INTERDIGITATED ARRAY DIFFUSION LAYER TITRATION OF DITHIOCARBAMATES WITH ELECTROGENERATED HYPOBROMITE

Peter TOMČÍK[1,*] and Dušan BUSTIN[2]

Department of Analytical Chemistry, Slovak University of Technology, 812 37 Bratislava, Slovak Republic; e-mail: [1] tomcik@cvt.stuba.sk, [2] bustin@cvt.stuba.sk

Received November 5, 1999
Accepted March 6, 2000

Presented at International Conference on Modern Electroanalytical Methods, Seč, September 19–23, 1999.

A simple but sensitive technique was developed for determination of dithiocarbamates. The proposed method is based on its oxidation with hypobromite under the formation of sulfate. The oxidation proceeds only in the close vicinity of interdigitated array microelectrode (IDA), the segments of which were used as working and indicator electrodes. Hypobromite was formed by disproportionation of galvanostatically generated bromine (from bromide) in weakly alkaline solution on one segment of IDA (generator). The unreacted flux of hypobromite was amperometrically detected on the second segment (collector-indicator). The hypobromite flux is influenced by dithiocarbamates present in solution, causing changes in the collector *versus* generator current plot (titration curve) which can be quantitatively evaluated. The sensitivity of the method is 7 795 l mol^{-1} μA and detection limit estimated according to the 3s criterion is $2.2 \cdot 10^{-6}$ mol l^{-1}. The technique was used in analysis of real samples, such as in determination of a pesticide residues in cucumber leaves.

Key words: Interdigitated array microelectrode; Dithiocarbamates; Pesticides; Electrogeneration; Diffusion layer titration; Electrochemistry.

Interdigitated array (IDA) microelectrode was used for the determination of some species in environmental[1] samples and chemicals[2] using titration in IDA diffusion layer. A chemical reaction of electrogenerated titrant with the determined species is used in this method in analogy with the case of rotating ring-disc electrode (RRDE) where the disc serves as a generator and the ring as a collector (detector). Similary to RRDE the chemical reaction also proceeds only in the close vicinity of the IDA microelectrode. In the case of IDA, there is no hydrodynamic transport and electroactive species are transported to the collector by diffusion only. Thus a transport direction change is possible. The collection efficiency with IDA is significantly higher

(70–90%) in comparison with RRDE, depending on the microelectrode geometry (mainly on the gap widths). The reaction agent (titrant) is generated on the generator array galvanostatically or using a slow galvanostatic scan. If no reaction with titrant occurs it is transported to the collector in the yield given by the collection efficiency. The potential of the collector is fixed on a value which corresponds to an electrochemical reaction reverse to the generator process. The titration agent should form a reversible or quasireversible redox system and should rapidly and quantitatively react with the determined species. A simple and sensitive method for determination of dithiocarbamates is described in this paper. The technique is based on generation of hypobromite which is formed in weakly alkaline solution by disproportionation from electrogenerated bromine and on amperometric detection of diffusion flux of unreacted hypobromite if dithiocarbamates are added to the solution. The method was used in analysis of Mancozeb, dithiocarbamate pesticide (water-insoluble coordination compound of zinc(II) and manganese(II) with *N*,*N′*-ethylenebis(dithiocarbamates)), which is widely used in agriculture to avoid post-harvest diseases. Mancozeb and its decomposition products are generally toxic, carcinogenic[3] and teratogenic[4] and hence can be hazardous. Therefore a strict monitoring of this pesticide is needed[5–7]. A sample of leaves was sprayed with Mancozeb suspension, treated with water and extracted with EDTA. In the extract, the residual content of nabam (water-soluble extraction product of Mancozeb) was determined.

EXPERIMENTAL

A planar interdigitated microelectrode array[8] (Fig. 1) formed on alumina-boron-silica glass with dimensions 15 × 3 × 0.6 mm was used. The widths of both the microelectrode segments and the gap between them were 5 μm.

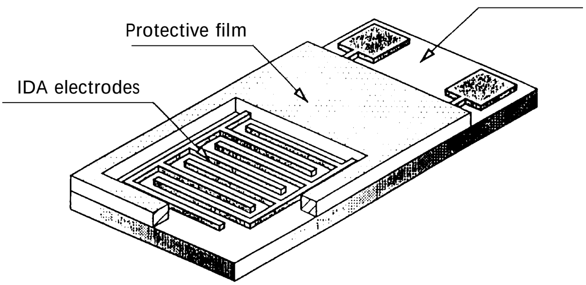


FIG. 1
A thin film of horizontally separated microelectrode array (not to scale)

Thin Pt films were deposited by radio frequence sputtering and the lift-off technique was used for the patterning of the IDA. The system was passivated with a polyimide protective film besides a 600 × 600 µm window and Pt contacts.

A model 366A bi-potentiostat (EG&G Princeton Applied Research, Princeton, NJ) was used for electrochemical measurements. The generator system was operated anodically in the galvanostatic mode producing hypobromite from 1 M KBr in 0.1 M sodium tetraborate. pH was adjusted to 9.1 with dilute H_2SO_4 and checked with a Metrohm pH-meter. Galvanostatic scans below 20 nA s^{-1} were used. Higher scans cause hysteresis of measured collector *vs* generator current plots.

The method was used for analysis of pesticide Mancozeb in cucumber leaves. Leaves were harvested by cutting above stalk, weighed (10–15 g) and extracted in ultrasonic bath with 40 ml of 0.1 M aqueous solution of EDTA at pH 9 (borate buffer) for 2 min. The extract was filtered and its volume was adjusted to 50 ml. From this solution, 1 ml was pipetted for analysis. The analysis time after titration should not exceed 7 min because of slow decomposition of nabam to avoid possible interferences of decomposition products[5]. Aqueous suspension of Mancozeb (0.1 g, 50 ml) was carefully sprayed onto individual leaves using a mechanical spray so that the leaves were fully wetted and there was no run-off onto the soil. Another set of leaves was treated with 20 ml of water before extraction and dried at ambient temperature.

All chemicals were used as received from commercial sources. Water treated with $KMnO_4$ and triply distilled was used for preparation of sample solutions.

RESULT AND DISCUSSION

Collection Efficiency of Hypobromite Transfer

Hypobromite was generated galvanostatically on the generator segment of IDA. The redox system of hypobromite is reversible on platinum electrode. The collector potential was fixed on a value which corresponds to the limiting cathodic current of titrant (0.0 V *vs* SCE). Its detection is based on the reaction

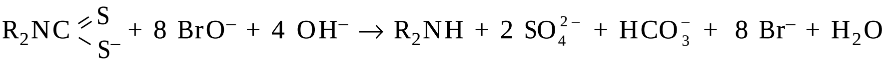
$$BrO^- + 2\ e + H_2O \rightarrow Br^- + 2\ OH^- \qquad (1)$$

The collection efficiency is the slope of a linear dependence of the collector current (I_{coll}) *versus* the generator current (I_{gen}). The slope at pH 9.1 was 0.74. This value is higher in comparison with the rotating ring-disc electrodes[9].

Diffusion Layer Titration of Dithiocarbamates

The transfer of hypobromite from the generator to the collector is influenced by the presence of dithiocarbamates in solution. The shape of the I_{coll}

vs I_{gen} curve significantly changes. Dithiocarbamates are anodically inactive at the potential of anodic generation of hypobromite. Chemical reaction of hypobromite and dithiocarbamates is rapid and quantitative in 1 M KBr solution so the surface concentration of hypobromite at the generator will remain zero until the current flowing through the IDA generator is such that the flux of outgoing hypobromite is larger than the flux of incoming dithiocarbamates. When the generator current increases, hypobromite spreads across the insulating gaps until it reaches the collector segments. Then the collector current increases from zero since the collector is set at the potential of limiting diffusion current of hypobromite reduction. The I_{coll} *vs* I_{gen} plot influenced by dithiocarbamate concentration can be utilized for its determination based on the reaction



$$\mathrm{R_2NC}\genfrac{}{}{0pt}{}{\mathrm{{=}S}}{\mathrm{{-}S^-}} + 8\ \mathrm{BrO^-} + 4\ \mathrm{OH^-} \rightarrow \mathrm{R_2NH} + 2\ \mathrm{SO_4^{2-}} + \mathrm{HCO_3^-} + 8\ \mathrm{Br^-} + \mathrm{H_2O} \qquad (2)$$

The I_{coll} *vs* I_{gen} plot is a coulometric diffusion layer titration curve with the IDA generator producing titrant and the IDA collector serving as an amperometric detector. Titration curves generated at different concentrations of dithiocarbamates are depicted in Fig. 2.

Extrapolation of the linear portion of the increasing part of the titration curve to the residual collector current gives the end-point value of the generator current, I_{genE}. As no chemical reaction actually takes place in the bulk phase of the sample, the "titration" can be extensively repeated in the same

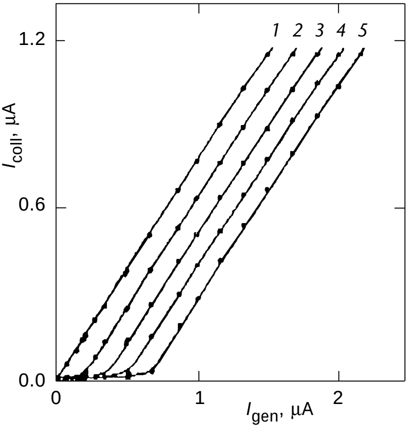


FIG. 2
Diffusion layer titration of sodium *N*,*N'*-diethyldithiocarbamate with electrogenerated hypobromite using IDA microelectrode. Generator polarized with galvanostatic scan 10 nA s^{-1}; collector potential fixed at 0.0 V *vs* SCE. Bulk concentration of sodium *N*,*N'*-diethyldithiocarbamate (μmol l^{-1}): 0 (*1*), 16 (*2*), 33 (*3*), 53 (*4*), 70 (*5*)

solution with excellent reproducibility of the I_{coll} *vs* I_{gen} plot. Standard deviation of 15 consecutive runs of the same solution, $1 \cdot 10^{-4}$ M sodium *N*,*N'*-diethyldithiocarbamate, is 2.0% for I_{genE} and 2.0% for the slope of the rising part of the titration curve.

I_{genE} (y) is a linear function of dithiocarbamate concentration (c). It fits the equation

$$y = B + A\,c\,, \qquad (3)$$

where B is the blank 47 nA and A is the slope 7 795 l mol^{-1} μA (both parameters were obtained by LS method approach). The precision and accuracy of the analysis are given by standard deviations (s) of its slope (156 l mol^{-1} μA) and intercept (5.6 nA). The intercept can be regarded as the blank and can be subtracted from the experimental I_{genE}. The detection limit estimated according to the 3s criterion is equal to about $2.2 \cdot 10^{-6}$ M sodium *N*,*N'*-diethyldithiocarbamate. Under the experimental conditions used (sample volume 10 ml), the limit is 5 μg of sodium *N*,*N'*-diethyldithiocarbamate.

Five standard samples of of sodium *N*,*N'*-diethyldithiocarbamate (37–185 μg) were analyzed; the results are summarized in Table I. Statistically, the means of parallel determinations do not differ from the known values in all standard samples. The confidence interval is relatively narrow.

TABLE I
Diffusion layer titration of sodium *N*,*N'*-diethyldithiocarbamate with electrogenerated hypobromite in standard samples[a]

Taken, μg	Found, μg	*s*, μg[b]	Confidence interval for 95% probability	
			μg	%
37.0	40.5	3.9	4.8	12.0
74.0	71.3	4.2	5.2	7.3
111.0	120.6	7.5	9.3	7.7
148.0	139.4	8.5	10.6	7.6
185.0	178.3	9.9	12.3	6.9

[a] Base electrolyte (1 M KBr with sodium tetraborate, pH 9.1, volume 10 ml); [b] number of analyses 5.

The low detection limit makes it possible to use the technique for determination of dithiocarbamates in pesticides applied on leaves. The standard addition method was used for evaluation of the end-point value of the generator current. The results are summarized in Table II. They are in good agreement with the results of liquid chromatographic analysis[5]. The nabam content (water-soluble extraction product of Mancozeb) in leaves decreases more rapidly if the leaves are treated with water.

TABLE II
Determination of residual content of Mancozeb in sprayed leaves[a], with and without water treatment, respectively

Time days	Mancozeb[b] µg/g of leaves	Confidence interval for 95% probability		Mancozeb[c] µg/g of leaves	Confidence interval for 95% probability	
		abs. µg/g	rel. %		abs. µg/g	rel.%
0	400	28	7.0	390	30	7.7
5	390	30	7.7	320	21	6.5
10	270	22	8.2	160	19	11.9
15	260	20	7.7	75	11	14.7

[a] Number of analyses 4; [b] treated without water; [c] treated with water.

This study was supported by the Slovak Grant Agency of Sciences, VEGA (Project No. 1/6103/99).

REFERENCES

1. Tomčík P., Jursa S., Mesároš Š., Bustin D.: *J. Electroanal. Chem.* **1997**, *423*, 115.
2. Bustin D., Jursa S., Tomčík P.: *Analyst* **1996**, *121*, 1795.
3. Borge M. U., Weisburger J. H., Weisburger E. K., Rice J. M., Cypher M.: *J. Natl. Cancer Inst.* **1972**, *49*, 583.
4. Bottomeley P., Hodless R. A., Smart N. A.: *Residue Rev.* **1985**, *95*, 45.
5. Lehotay J., Kisová D.: *J. Liq. Chromatogr.* **1993**, *16*(*5*), 1015.
6. Lehotay J., Holotík Š., Brandšteterová E.: *J. Liq. Chromatogr.* **1992**, *15*(*13*), 2397.
7. Brandšteterová E., Lehotay J., Liška O., Garaj J.: *J. Chromatogr.* **1984**, *291*, 439.
8. Tvarožek V., Ti Tien H., Novotný I., Hianik T., Dlugopolský J., Ziegler W., Leitmannová-Ottová A., Jakabovič J., Řeháček V., Uhlár M.: *Sens. Actuators, B* **1994**, *18–19*, 597.
9. Albery W. J., Hitchman M. L.: *Ring-Disc Electrodes*. Clarendon Press, Oxford 1971.