Theory of Cathodic stripping square-wave voltammetry

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Kinetic parameters for redox reactions of reactants immobilized at the working electrode surface are k_s/f, if a product is also immobilized, and $k_s/f^{0.75}$ if the product is soluble.

Cathodic stripping voltammetry is a valuable analytical method for the determination of traces of electroinactive anions which can form a thin film of insoluble salt on the surface of a mercury, or a silver working electrode (1-5). The method has been used to analyse traces of halides (1,3) sulfide (2,4), selenide (5) snd some other substances (1). Detection limits reported for different anions vary from $5\cdot10^{-9}$ M to $5\cdot10^{-7}$ M, depending on the stripping technique applied. One of the most advanced electroanalytical techniques, the square-wave voltammetry, is especially sensitive to quasireversible redox reactions of reactants immobilized at the working electrode surface (6). The immobilization can be achieved by different processes, such as the direct, or anion-induced adsorption, the electrodeposition of metal atoms on solid electrodes and insoluble salts on the surface of mercury and silver electrodes, the amalgam formation within the thin mercury film covered glassy-carbon electrode, or by the abrasive transfer of traces of solid analyte onto a surface of a graphite rod. All these processes can serve as a preconcentration step of an electroanalytical method and usually are followed by the chathodic, or the anodic square-wave stripping scan. A model of cathodic stripping square-wave voltammetry of insoluble mercuric salt accumulated at the mercury drop electrode surface is developed.

Theoretical relationships between the properties of responses and the parameters of both the redox reaction and the SWV signal are analysed. Both reversible and quasireversible redox reactions are considered and the nature of the so called "quasireversible maximum" is discussed. Similarity between responses of reactants which are immobilized by different processes is demonstrated. The kinetic parameters of these redox reactions are shown to be k_s/f, if the product is also immobilized, and $k_s/f^{0.75}$ if the product is soluble. Here, K_s is the standard reaction rate constant and f is the SW frequency. Numerical simulations are compared qualitatively with the SW stripping voltammograms of electrodeposited Hg_2CL_2 and Hg_2Br_2. The application of the method to the measurements of halides in the seawater and S^{2-} in anaerobic waters is discussed.

REFERENCES

WANG J., 1985.- Stripping analysis, VCH, Dearfield Beach.

FLORENCE T.M., 1979.- Cathodic stripping voltammetry, *J. Electroanal. Chem.*, 97, 219-236.

MANADHAR K. and PLETCHER D., 1977 - Determination of halide ions by cathodic stripping analysis, *Talanta*, 24, 387-390.

SHIMIZU K. and OSTERYOUNG R.A., 1981.- Determination of Sulfide by cathodic stripping voltammetry of Silver sulfide films at a rotating silver disk electrode, *Anal. Chem.*, 53, 584-588.

ZELIC M. and BRANICA M., 1990.- Study of electrochemical reduction of Selenium (+4) using square wave voltammetry, *Electroanalysis*, 2, 393-398.

LOVRIC M. and KOMORSKY-LOVRIC S., 1988.- Square-wave voltammetry of an adsorbed reactant, *J. Electroanal. Chem.*, 248, 239-253.

AAS - Determination of Mercury in marine reference materials after wet ashing by means of microwaves

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The application of microwaves (2450 MHz) to the mineralization of environmental samples for the purpose of the determination of mercury has been investigated.

The method was tested on 5 reference materials produced by the IAEA : MA-M-2/TM (mussel homogenate), MA-A-3/TM (shrimp homogenate), MA-B-3/TM (fish homogenate), IAEA-350 (tunny-fish, lyophilized) and SD-M-2/TM (deep-sea sediment). The concentration of mercury in these materials is either certified or known with an acceptable degree of accuracy.

The digester "Microdigest" - 300 (PROLABO) was used for the mineralization of these samples. Mineralization tests were done under various operating conditions : microwave energy, duration of operation, oxidizing reagents (HNO_3 - H_2O_2 and HNO_3 - H_2SO_4 - H_2O_2), condenser type (Vigreux column or Liebig column). Resulting solutions were analysed by cold-vapour atomic absorption spectrometry (HATCH 1 OTT, 1968). Results are given in Table 1. For each material the mean value of the individual determinations is compared with the consensus value (certified) or the expected value (non-certified). The agreement between these values is good (less than $\pm$ 10% deviation) in the case of shrimp homogenate MA-A-3/TM and lyophilized tunny-fish IAEA - 350 (the expected value for this sample was obtained in our laboratory by applying a conventional wet-ashing method). The mean value is lower than the certified value for the mussel homogenate MA-M-2/TM (-23%) and higher than the certified value in the case of the sediment SD-M-2/TM (+22%).

The applications of WILCOXON's non-parametric test showed that results of "strong attacks" (high microwave energy and long duration) are significantly higher than results of "weak attacks" for all analysed materials (p < 0.01). Results obtained by use of the Liebig condenser seem also to be higher than results obtained with the Vigreux column but the difference is less significant (p < 0.10). The effect of the addition of sulphuric acid is not systematic and depends on the material analysed.

Microwave mineralization coupled with cold-vapour atomic absorption spectrometry is a rapid and efficient analytical method for the determination of mercury in environmental materials. It takes about 15-30 minutes to solubilize mercury from the samples instead of several hours with the classical wet-ashing method.

Table 1. Results of Microwave mineralization

Sample N°	Oxidizing reagents (1)	Type of attack (2)	Condenser used
1	A	weak	Vigreux
2	A	strong	Vigreux
3	A	strong	Liebig
4	B	weak	Vigreux
5	B	strong	Vigreux
6	B	strong	Liebig

(1) A : 10 ml HNO3 65% followed by 2 ml H2O2 35%
 B : 7 ml HNO3 65% + 3 ml H2SO4 98% followed by 2 ml H2O2 35%

(2) weak attack : A : max energy 10%, duration 15 min.
 B : " " 5%, duration 20 min.

 strong attack : A : max energy 15%, duration 20 min.
 B : " " 15%, duration 35 min.

Results of mercury determinations ($\mu g\ g^{-1}$)

Sample N°	MA-M-2/TM	MA-A-3/TM	MA-B-3/TM	IAEA-350	SD-M-2/TM
1	0.70	1.53	0.45	3.11	0.065
2	0.75	1.69	0.43	3.94	0.080
3	0.75	1.82	0.53	4.31	0.076
4	0.68	1.64	0.41	4.24	0.057
5	0.75	1.82	0.47	4.39	0.064
6	0.73	1.96	0.47	4.65	0.057
Mean value	0.73	1.74	0.46	4.11	0.066
Expected value	0.95(1)	1.79(2)	0.51(1)	4.42(3)	0.054(1)
Rel. deviation	-23.2%	- 2.8%	- 9.8%	- 7.0%	+22.2%

(1) certified   (2) non-certified   (3) conventional wet-ashing

Correlation : mean value (y) - expected value (x) :

$$y = 0.938\ x - 0.028 \qquad r = 0.9987\ (p < 0.001)$$