DPV BEATS SWV: ADSORPTİVE STRİPPİNG DETERMİNATİON OF AN OXIDATİVE STRESS MARKER IN BIOLOGİCAL FLUID

Muharrem Öztürk¹, Behice Yavuz Erdoğan², Onur Dumanlı¹, A. Nur Onar¹

¹ Department of Chemistry, Art and Sciences Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey
E-mail: mcda55@hotmail.com; odumanli@omu.edu.tr; nonar@omu.edu.tr

² Department of Food Technology Programmes, Technical Vocational School of Higher Education, Ondokuz Mayıs University, Terme, 55600 Samsun, Turkey
E-mail: behicey@omu.edu.tr

Adsorptive stripping voltammetry is the best known analytical method that incorporates an electrolytic preconcentration step. This technique has the advantages of low detection limit, low determination limit, high sensitivity, wide spectrum of the test material and analytes, relative simplicity, insignificant matrix effect, speed, and low cost of equipment. The electrode of choice for stripping voltammetry is generally mercury[1,2]. Any number of potential waveforms can be used for the stripping step. The most common are differential pulse and square wave due to the discrimination against charging current.

Square-wave voltammetry has several advantages. Among these are its excellent sensitivity, the rejection of background currents, lower consumption of electroactive compounds in relation to DPV, and reduced problems with blocking of the electrode surface. The major advantage of square-wave voltammetry is its speed. The effective scan rate is of the order of 500 mV s⁻¹. As a result, the analysis time is drastically reduced. A complete voltammogram can be recorded within a few seconds, compared to 2–3 min in differential pulse voltammetry. In addition, SWV is also more sensitive than DPV, because both forward and reverse currents are measured in the former, but only the forward currents are measured in the latter. Frequencies of 1 to 100 square-wave cycles per second permit the use of extremely fast potential scan rates. For these reasons SWV is employed more often than differential pulse voltammetry (DPV) techniques [1,2].

In biological systems, 3-nitrotyrosine (3-NT) is believed to be the marker of a powerful oxidant peroxynitrite (ONOO⁻) which is the reaction product of oxygen radical and nitric oxide (NO)[3]. Electrochemical behaviour of 3-nitrotyrosine is evaluated and an adsorptive stripping SWV determination method was developed using phosphate buffer (0.30 M pH 9.0) as supporting electrolyte [4]. An irreversible reduction peak was observed at -0.497 V (vs. Ag/AgCl (3 M KCl)) at hanging mercury dropping electrode for 3-NT. LOD and LOQ values were found as 2.53x10⁻¹⁰ and 1.46x10⁻⁹ M respectively. Recovery was calculated as 96.29 ± 2.32%. However developed SWV method failed for the determination of 3-nitrotyrosine in cerebrospinal fluid. Similarly calibration curve preparation using adsorptive stripping SWV in the presence of synthetic cerebrospinal fluid at pH 7.24 was problematic, probably due to the albumin reduction peak that emerged as an envelope. The problem was solved by using DPV. The results will be discussed in this work.

References