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# VOLTAMMETRIC DETERMINATION OF ACLONIFEN AT A SILVER AMALGAM ELECTRODE IN DRINKING AND RIVER WATER

### WOLTAMPEROMETRYCZNE OZNACZANIE AKLONIFENU ZA POMOCĄ AMALGAMATOWEJ ELEKTRODY SREBRNEJ W WODZIE PITNEJ I RZECZNEJ

**Abstract:** A method for the determination of pesticide Aclonifen (AC) in drinking and river water by differential pulse voltammetry (DPV) on a meniscus modified silver solid amalgam electrode (m-AgSAE) using solid phase extraction (SPE) as a cleanup and preconcentration procedure is described. The limit of detection (*LOD*) for direct DPV determination of AC in deionized water is  $2.7 \cdot 10^{-8}$  mol·dm<sup>-3</sup>. *LOD* for DPV determination of AC in tap water after SPE is  $1.6 \cdot 10^{-10}$  mol·dm<sup>-3</sup>, the recovery being 55%. *LOD* for the determination of AC in Vltava river water is  $1.9 \cdot 10^{-9}$  mol·dm<sup>-3</sup>, the recovery being 65%. Humic acids interfere with the determination in river water; this problem can be resolved by adjusting the pH of the extracted sample to 6. The advantages of this approach are high sensitivity, low *LOD*, quick and easy sample preparation and fast determination.

Keywords: aclonifen, silver solid amalgam electrode, drinking water, river water, solid phase extraction

# Introduction

Aclonifen (AC) is a diphenyl ether herbicide (DPhEH) used for preemergent protection from weeds in potatoes, peas, carrot, rice and sunflowers [1]. It has been registered for use in the European Union since 2008. The need for herbicide use in modern agriculture is universal and increasing. This trend is not likely to be reversed due to the fact that weeds usually account for around 14% losses of crop each harvest [2]. AC exhibits side effects, as do other DPhEHs [3] and herbicides in general, such as high toxicity for aquatic organisms and hepatotoxicity in mammals in high doses [4]. It is a suspected human carcinogen and related substances are endocrine disruptors and have adverse effects on blood formation [5, 6]. The need for monitoring of this compound in the environment is therefore obvious. Various methods for the determination of AC are described in the literature [7-11]. The most powerful method for herbicide residue analysis is GC-MS with its ability to accurately

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quantify hundreds of substances in a single run. This technique is also suitable for the determination of residues of AC [12]. HPLC is a less convenient technique usually reserved for nonvolatile or thermally labile substances, but some researchers chose this approach nonetheless [13, 14]. The modern trend in herbicide determination by electrochemical methods is undoubtedly using nanoparticle based biosensors as shown in the review by Liang et al. [14]. The described methods all use extremely complicated sensor arrangements involving enzymes, nanoparticles, redox probes and conductive polymers. These sensors exhibit impressive sensitivity and selectivity [15-17]. The authors claim in each case that the sensors are robust and durable, but enzymes are unstable even in if covalently bonded to a support and many non-target substances present in real samples can inhibit them. It is therefore certain that easily renewable electrodes such as the meniscus modified silver solid amalgam electrode (m-AgSAE) offer an alternative that is much less complicated to work with, as its properties can be completely restored to a state as good as new in the matter of minutes by a very simple treatment.

More direct approach using silver amalgam based electrodes is also a recurring theme in the contemporary literature [18-22], all the works use a mercury film modified AgSAE for some reason, which uses small amounts of mercury for film renewal, but the mercury has to be in a toxic water soluble form, the film is much less stable than a meniscus and the electrode needs to be polished much more often, which is time consuming. Some works focus on the determination of herbicides at classical mercury electrodes [23] this method utilizes the excellent reproducibility of a hanging mercury drop electrode (HMDE) to deconvolute the signals of three herbicides to determine them in a mixture. HMDE has a slightly better performance than m-AgSAE, but lack its mechanical robustness, thus being more prone to mechanical failure. Boron doped diamond electrodes (BDDE) also have a place as sensors for herbicide determination, but their sensitivity is no match for an m-AgSAE [24]. None of the published methods uses voltammetry at m-AgSAE. This novel electrode is a valuable sensor for the determination of trace amounts of pollutants in the environment [25] including the determination of some DPhEHs [26, 27]. The modern trend on the herbicide market is not so much to invent new chemistries and modes of action but to develop new mixtures containing synergistic compositions of compounds that are already known to work well and to decrease the risk of resistance development by using mixtures of substances with different modes of action. This indicates that AC determination in environmental samples will probably stay relevant for a long period of time.

#### Chemicals

AC (2-chloro-6-nitro-3-phenoxybenzenamine 99%, Sigma-Aldrich, Germany) stock solution  $(1 \cdot 10^{-3} \text{ mol} \cdot dm^{-3})$  has been prepared by dissolving 0.02648 g of AC standard in 100 cm<sup>3</sup> of methanol. The stock solution was kept in the dark at 4°C. UV-VIS spectrophotometry was used to verify the stability of the stock solution. The stock solution was stable for more than 6 months. All chemicals used were of reagent grade purity. Acetic acid (99%), boric acid, phosphoric acid (85%), hydrochloric acid (35%), sodium hydroxide, and potassium chloride were purchased from Lachema (Brno, Czech Republic). Methanol g. r. (Merck, Germany) was used. Britton-Robinson buffers (BRB) of the desired pH were prepared from 0.2 mol·dm<sup>-3</sup> NaOH as the basic component and a solution consisting of 0.04 mol·dm<sup>-3</sup> boric acid, phosphoric acid, and acetic acid as the acidic component.

## Apparatus

Jenway 3510 (Jenway, Essex, Great Britain) pH-meter with a combined glass membrane electrode (type Jenway 924 005) was used for pH measurements. The electrode was calibrated by standard aqueous buffer solutions. Deionized water (Millipore, USA) was used. Voltammetric techniques were performed on the Palmsens Electrochemical Sensor Interface (Palm Instruments BV, Ruitercamp, The Netherlands) and the Palmsens PC software was used. The software was running under the Windows XP (Microsoft Corp.) operating system. For DPV pulse width of 100 ms and pulse height of -50 mV were used with scan rate of 20 mV/s, and potential resolution of 2 mV. All measurements were performed using a three electrode system. A silver/silver chloride electrode (1 mol·dm<sup>-3</sup> KCl, type RAE 113, Monokrystaly, Turnov, Czech Republic), a platinum wire auxiliary electrode, and a m-AgSAE (Polaro Sensors, Prague, Czech Republic) working electrode were used. After extended periods of storage and if the behavior of m-AgSAE started to change the meniscus was renewed by mechanical polishing (to remove old meniscus) and by immersing the electrode into a vial containing a small quantity of liquid mercury (to create a new meniscus; the process is called amalgamation). At the start of a series of measurements the electrode was activated in 0.2 mol·dm<sup>-3</sup> KCl solution by applying a negative potential of 2.2 V for 5 min, as described in [28]. Measured solutions of AC were prepared by adding an appropriate amount of the stock solution of AC to a 10  $\text{cm}^3$  volumetric flask, filling with methanol to a total volume of 5  $\text{cm}^3$  and then filling the flask up to 10 cm<sup>3</sup> with BRB of the appropriate pH. Calibration curves were constructed using arithmetic averages of 3 measurements. Error bars were derived from the same data. LODs were calculated according to the formula  $LOD = 3.3 \cdot \sigma/S$  where  $\sigma$  is the standard deviation of 10 measurements at the lowest concentration when the signal can still be evaluated and S is the slope of calibration curve in the vicinity of that concentration. Lichrolut RP-18 E 200 mg SPE columns were conditioned by passing 5 cm<sup>3</sup> of methanol and 5  $\text{cm}^3$  of deionized water through them. The model sample (100  $\text{cm}^3$ ) of AC in deionized, drinking, or river water was then passed through the conditioned cartridge, which was then washed by 5 cm<sup>3</sup> of deionized water and left to dry by passing air for 5 min. The cartridges were eluted by 2 cm<sup>3</sup> of methanol (modified procedure according to [11]). The eluate was then filled up to the mark in a 10 cm<sup>3</sup> volumetric flask with BRB pH 12 and DP voltammograms of the resulting solution were recorded. The SPE from 1 dm<sup>3</sup> of model samples was done analogously. To achieve even lower detection limits, we again started with 1 dm<sup>3</sup> of the sample, eluted the cartridge with 2 cm<sup>3</sup> of methanol, evaporated the resulting eluate, re-dissolved the residue in 1 cm<sup>3</sup> of mixture of 20% methanol and 80% BR buffer pH 12 and recorded DP voltammograms in the resulting 1 cm<sup>3</sup> of solution. The Palmsens potentiostat made by Palm Instruments (Ruitercamp, Netherlands) was used. The electrode was activated by applying a potential of -2200 mV in 0.2 mol·dm<sup>-3</sup> KCl for 5 min. The DP voltammograms were measured from -200 to -1600 mV with a scan rate of 20 mV/s, pulse height of -50 mV, and pulse width of 100 ms.

## Results

To develop a method for the determination of AC in a more complex matrix, we have started with SPE of AC from deionized water spiked with AC to verify that the extraction method is suitable for the substance. To establish the recovery, AC was extracted from 100 cm<sup>3</sup> of deionized water, the cartridges were eluted with 2 cm<sup>3</sup> of methanol. 8 cm<sup>3</sup> of BRB pH 12 were added and the DPV of resulting solution was recorded. The next step was trying to achieve the lowest possible LOD in model samples of drinking and Vltava river water. We have started with exactly the same settings, extracting 100 cm<sup>3</sup> of drinking and river water and performed the voltammetric determination in a solution of  $2 \text{ cm}^3$  of eluate and 8 cm<sup>3</sup> of BRB. To further increase the sensitivity of the method even more we have passed 1  $dm^3$  of the sample through the cartridge. Finally, we have started with 1  $dm^3$  of model sample, eluted the cartridge with  $2 \text{ cm}^3$  methanol, evaporated the resulting eluate and re-dissolved the residue in 1 cm<sup>3</sup> of mixture of 20% methanol and 80% BRB pH 12. This procedure gave satisfactory results for drinking water (Fig. 1), but in river water, high humic acid concentration interfered with the signal of the substance so only nanomolar and higher concentrations could be determined (Fig. 2). To circumvent this problem we have tried to adjust the pH to 2 by the addition of hydrochloric acid in hope to reduce the solubility of humic acid. However, results were not satisfactory. Addition of disodium EDTA to break up humic acid - metal complexes (we have suspected they were actually the interfering species) was also fruitless. Increasing the pH was not practical due to the possible dissolution of the silica gel used as support of the stationary phase of the SPE cartridges. Contrary to our expectations we have succeeded by adjusting the pH of the sample to the value slightly below neutral. When adjusting the pH to 6 prior to SPE the signal of the substance was free of humic acid interference, but the repeatability suffered greatly so even this method was not too suitable for practical determination of subnanomolar concentrations of AC (Fig. 3). The results of the determinations are summarized in Table 1.



Fig. 1. DP voltammograms of AC at m-AgSAE after SPE from 1 dm<sup>3</sup> of model sample of drinking water. Eluate was evaporated and dissolved in 1 cm<sup>3</sup> of mixture of 20% methanol and 80% BR buffer pH 6. AC concentration in drinking water model sample 0 (1) 0.2 (2), 0.4 (3), 0.6 (4), 0.8 (5) and 1 (6) nmol·dm<sup>-3</sup>



Fig. 2. DP voltammograms of AC at m-AgSAE after SPE from 1 dm<sup>3</sup> of model sample of Vltava river water. 2 cm<sup>3</sup> of methanolic eluate was mixed with 8 cm<sup>3</sup> of BR buffer pH 12. AC concentration in model river water sample was 0 (1) 2 (2), 4 (3), 6 (4), 8 (5) and 10 (6) nmol·dm<sup>-3</sup>



Fig. 3. DP voltammograms of AC at m-AgSAE after SPE from 1 dm<sup>3</sup> of model sample of Vltava river water with pH adjusted to 6. 2 cm<sup>3</sup> of methanolic eluate were evaporated to dryness and dissolved in 1 cm<sup>3</sup> of mixture of methanol - BR buffer pH 12 (2:8). AC concentration in Vltava water model sample was 0 (1), 0.2 (2) 0.4 (3) 0.6 (4) 0.8 (5), and 1 (6) nmol·dm<sup>-3</sup>. The corresponding calibration dependence showing very low repeatability is in the inset

Table 1

Parameters of calibi	ation straight li	ines for direct	determination	of AC in w	ater samples
	6				

c [mol·dm <sup>-3</sup> ]	Technique	Water	k [nA·mol <sup>-1</sup> ·dm <sup>3</sup> ]	q [nA]	σ [nA]	R	LOD [mol·dm <sup>-3</sup> ]
$(2-10) \cdot 10^{-6}$	direct DPV	drinking	$-3.82 \cdot 10^{6}$	3.9		-0.9994	
$(2-10) \cdot 10^{-7}$	direct DPV	drinking	$-4.32 \cdot 10^{6}$	-0.32	0.048	-0.9970	8·10 <sup>-7</sup>
$(2-10) \cdot 10^{-6}$	direct DPV	river	$-4.82 \cdot 10^{6}$	1.9		-0.9983	
$(2-10) \cdot 10^{-7}$	direct DPV	river	$-3.51 \cdot 10^{6}$	-0.15		-0.9901	
$(2-10) \cdot 10^{-8}$	direct DPV	river	$-5.14 \cdot 10^{6}$	-0.016	0.036	-0.9754	2.3.10-8
$(2-10) \cdot 10^{-8}$	DPV/SPE 100 cm <sup>3</sup>	deionized	$-35.2 \cdot 10^{6}$	0.08	0.288	-0.9918	2.7.10-8
$(2-10) \cdot 10^{-8}$	DPV SPE 100 cm <sup>3</sup>	drinking	$-41.5 \cdot 10^{6}$	0.014	0.296	-0.9988	$2.4 \cdot 10^{-8}$
$(2-10) \cdot 10^{-9}$	DPV SPE 1 dm <sup>3</sup>	drinking	$-4.90 \cdot 10^8$	0.61	0.13	-0.9954	$9.10^{-10}$
$(2-10) \cdot 10^{-10}$	DPV SPE 1 dm <sup>3</sup>	drinking	$-1.65 \cdot 10^{9}$	0.001	0.08	-0.9961	$1.6 \cdot 10^{-10}$
$(2-10) \cdot 10^{-8}$	DPV SPE 100 cm <sup>3</sup>	river	$-4.66 \cdot 10^7$	-0.51	0.304	-0.9986	$2.2 \cdot 10^{-8}$
$(2-10) \cdot 10^{-9}$	DPV SPE 1 dm <sup>3</sup>	river	$-3.83 \cdot 10^8$	-0.034	0.218	-0.9952	$1.9 \cdot 10^{-9}$
$(2-10) \cdot 10^{-10}$	DPV SPE 1 dm <sup>3</sup>	river					

c - AC concentration, k - the slope of the calibration dependence, q - the intercept of the calibration dependence,  $\sigma$  - the standard deviation of ten consecutive measurements of the lowest calibration point, R - the correlation coefficient of the calibration data, LOD - the limit of detection

# Conclusions

The new method for the determination of AC by DPV at m-AgSAE after preliminary separation and preconcentration using SPE has been successfully developed. The calibration dependencies are linear in the concentration range from  $2 \cdot 10^{-10}$  to  $1\cdot 10^{-6}$  mol·dm<sup>-3</sup> in drinking water and  $2\cdot 10^{-9}$  to  $1\cdot 10^{-6}$  mol·dm<sup>-3</sup> in Vltava river water. The detection limits obtained are  $1.6 \cdot 10^{-10}$  mol·dm<sup>-3</sup> in drinking water and  $1.9 \cdot 10^{-9}$  mol·dm<sup>-3</sup> in river water. The effectiveness of the method was demonstrated by successful determination of trace amounts of AC in spiked drinking water and river water samples. Due to its high sensitivity and simplicity the new method can be a useful alternative to chromatographic methods for the purpose of screening for AC residues in the environment. The method is sensitive and fast, it is performed on a portable electrochemical instrument (Palmsens), and it would be easy to make the method as a whole suitable for field measurements by employing a pipette tip SPE as in [29]. This is possible due to the increased mechanical stability of m-AgSAE compared to traditional electrodes utilizing liquid mercury. Due to the use of m-AgSAE this method is more sensitive than comparable methods using f-AgSAE [22] and BDDE [24] and the electrode is less prone to passivation and easier to maintain. This is even more true when compared to the more sensitive but much more complex electrochemical nanobiosensors [15-17].

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