

Sensitive voltammetric method for determination of herbicide triasulfuron using silver solid amalgam electrode



Lenka Bandžuchová^{a,*}, Renáta Šelešovská^a, Tomáš Navrátil^b, Jaromíra Chýlková^a

^a University of Pardubice, Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering, Studentská 573, 532 10 Pardubice, Czech Republic

^b J. Heyrovský Institute of Physical Chemistry of the ASCR, v.v.i, Dolejškova 3, 182 23 Prague 8, Czech Republic

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ABSTRACT

Voltammetric behavior of triasulfuron (TS), sulfonylurea herbicide, was investigated using mercury meniscus modified silver solid amalgam electrode (m-AgSAE) and hanging mercury drop electrode (HMDE). It was found that TS provided one well-developed reduction peak and the highest current response was recorded in Britton–Robinson buffer of pH 3 (m-AgSAE) and 2.5 (HMDE), respectively. Differential-pulse voltammetry (DPV) with optimized working parameters was applied for analysis of model solutions containing TS with good sensitivity ($LD(m-AgSAE) = 6.4 \times 10^{-8} \text{ mol L}^{-1}$ and $LD(HMDE) = 2.7 \times 10^{-9} \text{ mol L}^{-1}$, respectively). Proposed method was successfully applied in analysis of herbicide preparation and river water.

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1. Introduction

Triasulfuron (TS, Fig. 1, CAS: 82097-50-5) is a member of group of sulfonylurea herbicides firstly introduced by DuPont Agricultural Products in 1982 [1]. This group of herbicides is wide-spread used all over the world in more than 40 countries [1]. The main reasons for their rapid acceptance are very low acute and chronic mammalian toxicity, but extremely high phytotoxicity to weeds, low application rate and broad-spectrum weed control [2,3]. TS and other members of this group of herbicides act through inhibition of enzyme acetolactate synthase (EC 4.1.3.18), which is a key enzyme in biosynthesis of the branched-chain amino acids (valine, leucine, and isoleucine). It leads to rapid break of cell division and growth [2–4]. It was confirmed that TS provided excellent weed control at low rates (10–30 g TS/10,000 m²). TS is mostly used in commercial preparation for protection of barley, oat, wheat or rye [5].

Detention and retention processes are among the most important factors influencing the fate of used agrochemicals in the environment. TS, as the other sulfonylureas, is a weak acid readily soluble in water, very mobile in soils, more persistent in neutral or weakly alkaline media and susceptible to hydrolysis in media of

acidic pH [4,6–10]. Cleavage of the sulfonylurea bridge was identified as the main degradation pathway of TS [10]. Many papers, e.g. [11–15], dealt with degradation of TS in various types of soils. It was found that soil pH, soil type, depth, presence of microorganisms, application rate or rainfalls play very important role in the degradation of the mentioned herbicides [11–15]. The degradation time for 50% of TS ($DT_{50}(TS)$) was found longer under laboratory conditions in sterile soils than under field conditions in non-sterile soils, e.g., James et al. found $DT_{50}(TS)$ from 31 to 44 days in five controlled temperatures/soil moisture regimes (10–30 °C and 40–80%, respectively) under laboratory conditions. However, the half-lives in the field were considerably shorter (12–13 days) [14]. Residues of the TS and other sulfonylureas are usually determined by various chromatographic methods, e.g., high performance liquid chromatography (HPLC) [7,10,12,13], reversed phase HPLC [4], liquid chromatography in connection with UV or mass spectroscopy [16], affinity chromatography [17], micellar electrokinetic capillary chromatography [18], gas and gel permeation chromatography [14]. Beside chromatographic methods capillary electrophoresis [9,19], capillary zone electrophoresis [20] or immunoassay methods [21,22] were proposed for determination of TS.

Electrochemical methods represent a suitable alternative to the above mentioned techniques, particularly due to the relatively low costs of instrumentation, possibility of miniaturization and fast and sensitive performance of analysis. Only a few papers dealing with electrochemical behavior or determination of sulfonylurea

* Corresponding author. Tel.: +420 466038080.

E-mail addresses: lenka.bandzuchova@upce.cz, lenicka.b@seznam.cz (L. Bandžuchová).

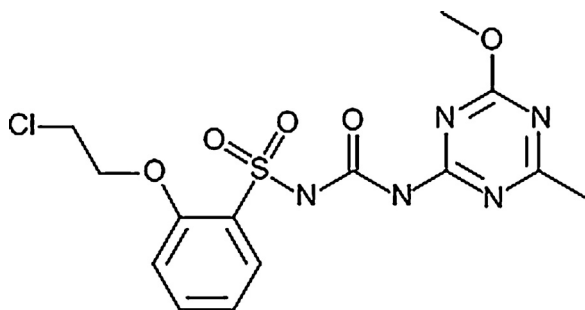


Fig. 1. The chemical structure of triasulfuron.

herbicides have been published. Olmedo et al. described electrochemical behavior of herbicide tribenuron with dropping mercury electrode (DME) using DC, tast and DP polarography and with hanging mercury drop electrode (HMDE) using adsorptive stripping voltammetry (AdSV) [23]. Tribenuron provided 2 reduction signals, but only the first one ($E_{p1} = -1150$ mV vs. SCE in medium of pH 4) was suitable for analytical purposes. The reduction mechanism of tribenuron was described as a $4H^+/4e^-$ reduction. The proposed method (AdSV) exhibited high sensitivity ($LD = 2.6 \mu\text{g L}^{-1} = 6.6 \text{ nmol L}^{-1}$) and it was applied for analysis of agricultural preparations [23]. Authors Sarigul and Inam studied two members of sulfonylurea herbicides cyclosulfamuron [24] and TS [25] on static mercury drop electrode (SMDE). Voltammetric behavior of cyclosulfamuron was examined using cyclic (CV) and square-wave voltammetry (SWV). This compound provided one well-defined reduction signal ($E_p = -1350$ mV vs. Ag/AgCl, pH 6) in media of pH 3–7. SWV was utilized for determination of cyclosulfamuron in agricultural preparations and tap water with good sensitivity ($LD = 3.5 \mu\text{g L}^{-1} = 8.3 \text{ nmol L}^{-1}$) [24]. Electrochemical behavior of TS was studied applying CV and differential pulse voltammetry (DPV) and it was found that TS provided also one well-developed reduction signal ($E_p = -1030$ mV vs. Ag/AgCl/NaCl (3 M), pH 3) in an acidic medium. DPV in connection with SMDE was evaluated as sensitive for TS determination ($LD = 0.15 \mu\text{mol L}^{-1}$). This method was successfully applied in analysis of pesticide formula, soil and dam water [25]. Authors also described the effect of heavy metals or other commonly used pesticides on voltammetric response of cyclosulfamuron and triasulfuron [24,25].

Development of new electrode materials which could replace liquid mercury, due to its alleged toxicity, is one of the trends of current electroanalytical chemistry in voltammetric measurements. Silver solid amalgam electrodes are very sensitive for voltammetric determinations of reducible compounds and exhibit high hydrogen overvoltage like mercury electrodes, but they are mechanically stable and made from non-toxic solid material (alloy) like solid electrodes [26–29]. Solid amalgam electrodes can be formed in different forms (polished, paste, meniscus covered, composite) and the amalgams can be prepared from different metals (Au, Cu, Ag, Sb, etc.). The most suitable added materials (in case of paste and composite SAEs) and chosen amalgam forming metals can be applied in dependence on determined material. The additives define wider or narrower potential window [29–33]. The silver solid amalgam electrodes (AgSAE) described in [26–28] in various modifications have been already utilized as an efficient tool in voltammetric analysis of, e.g., heavy metals [26–30], inorganic anions [28–30], organic nitro compounds [31–36], carcinogens [34,37,38], antineoplastic drugs [39–41,43–45], DNA [42–44,46–49], peptides [45–47], vitamins [32,47–50], and folate structure compounds [39,40,47,48].

The voltammetric behavior of TS has been examined using m-AgSAE and HMDE in the present paper. Various voltammetric techniques have been applied for voltammetric monitoring of this herbicide. Optimum working conditions for DPV determination of

TS were found and proposed sensitive method was applied in analysis of real samples containing TS.

2. Experimental

2.1. Materials

All chemicals used for preparation of supporting electrolytes, standard and other solutions were of p.a. purity. All solutions were prepared in deionized water from Milli-Q-Gradient, Millipore, Prague, Czech Republic (conductivity $< 0.05 \mu\text{S cm}^{-1}$). The Britton–Robinson (BR) buffers of pH values from 1.8 to 9 were prepared by mixing the alkaline component consisting of 0.2 mol L^{-1} NaOH (Lachema, Brno, Czech Republic) with the acidic component which consisted of 0.04 mol L^{-1} H_3PO_4 , 0.04 mol L^{-1} H_3BO_3 and 0.04 mol L^{-1} CH_3COOH (all p.a., Lachema, Brno, Czech Republic). 0.04 mol L^{-1} H_2SO_4 was prepared by dissolution of an appropriate amount of 98% H_2SO_4 (Penta, Czech Republic) in deionized water. Triasulfuron (Sigma–Aldrich) was dissolved in 50% acetonitrile (Lach-ner, Czech Republic) and the standard solution of concentration $1 \times 10^{-3} \text{ mol L}^{-1}$ was stored in glass flask in a refrigerator. The solution of 2 mol L^{-1} KCl was prepared by dissolution of the appropriate amount of KCl (Lachema, Brno, Czech Republic). Herbicide formula “Logran® 20WG” with content of TS 200 g/kg was provided by Syngenta (Syngenta Crop Protection AG, Basel, Switzerland). The river water was sampled from the river Elbe (Labe) in the city of Pardubice, Czech Republic.

2.2. Instrumentation

All voltammetric measurements were carried out with the computer controlled Eco-Tribo Polarograph PC-ETP (Eco-Trend Plus, Prague, Czech Republic) equipped by software POLAR.PRO (version 5.1) for Windows XP. All measurements were provided in a 3-electrodes set up, where m-AgSAE (working surface: 0.39 mm^2) and HMDE (working surface: 0.73 mm^2) (both Eco-Trend Plus, Prague, Czech Republic) served as the working electrodes, silver/silver chloride/saturated KCl (Ag/AgCl/KCl (sat.)) as the reference and platinum wire as the auxiliary electrode (both Monokrystaly, Turnov, Czech Republic). Air oxygen was removed from solutions by bubbling for 5 minutes by nitrogen (purity class 4.0; Linde, Prague, Czech Republic) before every analysis. The pH values were measured by pH-meter Hanna 221 (Hanna Instruments, Inc., USA). Solution of “Logran® 20 WG” was prepared using ultrasonic bath Bandelin Sonorex (Schalltec GmbH, Germany). All the measurements were carried out at laboratory temperature.

2.3. Procedures

2.3.1. Preparation and pretreatment of the working amalgam electrode

The preparation and pretreatment of m-AgSAE is described more in detail in our previous papers [43,44,50–53]. The parameters of the electrochemical regeneration of the amalgam electrode surface before each measurement were incorporated directly into the controlling software. Optimum conditions found for the surface regeneration of m-AgSAE in BR buffer (pH 3) for determination of TS were 30 regeneration cycles between 0 and -1400 mV (the limiting potentials were kept constant for 0.3 s in each cycle).

2.3.2. Voltammetric measurements

CV (cyclic voltammetry) was used for investigation of dependence between voltammetric response of TS and pH of the supporting electrolyte. DCV (direct current voltammetry) was utilized for studying the effect of scan rate on voltammetric behavior of TS. DPV (differential pulse voltammetry) with pulse height of

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