions improves the reproducibility owing to easier removal of air bubbles from the flow system. The anionic sodium dodecylsulphate decreases the Cr(VI) signal already at concentrations above 3-5 mg/L. Sorption of the anionic surfactant on the positively charged electrode surface may be a plausible explanation. On the contrary, the cationic Hyamine enhances the signal significantly. In the presence of Hyamine is the coulombic content of the reduction peak much higher than expected from the Cr(VI) content in the porous electrode, so a sorption of Cr(VI) during the filling of the electrode with the sample seems to occur. However, the explanation of this phenomenon would need further investigation.

Total Cr can only be assessed with this method after oxidising Cr(III) to Cr(VI) and measuring it with the above procedure. The oxidation of Cr(III) with hydrogen peroxide in alkaline solution is simple and fast. However, on acidifying the resulting solution the formed Cr(VI) is immediately reduced back by the excess of hydrogen peroxide remaining in the solution after oxidation. Oxidation with $K_2S_2O_8$ in acidic media produced Cr(VI) as well but the excess persulphate interfered in the Cr(VI) measurement giving an intense reduction peak completely obscuring the Cr signal. The only applicable procedure found was the oxidation with permanganate in solutions acidified with HCl. The procedure is simple but time consuming owing to the need of a long boiling of the reaction mixture. The excess of permanganate is automatically removed by addition of EDTA after completing the oxidation.

The completeness of the oxidation and recovery were checked by means of synthetic samples in the concentration range of 10 to 500 $\mu\text{g dm}^{-3}$, as well as by means of real water samples spiked with known amounts of Cr. Satisfactory recoveries (90-110 %) were achieved in all cases.

Tap water, mineral water and river water samples were analysed by the elaborated procedure. The accuracy for total Cr content was checked by GF AAS measurements (Table 5). No values above the detection limit of the methods were found in these samples so the samples were spiked with Cr(VI) and Cr(III) for recovery tests. Recoveries about 100 % were obtained in all cases.

Sample	Cr(VI) found $\mu\text{g/L}$	Total Cr found $\mu\text{g/L}$	Spike recovery %	Total Cr ^a $\mu\text{g/L}$
Tap water	< 1.9	< 1.9		< 0.8
+ 50 $\mu\text{g/L}$ Cr(VI)	49.6 $\pm$ 1.9		99.2	46.7 $\pm$ 3.1
+ 50 $\mu\text{g/L}$ Cr(III)	< 1.9	49.8 $\pm$ 2.0	99.6	
Mineral water ^b	< 1.9	< 1.9		< 0.8
+50 $\mu\text{g/L}$ Cr(VI)	48.5 $\pm$ 2.1		97.0	47.9 $\pm$ 3.8
+50 $\mu\text{g/L}$ Cr(III)	< 1.9	51.5 $\pm$ 2.2	103	
River water ^c	< 1.9	< 1.9		< 0.8
+ 50 $\mu\text{g/L}$ Cr(VI)	51.0 $\pm$ 2.4		102	48.3 $\pm$ 4.1
+ 50 $\mu\text{g/L}$ Cr(III)	< 1.9	48.6 $\pm$ 2.8	97.2	

Table 5. Recovery test with water samples. a Found by GF AAS; b Mineral water "Mitická ticha" (Slovakia); c River L' Arve at Geneve, Switzerland (b Manova et al., 2007)

6. Conclusions

The stripping chronopotentiometric determination of sulphides provided reliable results for waste water samples from a tannery. The sample preparation is simple, even if in some cases the prepared sample should be heated prior to the measurement to obtain values corresponding with the control method. There is no need for a pre-separation step such as in titrimetric and photometric methods. The automatic on-line matrix exchange in the flow system after deposition minimises possible interferences from the sample matrix making this technique advantageous over the static batch ones. In general, the presented procedure allows the measurement of sulphide compounds, which form soluble sulphide in alkaline solution. It is evident, that different sample preparation procedures, e.g. boiling with mineral acids and distillation, may address some sulphide species not measured by this technique. The main advantages of the elaborated procedure are the simple sample preparation, no interference from dissolved oxygen and sample matrix, low detection limit, fast and full automatic measurement.

The determination of lead by flow-through chronopotentiometry proved to be a simple, sensitive, and accurate method for waste water analysis. The measurement, including sample preparation is fast, an average measurement cycle does not exceed 3-6 min. Due to the broad linear concentration range and low detection limit the method can successfully deal with samples with different lead concentrations.

The in-electrode coulometric titration of Cr(VI) in porous electrodes proved to deliver reproducible and accurate results in a concentration range of about 5 to 500 $\mu\text{g/L}$. Owing to the preconcentration effect the detection limits of the adsorptive stripping methods are much lower (Table 1) but the presented procedure offers some significant advantages. The limit of detection enables to use the method for assessment of chromium content in drinking water below the threshold value (50 $\mu\text{g/L}$). The sample preparation for Cr(VI) determination is simple and fast and dissolved oxygen need not to be removed. Owing to the long lifetime of the porous carbon electrode, the procedure is also suitable for field applications and long-term unattended measurements, e.g. in process systems. Compared to photometric methods for Cr(VI), coloured species do not interfere. However, total Cr can only be assessed after a chemical oxidation of Cr(III) to chromate. Colloidal and solid particles in the solutions may clog the pores of the electrode and therefore must be removed. High contents of organic substances in some waste waters may interfere and the elimination of such interferences is the main goal in the improvement of the presented procedure.

The intrinsic simplicity of chronopotentiometric measurements, especially in flow-through mode has made this method a suitable tool for routine and on-line control of electrochemically active species in environment, waste water treatment and chemical technologies. Heavy metals, some anions and simple compounds can be targeted by the technique. Obviously, the direct contact of the sensor (electrode) with the sample may be a source of various interferences not only due to possible presence of electrochemically similar species but predominantly due to electrode failure caused by sorption and deposition of matrix components on the electrode surface. Yet, proper sample pre-treatment and adequate experimental parameters minimize or even completely eliminate these effects. As a consequence, this measurement principle is becoming preferred now predominantly in industrial applications for unattended on-line monitoring purposes.

7. Acknowledgement

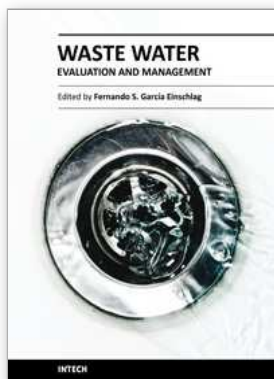
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Fresh water resources are under serious stress throughout the globe. Water supply and water quality degradation are global concerns. Many natural water bodies receive a varied range of waste water from point and/or non point sources. Hence, there is an increasing need for better tools to assess the effects of pollution sources and prevent the contamination of aquatic ecosystems. The book covers a wide spectrum of issues related to waste water monitoring, the evaluation of waste water effect on different natural environments and the management of water resources.

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