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Trace Analysis of Metal Ions Using a Coulometric Thin Layer Flow Cell Technique*

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Abstract

An electroanalytical method is presented based on sample injection into a flowing electrolyte phase followed by exhaustive collection and subsequent quantitative determination of the sample in a flow-through thin layer cell within a time scale of $\approx$ 10 min. The method is suitable for trace analysis of reversibly reducible metallic species at the picomole level and has been tested experimentally by investigating the analysis of Tl^{+}- and Pb^{2+}-sample solutions. By optimizing the cell parameters a further lowering of the present detection limit ($\approx$ nanomoles/l) should be possible.

Voltammetric techniques have gained increasing importance for the trace analysis of metallic and organic compounds in aqueous systems to the picomole level. Recent investigations are based mainly on anodic stripping voltammetry of deposits precollected at thin metal film electrodes (e. g. mercury films) under defined conditions of convection such as rotating electrodes [1,2] or flow cells [3]. In all these cases only a fraction of the electroactive compound present in the sample solution is converted in the electrode process, and therefore, the quantitative evaluation of the stripping current transient is based on a calibration procedure using standards of known concentration, preferably

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In this communication an experimental method is presented based on a previously described coulometric thin layer flow cell [4] combined with the possibility for sample injection. The method allows the absolute determination of reversibly reducible metal ions such as Pb^{2+}, Cd^{2+}, Tl^{+} and Cu^{2+} in the picomole range without a calibration process. Its basic features and working principle are as follows:

The *electroanalytical assembly* (Fig. 1a) consists of a coulometric flowthrough thin layer cell [4] equipped additionally with a sample injection valve SI located between the flow propulsion system FP and the thin layer TL. The thin layer contains two potential controlled electrodes,

- a collector electrode C (metal U, variable potential E_C) mounted in the upstream part ($R_o \leq r \leq R_1$) of the thin layer and
- a detector electrode D (metal U, constant potential $E'_D \rightarrow -\infty$) downstream from the collector electrode ($R_1 < R'_o \leq r \leq R'_1$).

The assembly is supposed to ascertain the coulometric function of both electrodes (i.e. the exhaustive scavenging of the reducible species) under cathodic limiting current conditions [4] by proper choice of the solution flow rate $J = \mathrm{d}V/\mathrm{d}t$ and of the electrode and thin layer dimensions.

The *operating principle* of the cell is shown in Fig. 1.

In the *sampling sequence* $0 \leq t \leq t_s$ (Figs. 1a-c) degassed and prepurified supporting electrolyte is flowing at constant volume flow rate J along the collector ($E_C = E_s \rightarrow -\infty$) and detector electrodes. At $t = 0$ (Fig. 1a) a known small volume V_s of the sample solution S, containing the reducible metal species Me^{z+} in unknown concentration C_{Me}, is delivered into the flow stream by means of the sample injection valve. The sample volume is carried into the thin layer (Fig. 1b) by the flowing electrolyte phase, and the total amount

$$N_{Me} = C_{Me} \cdot V_s$$

of metallic species is collected quantitatively at the collector electrode under limiting current conditions by the electrode process

$$Me^{z+} + z\,e^- \xrightarrow{U} Me/U\,.$$

At $t = t_s = J(V + V_s)$ (sampling time, depending on the volume flow rate J, the sample volume V_s and the total electrolyte volume V between sample injection valve and downstream edge of the collector electrode) the collection process is completed (Fig. 1c), and the currents i_C and i_D at the collector and detector electrode correspond to a steady state residual value $i_{ss} \rightarrow 0$. Soluble reduction products of additional electroactive systems present in the sample solution (e.g. oxygen) will be rinsed through the thin layer during the sampling process without affecting the quantitative determination.

In the subsequent *stripping sequence* $t_s < t_o \leq t \leq t_e$ (Figs. 1d,e) the metal deposited at the collector is stripped by scanning the collector potential anodically:

$$E_C = E_C(t) = E_s + v \cdot t \qquad (v > 0)$$

The stripping process can be carried out in two different ways:

- In the *flow stripping method* (Fig. 1d) the solution flow through the thin layer is maintained. The metal stripped from the collector electrode is deposited quantitatively under limiting current conditions at the detector electrode, causing the detector current

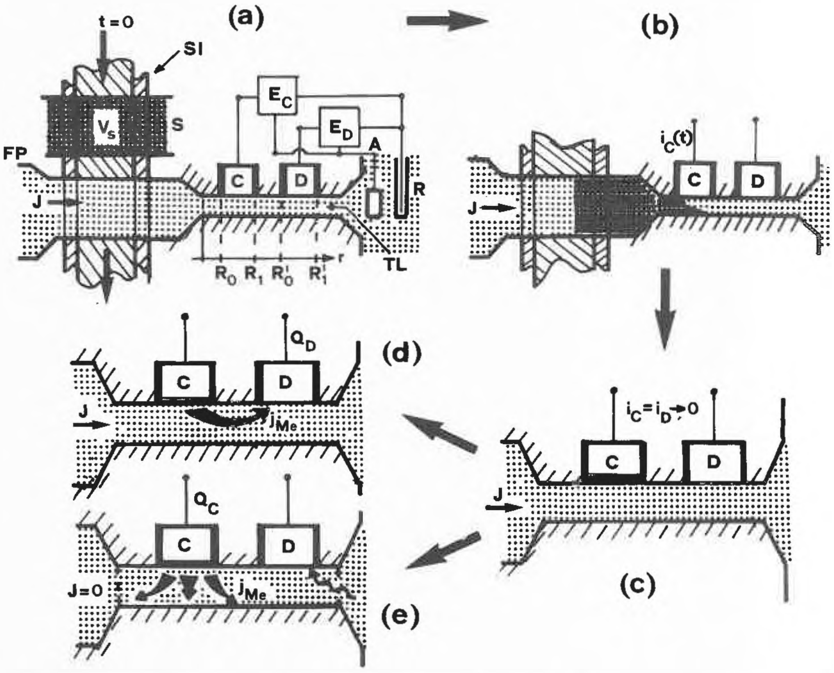

Fig. 1: Operating principle of electroanalytical flow cell: S = sample solution; FP = flow propulsion system; SI = sample injection valve; TL = thin layer; C = collector electrode; D = detector electrode; A, R = auxiliary and reference electrodes. *Fig. 1a:* Sampling sequence, $t = 0$. *Fig. 1b:* Sampling sequence, $0 \leq t \leq t_s$. *Fig. 1c:* End of sampling sequence, $t = t_s$. *Fig. 1d:* Flow stripping sequence, $t_o \leq t \leq t_e$. *Fig. 1e:* Stationary stripping sequence, $t_o \leq t \leq t_e$.

to deviate from its steady state value in a cathodic transient $i_D(t)$ with the finite integral

$$Q_D \equiv \lim_{t=t_e \to \infty} \int_{t_0}^{t} i_D(t) \cdot dt = -N_{Me} \cdot z \cdot F$$

and allowing the direct coulometric determination of N_{Me} and C_{Me}:

$$C_{Me} = N_{Me}/V_s = -\frac{Q_D}{zFV_s}$$

- In the *stationary stripping technique* the solution flow is stopped and the metal stripped anodically into the quiescent electrolyte phase within the thin layer, giving rise to an anodic collector current transient with the finite integral

  $$Q_C \equiv \lim_{t=t_e \to \infty} \int_{t_0}^{t} i_C(t) \cdot dt = N_{Me} \cdot z \cdot F$$

  and enabling a similar absolute coulometric evaluation of C_{Me}. In this method the detector electrode acts merely as a scavenger for possible electroactive contaminants entering the thin layer from its diffusionally unscreened downstream end.

While a full assessment of the specific advantages of the two different stripping techniques is not yet possible, it is to be expected that the flow technique has to be chosen in cases of potential controlled adsorption of anions during the anodic stripping process [4], whereas the stationary method is less sensitive to soluble contaminants causing interfering faradayic electrode processes.

Besides offering the possibility for absolute analysis without the need of calibration, the above method can be used without degassing the sample solution injected into the flow stream. Its performance has been examined for the analysis of Tl^+ and Pb^{2+}.

In the *experimental test* a flow-through thin layer cell described previously [4] was equipped with a Rheodyne sample injection valve (type 50–20). The collector and detector electrodes were made from amalgamated Ag, and the experiments were carried out at a volume flow rate $J = 2 \cdot 10^{-4}\ cm^3/s$. $NaClO_4$ (0.05–0.01 M, suprapur) + $HClO_4$ (0.01 M suprapur) was used as supporting electrolyte. The supporting electrolyte for the flow system was degassed and prepurified electrochemically (by passing a sufficient volume through the thin layer in the reverse direction). Pb^{2+}- and Tl^+-sample solutions were prepared with the same (but not prepurified and not degassed) supporting electrolyte from 10^{-2} M stock solutions. Each determination was followed by a blank test by injecting the same volume of unpurified and undegassed supporting electrolyte. The results presented below have been corrected for the blank value.

The results obtained by investigating Pb^{2+}- and Tl^+-samples of known concentration, using both the stationary and flow stripping technique, are presented in Table 1, and a selection of typical experimental curves is shown in Fig. 2. The data show good agreement between calculated and measured values to minimum concentrations $C_{Me} \approx 5 \cdot 10^{-9}$ M, and the results obtained for the Tl^+-Pb^{2+}-mixture (curve A in Fig. 2) indicate that the method is also suitable for the quantitative investigation of samples containing various

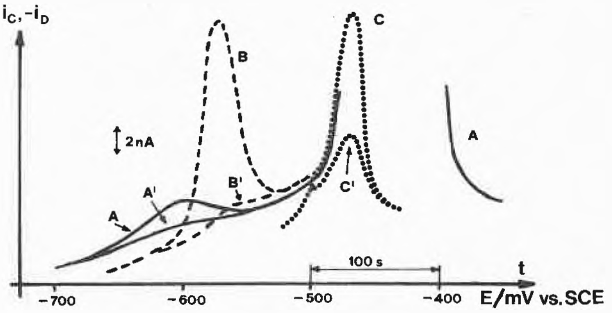

Fig. 2: Anodic stripping voltammograms of Tl^+ and Pb^{2+}: $J = 2 \cdot 10^{-4}\ cm^3/s$; $\nu = 1$ mV/s. Supporting electrolyte: $NaClO_4$ (0.01 M) + $HClO_4$ (0.01 M); stationary (——) and flow (- - - -) stripping curves. *Curve A:* $5 \cdot 10^{-9}$ M Tl^+ in mixture with ≈ 1000 fold excess of Pb^{2+} ($V_s = 132.4\ \mu l$). *Curve B:* 10^{-7} M Tl^+ ($V_s = 33.1\ \mu l$). *Curve C:* 10^{-8} M Pb^{2+} ($V_s = 33.1\ \mu l$). *Curves A', B', C':* Blank curves.

Table 1: Quantitative analysis of Pb^{2+} and Tl^+ in $NaClO_4$ (0.05–0.01 M) + $HClO_4$ (0.01 M)

System Me^{z+}	C_{Me}	$V_s [\mu l]$	C_{NaClO_4}	N_{Me} [moles] calculated	N_{Me} [moles] measured	stripping method
Pb^{2+}	10^{-6} M	33.1	0.05 M	$3.31 \cdot 10^{-11}$	$3.16 \cdot 10^{-11}$	flow
	10^{-6} M	33.1	0.01 M		$3.30 \cdot 10^{-11}$	flow
	10^{-7} M	33.1	0.05 M	$3.31 \cdot 10^{-12}$	$3.17 \cdot 10^{-12}$	flow
	(20 ppb)	33.1	0.01 M		$2.89 \cdot 10^{-12}$	flow
	10^{-8} M	132.4	0.01 M	$1.32 \cdot 10^{-12}$	$1.23 \cdot 10^{-12}$	flow
	(2 ppb)	132.4	0.01 M		$1.21 \cdot 10^{-12}$	stat.
	$5 \cdot 10^{-9}$ M (1 ppb)	132.4	0.01 M	$0.66 \cdot 10^{-12}$	$0.50 \cdot 10^{-12}$	flow
Tl^+	10^{-7} M	33.1	0.01 M	$3.31 \cdot 10^{-12}$	$3.32 \cdot 10^{-12}$	flow
Tl^+/Pb^{2+} mixture $C_{Pb} \approx 1000 \cdot C_{Tl}$	$5 \cdot 10^{-9}$ M (Tl^+)	132.4	0.01 M	$0.66 \cdot 10^{-12}$	$0.70 \cdot 10^{-12}$	stat.

different metallic species. In this case, the performance of the technique for separate quantitative investigation of the different species will depend greatly on their formal potentials, the electrode kinetics of the stripping processes and the substrate material of the collector electrode and may be influenced additionally by the flow rate (in the flow stripping technique).

The above data allow the conclusion that the presented technique is a valuable tool for trace analytical purposes. The concentration limit can be lowered by increasing the sample volume V_s accordingly. If the total sampling and stripping time t_e is to remain constant, it involves a corresponding increase of the volume flow rate J without loss of the coulometric cell function. An estimation, based on the analysis of convective diffusion in the thin layer [5], reveals that on choosing optimum thin layer and electrode dimensions the flow rate can be increased by a factor up to 50, resulting in a 50 fold increase of sensitivity at the unaltered sampling time range $t_s \approx 10$ min. used in the above experiments. In cases where large sample volumes (≈ 50 ml) and long sampling times (several hrs.) are acceptable, it should be possible to lower the detection limits by another two orders of magnitude. Work in progress* will show how these estimations can be realized in practice, and how this experimental method can be extended to additional applications, such as separation techniques or the determination of non-metallic trace compounds.

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