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Electro-oxidation of herbicide halosulfuron methyl on glassy carbon electrode and applications

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ABSTRACT

Halosulfuron methyl, a fast-acting herbicide and is absorbed into leaf tissue within 1–2 days and translocated through the vascular system, interrupting amino acid production within the plant, can be detected using glassy carbon electrode the technique of adsorptive stripping voltammetry. The adsorptive stripping voltammetric behavior of halosulfuron methyl was investigated in pH range 1.0–10.0. Halosulfuron methyl was irreversibly oxidized at a glassy carbon electrode. Electrochemical techniques including adsorptive stripping voltammetry and cyclic voltammetry were employed to study the oxidation mechanism. The experimental parameters such as the accumulation potential, accumulation time and frequency were optimized. The linear range, detection limit and quantification for halosulfuron methyl were evaluated by adsorptive stripping voltammetry. Under the optimized conditions, the peak current is linear to halosulfuron methyl concentration in the range 4.1–50.0 μg mL^{-1}. Limit of detection and limit of quantification were 1.23 and 4.10 μg mL^{-1}, respectively. The interference of inorganic species and other some pesticides on the voltammetric response have been studied. The applicability to spiked soil and natural water was described and the recoveries for the standards added are 103.8% and 108.2%, respectively. The method is successfully applied for the determination of halosulfuron methyl in commercial formulation.

1. Introduction

Sulfonylurea herbicides were developed in the mid-1970s by DuPont and first commercialized for wheat and barley crops in 1982. This class of herbicides are spread over 20 compounds, and widely used as control chemicals for most broad-leaved weeds and common grasses in agricultural crops. Sulfonylurea herbicides are characterized by their effectiveness in very low doses, excellent selectivity, and low mammalian toxicity [1]. However, under persistent conditions, residues can affect the growth of susceptible plants more than 1 year after application, because of their high phytotoxicity [2]. Sulfonylureas are weak acids and have p*K*a values generally ranging from 3 to 5. They exist in aqueous solution primarily in the neutral form at pH values below p*K*a, and in the anionic form at pH levels above the p*K*a. Therefore, the herbicides are predominantly anionic in most agricultural soils, and the relative concentrations of the neutral form are greatest in soils of low pH [3]. Sulfonylurea herbicides are subject to pH-dependent hydrolysis of the sulfonylurea linkage and the hydrolysis half-lives ($t_{1/2}$) for several sulfonylurea herbicides are reported by Sarmah and Sabadie [4]. Compared to other herbicides, sulfonylureas and ureas are used in much lower concentrations and are degraded in soil more rapidly. Therefore, there is an increasing need for rapid, reliable methods to measure trace levels of these compounds in crops, soil and in natural waters to minimize the risks associated with pesticide use.

Halosulfuron-methyl chemically known as methyl 3-chloro-5-[(4,6-dimethoxypyrimidin-2-yl) carbamoylsulfamoyl]-1-methylpyrazole-4-carboxylate), is a member of the sulfonylurea family which inhibit the actions of plant enzymes thus stopping plant growth. It is a fast-acting sulfonylurea herbicide and is absorbed into leaf tissue within 1–2 days and translocated through the vascular system, interrupting amino acid production within the plant (Scheme 1).

Environmental Protection Agency (EPA) established tolerances for halosulfuron-methyl of 0.05 parts per million (ppm) in field corn grain and sorghum grain and forage; 0.2 ppm for field corn forage; 0.8 ppm for field corn fodder; and 0.1 ppm for sorghum fodder. Halosulfuron-methyl and some of its degradation species have soil adsorption coefficients (Koc's) of less than 400. This indicates high soil mobility and therefore a high capacity to leach through soil and contaminate groundwater. Hydrolysis of halosulfuron-methyl

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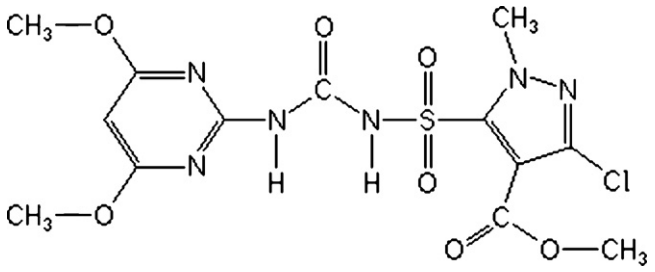


Scheme 1. Structure of halosulfuron-methyl.

is pH dependent, with a hydrolytic half-life of 27 days at pH 5, 14 days at pH 7, and 0.75 days at pH 9.

A number of analytical techniques, mostly chromatographic methods, are reported in the literature for the analysis of sulfonylurea herbicides. High performance liquid chromatography (HPLC) with ultraviolet detector or diode array detector was the most common approaches used [5,6], other methods such as liquid chromatography with mass spectrometry [7–9], capillary electrophoresis [10,11], supercritical fluid chromatography [12], bioassay [13] and enzyme immunoassay [14] are also reported.

Some electrochemical methods such as differential pulse polarography (DPP) [15–17] and square wave voltammetry (SWV) on a hanging mercury drop electrode [18] were described for the determination of sulfonylurea herbicides. Only a few works for the determination of halosulfuron in water samples [9] and vegetables [19] using HPLC were reported in the literature. To the best of our knowledge, no publications of electroanalytical techniques for halosulfuron quantification were available in the literature. The electrochemical behavior of halosulfuron methyl on glassy carbon electrode was established and studied for the first time. Electroanalytical methods are known to attend the demand for minimal sample treatment and low consumption of organic solvents. On the other hand, the voltammetric procedures have other advantages such as their low cost, short time for analysis, possibility of analysis without the need of extraction or pre-treatments, useful applications in kinetic and equilibria studies.

The aim of this work was the development of new, rapid, simple, selective and inexpensive square wave voltammetric method at a glassy carbon electrode for the direct determination of halosufuron in real samples without any time-consuming extraction or evaporation steps prior to herbicide assay. The voltammetric behavior and oxidation mechanism of halosulfuron methyl using the cyclic and SWV techniques were also described.

2. Material and methods

2.1. Apparatus

The square wave voltammograms were obtained with a Bioanalytical Systems-epsilon potentiostat/galvanostat (BAS, West Lafayette, IN, USA) analyzer coupled with a BAS C-3 solid electrode cell stand. A three-electrode system was used, consisting of a platinum counter electrode, an Ag/AgCl (3 mol L^{-1} NaCl) reference electrode and BAS MF-2012 glassy carbon electrode (GCE) as a working electrode. All the experiments were performed at room temperature. pH was measured with a Hanna HI 8521 (Hanna Instruments, Singapore) pH meter with combined glass electrode.

2.2. Reagent

A stock solution of 500 μg mL^{-1} halosulfuron methyl (with a purity of 99.5%) was prepared by dissolving halosulfuron methyl in 50% acetone–water and diluting to 10.0 mL. Working solutions were prepared by diluting appropriate amount of this stock in distilled water and stored in dark at 4 °C. Salts used for supporting electrolyte, solvents and other reagents were of analytical reagent grade (Merck, Darmstandt, Germany). Britton–Robinson buffer (B–R buffer) solutions were prepared from a stock solution containing 0.04 mol L^{-1} phosphoric, boric and acetic acids (Merck) by adding appropriate amount of 2 mol L^{-1} NaOH to obtain pH values ranging from 2 to 10.

2.3. Analytical procedure

The glassy carbon electrode was thoroughly cleaned before use and between scans by polishing with alumina on a polishing pad (BAS microcloth pads, MF-1040), followed by a rinse with water, then dilute acid, ethanol, followed by a rinse with distilled water. The voltammetric response of halosulfuron methyl at glassy carbon electrode (GCE) was obtained in H_2SO_4 and B–R buffers with pH varying in the range of 3.0–5.0. The optimum of pH 1.0 (H_2SO_4) for the halosulfuron methyl analysis was selected by the maximum peak current value obtained. For this purpose, 10.0 mL of supporting electrolyte solution of H_2SO_4 was placed into the voltammetric cell and de-oxygenated with high-purity nitrogen (99.999%) for ca. 5 min. The analytical curves for halosulfuron methyl were obtained by standard addition of the pesticide into the electrolyte.

The selected accumulation potential (E_{acc} = +200 mV) was applied during the accumulation period (t_{acc} = 60 s) while the solution was kept under stirring and nitrogen atmosphere. The voltammograms were obtained by scanning the potential from +200 mV to ca. +1700 mV to (versus Ag/AgCl). The quantifications were performed by the standard addition method, from the SW peak obtained at +1525 mV versus Ag/AgCl (pH 1.0; 20 ± 2 °C). The square wave parameters used were a frequency (f) of 200 Hz, amplitude (ΔE) of −50 mV and staircase step (ΔE_s) of 6 mV. Halosulfuron methyl spiked in soil and dam water samples was successfully determined from the peak appeared at +1525 mV (versus Ag/AgCl).

3. Result and discussion

3.1. Square wave voltammetric behavior of halosulfuron methyl

The cyclic voltammetric behavior of halosulfuron methyl was studied at a concentration level of 50 μg mL^{-1} in 0.1 mol L^{-1} H_2SO_4. The cyclic voltammogram showed that this pesticide exhibited a peak of oxidation at potential of +1540 mV versus AgCl/Ag. The absence of any cathodic peak on the reverse scan indicated the irreversibility of the electrode process at scan rate 200 mV/s (Fig. 1). According to our previous experiments, no oxidation or reduction

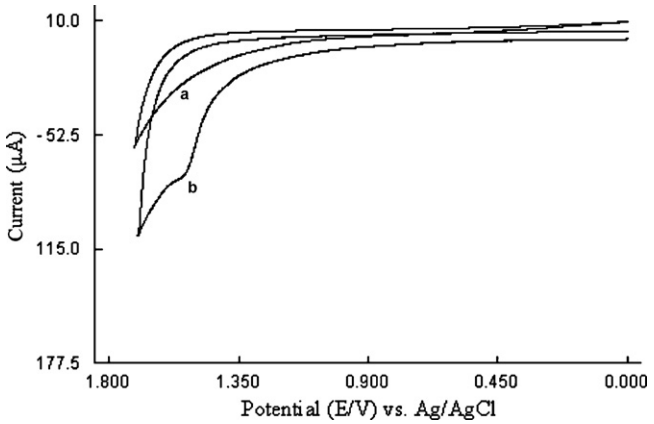


Fig. 1. Cyclic voltammogram of: 50 μg mL^{-1} halosulfuron methyl at 0.1 mol L^{-1} H_2SO_4 (scan rate: 200 mV/s). (a) 0.1 M H_2SO_4; (b) 50 μg mL^{-1} halosulfuron methyl.

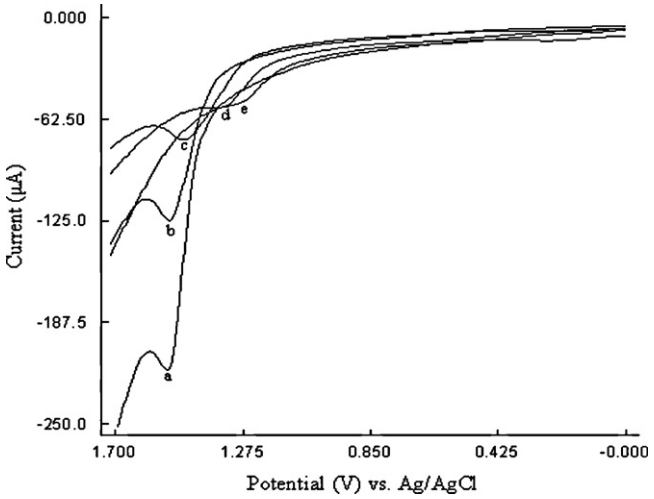


Fig. 2. SWS voltammograms of: 20 μg mL^{-1} halosulfuron methyl in different pH. (a) In 0.1 mol L^{-1} H_2SO_4; (b) in 0.01 mol L^{-1} H_2SO_4; (c) in pH 3.0 B–R buffer; (d) in pH 4.0 B–R buffer; (e) in pH 5.0 B–R buffer.

peak was observed on mercury electrode within the full potential range of 0.0 to −1500 mV.

The influence of the scan rate (υ) on the peak potential (E_p) was studied within the range 10–2000 mV/s. The peak potential shifted to the more positive in the anodic direction when the scan rate increased according to the following equations for 10–2000 mV/s.

$$E(\text{mV}) = 0.2293\upsilon(\text{mV/s}) + 1498.3 \quad r = 0.984 \quad (10 - 200\text{mV/s})$$

$$E(\text{mV}) = 0.0216\upsilon(\text{mV/s}) + 1539.2 \quad r = 0.991 \quad (200 - 2000\text{mV/s})$$

This observation also supported the irreversibility of the electrode process obtained from Fig. 1.

The dependence of peak current (I_p) on scan rate (υ) was studied in the range 10–2000 mV/s, to assess whether the processes on glassy carbon electrode were under diffusion or adsorption controlled. A linear relationship was observed between peak current and square root of the scan rate corresponding to the equation:

$$I_p(\mu\text{A}) = 0.9653\upsilon^{1/2} - 4.9405 \quad r = 0.990$$

A plot of logarithm of peak current ($\log I_p$) versus logarithm of scan rate range ($\log \upsilon$) gave a straight line. The linear relationship was obtained as follows:

$$\log I_p = 0.77 \log \upsilon - 0.9095 \quad r = 0.988$$

The slope of 0.77 between the theoretical value of 0.5 (diffusion controlled) and 1.0 (adsorption controlled) is expressed for the mixed or mainly adsorption controlled electrode process [20].

The influence of pH on the voltammetric behavior of halosulfuron methyl has been studied using SWSV in the pH range of 1–10. Halosulfuron methyl exhibited a single oxidation peak over the pH range of 1.0–5.0. No cathodic peak was appeared on the reverse scan. The peak current exhibited a maximum intensity in 0.1 mol L^{-1} H_2SO_4 (Fig. 2).

The plot of the peak potential (E_p) versus pH showed two linear segments with a break at pH 3.0 (Fig. 3), which corresponded to the p*K*a value of halosulfuron methyl, and their slopes were 24.7 and 82.1 mV, respectively. The linear segments can be expressed by the following regression equations:

$$E(\text{mV}) = -24.7\,\text{pH} + 1554.9 \quad r = 0.952$$

$$E(\text{mV}) = -82.1\,\text{pH} + 1706 \quad r = 0.944$$

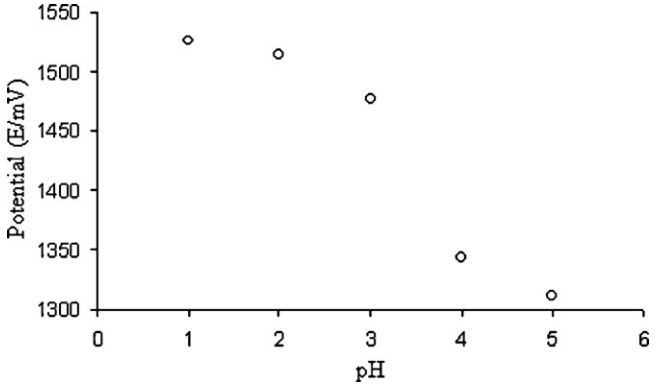


Fig. 3. Dependence of peak potentials of 20 μg mL^{-1} halosulfuron methyl in different pH.

The p*K*a value of halosulfuron methyl which is 3.44 is close to our experimental value. There was no oxidation peak for the molecule at pH higher than about 5.0.

The potential shift to less positive values with increasing pH was not so effective at pH lower than p*K*a. It can be concluded that the electro active-grouping responsible for the oxidation process was in acid–base equilibrium with p*K*a of about 3.

Square wave frequency (f) is of the utmost importance in SWV since it determines the intensity of the signal and, in turn, the sensitivity of the technique. Moreover, for that type of system the peak potential should vary linearly with the logarithm of the frequency following the relationship [21]:

$$\frac{\Delta E_p}{\Delta \log f} = \frac{2.3\text{RT}}{\alpha n F}$$

where α is the transfer coefficient and n is the number of electrons involved in the reaction. Fig. 4 shows the dependence of E_p with $\log f$.

$$E_p(\text{V}) = 0.0512 \log f + 1.4361 \quad r = 0.973$$

By means of this equation, a value 1.1533 was determined for αn. Therefore n was calculated 2, if the value of α regard as 0.5 for irreversible reactions.

Halosulfuron methyl was electroactive in acidic solution, because anodic oxidation in aqueous sulphuric acid leads to loss of the methoxy substituent. The elimination of methanol is catalyzed by protons by a mechanism illustrated in Scheme 2. This behavior indicated the involvement of protons in the rate determination step and proton transfer precedes the electron transfer [22].

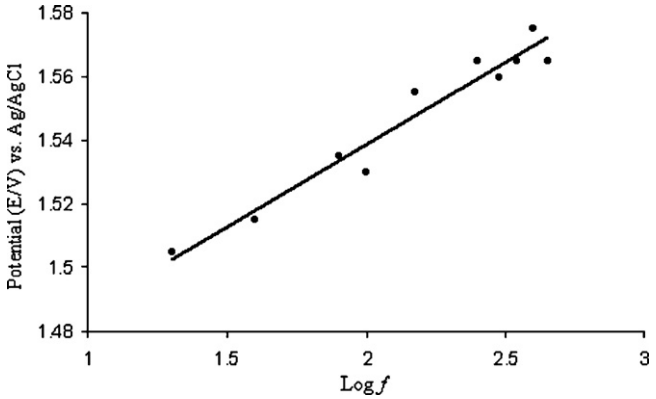
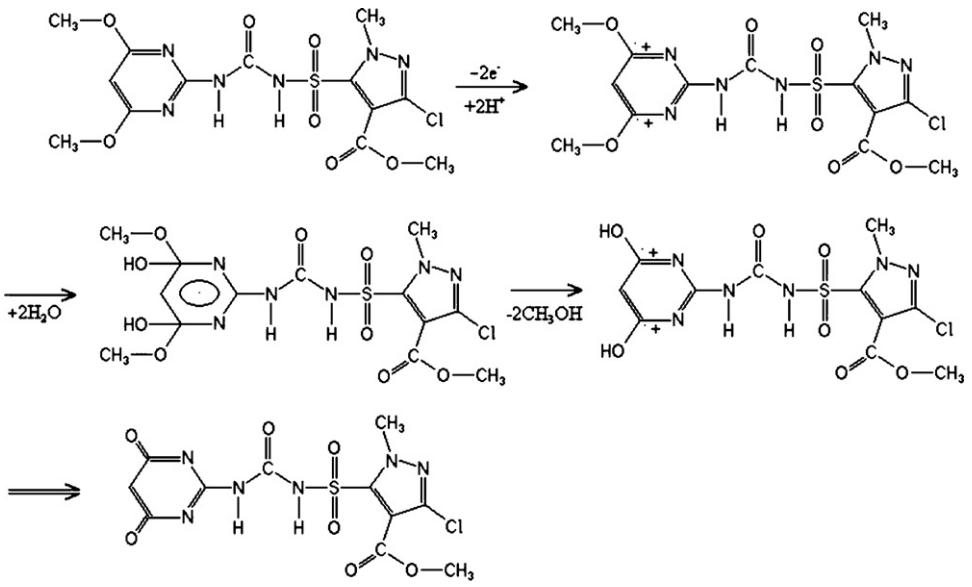


Fig. 4. Linear dependence of the peak potential with the logarithm of square wave frequency.



Scheme 2. Oxidation mechanism of halosulfuron methyl.

3.2. Quantitative study

For the optimizations of instrumental conditions, the square wave frequency (f), the step potential (ΔE_s), and the pulse amplitude (ΔE) were examined. The variable ranges were: 1–10 mV for the step potential; 20–450 Hz for the frequency and 10–100 mV for the pulse amplitude. The peak current increases by increasing all of these instrumental parameters. However, the baseline current also increased. Finally, the conditions selected were $\Delta E_s = 6$ mV, $f = 200$ Hz and $\Delta E = -50$ mV owing to the regularity of current responses.

The dependence of peak current on deposition time was studied between 15 and 120 s. Within this range the peak current increase by increasing deposition time. However, longer deposition times gave broad and irregular peaks, and thus a deposition period of 60 s was selected for further investigations. Initial deposition potential (E_d) is an important parameter in controlling the peak characteristics. The voltammograms of halosulfuron were obtained after applying different deposition potentials in the range of 0–1600 mV. The peak current decreased with increasing deposition potential from 200 to 1600 mV. The maximum value of peak current was obtained at +200 mV at study of influence of the deposition potential. This value was chosen as deposition potential. Relationship between peak current and concentration was studied using the selected conditions. The peak currents obtained from voltammograms were linearly related to pesticide concentration between 4.1 and 50 $\mu g\,mL^{-1}$ (Fig. 5).

Relationship between peak current and concentration is given by the following equation (Fig. 6):

$$I(\mu A) = 2.2505C\ (\mu g\ mL^{-1}) + 39.508(\mu A) \quad r = 0.991$$

Limit of detection (LOD) and limit of quantification (LOQ) were obtained as 1.23 $\mu g\,mL^{-1}$ and 4.10 $\mu g\,mL^{-1}$, respectively (Table 1). LOD and LOQ were calculated using the following equations [23]:

$$LOD = 3s/m \quad LOQ = 10s/m$$

where s is the standard deviation of peak current and m is the slope of the calibration curve. As seen from Table 1, LOD and LOQ values obtained in supporting electrolyte is about one-third of the dam and soil water. The difference in sensitivities could be attributed to the matrices effect resulting from the real samples.

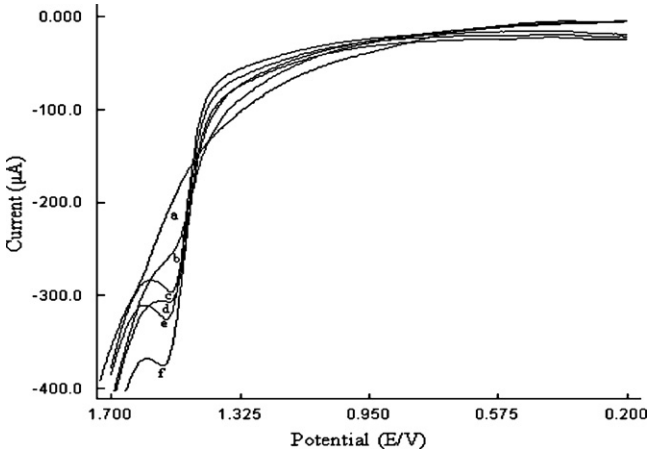


Fig. 5. Square wave voltammograms obtained for the determination of halosulfuron methyl. (a) 10 mL 0.1 mol L^{-1} H_2SO_4; (b) 2.5 $\mu g\,mL^{-1}$ halosulfuron methyl; (c) 20 $\mu g\,mL^{-1}$ halosulfuron methyl; (d) 25 $\mu g\,mL^{-1}$ halosulfuron methyl; (e) 30 $\mu g\,mL^{-1}$ halosulfuron methyl; (f) 40 $\mu g\,mL^{-1}$ halosulfuron methyl

3.3. Interference study

For the analysis of complex matrices such as soil samples or environmental water, there is possibility of interferences from other species present in the sample. The influence of some inor-

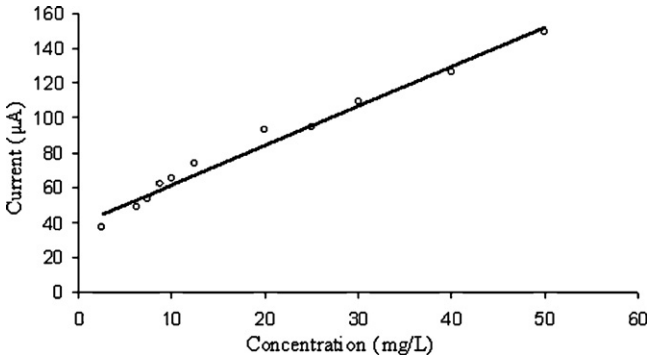


Fig. 6. Dependence of concentration on peak current of halosulfuron methyl.

Table 1
Regression data of the calibration equation for determination of halosulfuron methyl by SWSV.

Parameter	Supporting electrolyte	Dam water		Soil
Measured potential (mV)	1525.6	1658		1656
Linearity range ($\mu g\,mL^{-1}$)	4.1–50	1.4–4.0	4.0–30.0	1.4–20.0
Slope ($\mu A/\mu g\,mL$)	2.2505	15.41	3.5884	6.4739
S.E. of slope	0.10	1.29	0.21	0.31
Intercept (μA)	39.508	15.5	62.58	31.233
S.E. of intercept	2.50	3.52	3.07	2.86
Correlation coefficient	0.991	0.993	0.990	0.991
LOD ($\mu g\,mL^{-1}$)	1.23[a]	0.42[a]		0.43[a]
LOQ ($\mu g\,mL^{-1}$)	4.10[a]	1.40[a]		1.44[a]
Repeatability of peak potential (RSD, %)	0.28	0.17		0.41
Repeatability of peak current (RSD, %)	1.51	4.69		5.01

[a] $N = 5$.

ganic species and other pesticides was investigated; at halosulfuron methyl mass ratio 1:1, 2:1, and 5:1. As interfering species, some ions and other commonly used pesticides, e.g. anilazine and cyromazine were selected according to some criteria such as their mostly presence in natural samples and common usages, respectively. The sufficiently good recoveries could be attributed to the ions or pesticides in which they do not oxidize or form complex with the analyte species. Recovery results in the presence of co-existing species are shown in Table 2.

3.4. Determination of halosulfuron methyl in soil and dam water

The linear calibration plot in dam water was separate into two linear sections. The consecutive additions of halosulfuron methyl into dam water gave a linear relationship between the peak currents and concentrations in the range of 1.4–30.0 $\mu g\,mL^{-1}$ with the linear regression equation given by:

$$I(\mu A) = 15.41C(\mu g\ mL^{-1}) + 15.5 \quad r = 0.993$$

$$I(\mu A) = 3.59C(\mu g\ mL^{-1}) + 62.6 \quad r = 0.990$$

The consecutive additions of halosulfuron methyl into soil (Fig. 7) gave a linear relationship between the peak currents and concentrations in the range of 1.4–20.0 $\mu g\,mL^{-1}$ with the linear regression equation given by:

$$I(\mu A) = 6.47C(\mu g\ mL^{-1}) + 31.2 \quad r = 0.991$$

Regression data of calibration lines for quantitative determination of halosulfuron methyl soil and dam water were summarized in Table 1.

The propesed method was applied to the analysis of the halosulfuron methyl spiked in dam water and soil samples. The recoveries were estimated by measuring the peak currents of extracted spiked halosulfuron methyl and comparing them with peak currents obtained after the standard additions of the same concentrations. The results are shown in Table 3.

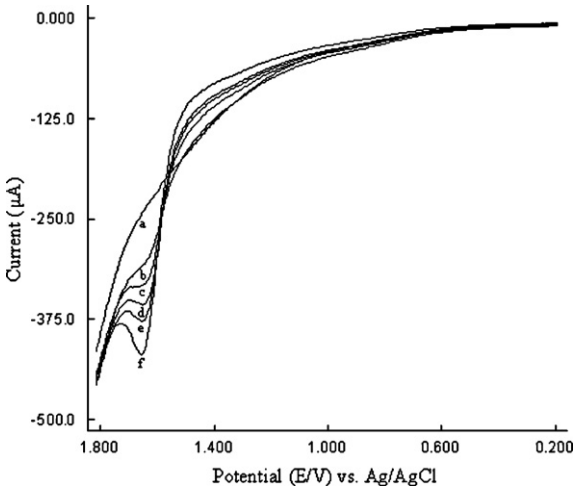


Fig. 7. SWS voltammograms for linear calibration curve in soil. (a) 9 mL 0.1 mol L^{-1} H_2SO_4 + 1 mL soil sample; (b) 2.0 $\mu g\,mL^{-1}$ halosulfuron methyl; (c) 4.0 $\mu g\,mL^{-1}$ halosulfuron methyl; (d) 6.0 $\mu g\,mL^{-1}$ halosulfuron methyl; (e) 10 $\mu g\,mL^{-1}$ halosulfuron methyl; (f) 20 $\mu g\,mL^{-1}$ halosulfuron methyl.

3.5. Application to agrochemical formulation

Pesticide formulation Inpul 75 WG (Sumitomo Corp., Japan) equivalent to 500 $\mu g\,mL^{-1}$ halosulfuron methyl was accurately prepared in a 10.0 mL of 50% acetonitryl solution. The halosulfuron methyl content in herbicide formulation was analyzed, by the standard addition method. These data are shown in

Table 2
Effect of inorganic species and other pesticides on the determination of halosulfuron methyl.

Interferent	Interferent:analyte-mass ratio	Recoveries (%)	Interferent:analyte-mass ratio	Recoveries (%)	Interferent:analyte-mass ratio	Recoveries (%)
Ni^{2+}	1:1	95.2	2:1	97.1	5:1	100
Co^{2+}	1:1	95.0	2:1	90.0	5:1	85.0
Zn^{2+}	1:1	94.7	2:1	94.7	5:1	92.6
Pb^{2+}	1:1	97.8	2:1	102.2	5:1	94.4
Cu^{2+}	1:1	97.2	2:1	92.9	5:1	90.0
Mg^{2+}	1:1	97.6	2:1	93.8	5:1	93.8
Na^{+}	1:1	97.7	2:1	100	5:1	105.9
NO_3^-	1:1	105.9	2:1	108.2	5:1	91.8
PO_4^{3-}	1:1	103.2	2:1	94.7	5:1	92.6
Anilazine	1:1	98.6	2:1	101.0	–	–
Cyromazin	1:1	105.3	2:1	98.5	–	–

Table 3
Determination of spiked halosulfuron methyl in soil and dam water samples.

Dam water					Soil				
Added ($\mu g\,mL^{-1}$)	Founded ($\mu g\,mL^{-1}$)	Recovery (%)	RSD (%)	Bias (%)	Added ($\mu g\,mL^{-1}$)	Founded ($\mu g\,mL^{-1}$)	Recovery (%)	RSD (%)	Bias (%)
–		–	–	–	–		–	–	–
10	10.67	106.7	2.45	6.7	10	10.91	109.1	0.78	9.1
15	15.88	105.9	1.80	5.9	15	16.39	109.3	0.66	9.3
20	21.10	103.8	2.72	3.8	20	21.64	108.2	0.89	8.2

$N = 3$.

Table 4
Results obtained for halosulfuron methyl in agrochemical formulation using SWSV and CV.

	SWSV	CV
Labeled claim (%)	75	75
Amount found (%)	79.6	74.4
RSD (%)	3.22	6.10
Bias (%)	6.08	0.40
$t_{calculated\ value}$	1.98[$t_{theoretical\ value} = 2.45$][a]	
$F_{calculated\ value}$	3.12[$F_{theoretical\ value} = 6.94$][a]	

[a] $N = 3$.

Table 4. The results obtained were compared statistically with cyclic voltammetric (CV) method using Student's *t*-distribution and variance ratio *F*-test. Statistical analysis of the results by both methods showed no significant difference between the performance of the two methods regarding the accuracy and precision.

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