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Original scientific paper

## Electrochemical determination of 5-dodecylsalicylaldoxime and 2'-hydroxy-5'-nonylacetophenone oxime in commercial extractants

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**Abstract:** A differential pulse voltammetric method using a hanging mercury drop electrode (HMDE) was optimized for the determination of 5-dodecylsalicylaldoxime in hydro-alcoholic solutions using factorial and central composite designs. The Taguchi design methodology was used to extend the formerly optimized method to the determination of 2'-hydroxy-5'-nonylacetophenone oxime. The method was successfully applied to quantify 5-dodecylsalicylaldoxime and 2'-hydroxy-5'-nonylacetophenone oxime in samples of commercial extractants over the concentration range 0.05–2.45 and 0.07–0.82 mg L<sup>-1</sup>, respectively, with detection limits of 0.034 and 0.019 mg L<sup>-1</sup>, respectively.

**Keywords:** voltammetry; hydroxyoxime-based extractants; factorial design.

### INTRODUCTION

5-Dodecylsalicylaldoxime (DSAO) is the active component of the commercial extractants LIX860, LIX860-I and LIX622. On the other hand, 2'-hydroxy-5'-nonylacetophenone oxime (HNAPO) is the active component of LIX84 and SME 529. These reagents, that are being mainly used for copper removal from industrial acidic effluents, are commercialized diluted in an organic solvent and they may contain small amounts of 4-nonylphenol (LIX84), 4-dodecylphenol (LIX860, LIX860-I and LIX622)<sup>1</sup> or modifiers, such as tridecyl alcohol (LIX622).<sup>1,2</sup>

In the study of fundamental metal extraction processes directed towards the determination of the stoichiometry of the extracted metal complexes and the values of their equilibrium constants, the composition of the extractants must be known. Consequently, it becomes necessary to develop methods for the quantification of the active component in industrial formulations since the manufac-

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turers usually do not provide precise information about the composition of commercial reagents.

Some electrochemical methods are reported in the literature for the analysis of the active components of several extractants. Thus, the electrochemical behaviour<sup>3,4</sup> and determination<sup>3</sup> of 4-methyl-*N*-quinolin-8-ylbenzenesulfonamide, a compound closely related to the active component in LIX 34 (4-alkaryl-*N*-quinolin-8-ylbenzenesulfonamide) were studied. The electrochemical quantification of 1-phenyldecane-1,3-dione<sup>5</sup> and 7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-quinolinol,<sup>6</sup> the active components of LIX 54 and Kelex 100, respectively, was also performed.

As far as hydroxyoxime-based extractants are concerned, GC and HPLC methods have been developed for either the identification or quantification of their active components.<sup>7–13</sup> Voltammetry has been used for both qualitative and quantitative determination of HNAPO and 5-nonylsalicylaldoxime<sup>14</sup> (the active component of LIX 622N, LIX 860N-I, LIX 860N-IC, Acorga P5100 and Acorga PT5050). Finally, the electrochemical behaviour of 2-hydroxy-5-methylbenzophenone oxime,<sup>15</sup> a compound similar to the active component of the commercial extractant LIX 65N (2-hydroxy-5-nonylbenzophenone oxime), was reported.

In this work, a voltammetric method based on the electrochemical reduction of the oxime group of the hydroxyoximes DSAO and HNAPO to give the corresponding amines<sup>16</sup> is proposed. The voltammetric behaviour of DSAO in hydro-alcoholic solutions using differential pulse voltammetry (DPV) is reported. An experimental design methodology was used to establish the optimum values of the instrumental variables to determine DSAO. The Taguchi<sup>17</sup> design methodology was used in order to extend the former optimized method to the determination of HNAPO. The method was applied to quantify the DSAO and HNAPO contents in samples of commercial extractants.

## EXPERIMENTAL

### *Reagents and chemicals*

Standards of DSAO were prepared from samples of LIX 860-IC (90 % DSAO), kindly supplied by Cognis. A sample of pure HNAPO (98.8 % purity) was obtained from the commercial extractant SME 529 (Shell Chemical Co.) according to the method proposed by Preston and Whewell.<sup>18</sup>

Hydro-alcoholic solutions of the standards and the commercial samples were prepared using methanol (Carlo Erba, *p.a.*) as diluent, KCl (Panreac, *p.a.*) as ionic medium and Britton–Robinson buffer containing 0.04 M of each phosphoric acid (Carlo Erba, *p.a.*), acetic acid (Carlo Erba, *p.a.*) and boric acid (Fluka, *p.a.*) to adjust the pH.

The analyzed commercial extractants were LIX 860, LIX 860-I, LIX 622 (Cognis) and LIX 84 (Henkel). Isotridecanol N (BASF), 4-dodecylphenol (Aldrich) and 4-nonylphenol (Acros), that could be present in the commercial formulations,<sup>1,2</sup> and the diluent ShellSol D70 (Shell) were also tested.

### Experimental procedure

Voltammetric measurements were performed with an Autolab/general purpose electrochemical system (GPES) package, equipped with a potentiostat model III connected to a Metrohm 647 VA stand. A three-electrode electroanalytical cell (50 mL) with a hanging mercury drop electrode (HMDE) as the working electrode, a platinum auxiliary electrode and an Ag/AgCl reference electrode (3 M KCl) was used for all measurements, and all potentials in the paper refer to this electrode. The electrodes were washed with mixtures of ultra-pure water (Milli-Q water purification system) and methanol and tested prior to each experiment. The pH of the solutions was measured using a Radiometer pHM64 fitted with an Ingold combined Ag/AgCl glass electrode. All the experiments were performed at  $298.0 \pm 0.5$  K. Oxygen was removed from the solutions by purging with nitrogen gas for 4 min.

## RESULTS AND DISCUSSION

### Preliminary voltammetric experiments

The differential pulse voltammograms of the DSAO-based extractant LIX 622 are shown in Fig. 1. It could be observed that methanol percentage and pH affect both the peak potential and the peak intensity. The intensity of the reduction peak increased with increasing methanol percentage (Fig. 1a). However, in order to avoid precipitation of the reagent and, simultaneously, maintain a minimum methanol percentage in the solutions, 40 % methanol was chosen. On the other hand, the intensity of the reduction peak of DSAO decreased with pH (Fig. 1b). Taking into account that the solutions were not stable with time at pH values below 2.0, this pH value was selected. Finally, an ionic medium of 0.1 M KCl was always used to keep the ionic strength constant. It could be observed that under these conditions (40 % methanol, pH 2.0), the reduction peak of the oxime group in DSAO appeared at around  $-0.80$  V. None of the other compounds that the extractants might contain gave rise to reduction peaks in the studied potential range.

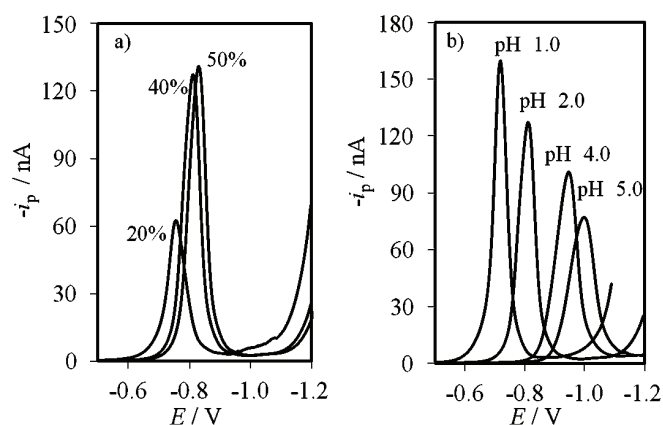


Fig. 1. Differential pulse voltammograms of the DSAO based LIX 622 extractant ( $5.84 \text{ mg L}^{-1}$ ) as a function of: a) methanol content and b) pH;  $t_m = 0.05$  s,  $t_i = 0.3$  s,  $s_p = 5$  mV and  $a_m = 50$  mV.

*Optimization of the instrumental variables in the differential pulse voltammetric (DPV) determination of DSAO*

To establish the optimum conditions for the determination of DSAO by the DPV technique, a two-level factorial design was performed. The response variable was the peak intensity ( $i_p$ ), which could be influenced by a large number of instrumental and chemical variables. In this work, only the instrumental variables, modulation time ( $t_m$ ), interval time ( $t_i$ ), potential step ( $s_p$ ) and modulation amplitude ( $a_m$ ) were optimized. A  $2^4$  factorial design was applied to estimate the residual error.

Prior to performing a design of experiments, the maximum and minimum values for each factor were established. All the experiments were realized in a random order and repeated. The values corresponding to the minimum (–) and maximum (+) levels for each factor were the following: 0.1 and 0.4 s (interval time), 2 and 15 mV (potential step), 0.002 and 0.060 s (modulation time) and 20.0 and 75.0 mV (modulation amplitude), respectively.

By using the Unscrambler program,<sup>19</sup> the  $P$  factors for each variable and for the interactions between them were calculated,  $P$  being the probability of their coefficient being zero (null hypothesis). If the  $P$  value for a parameter is higher than 0.05, the parameter has no significant effect on the model (at a confidence level of 95 %) and it could be eliminated.

For analysis, the results were presented as a Pareto chart, shown in Fig. 2. The bar lengths are proportional to the  $P$  value of each variable. As could be seen, the modulation time and modulation amplitude are the significant factors and there is an interaction between these factors. On the other hand, it was proven that the intermediate values of interval time and potential step, non-significant parameters, gave rise to good results and provided an acceptable scan rate ( $50 \text{ mV s}^{-1}$ ). Consequently, the interval time and potential step were fixed at 0.2 s and 10 mV, respectively.

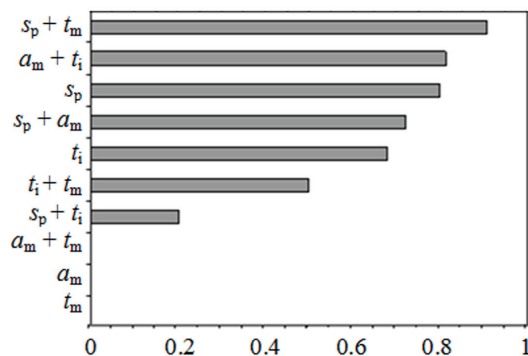


Fig. 2. Pareto chart showing the results of the experimental design applied to the DPV technique.

Once the significant variables were found, a central composite design with three replications at the central point was performed. The values corresponding to the minimum (-), maximum (+) and centre point (0) levels were, respectively, 0.012 s (-), 0.060 s (+) and 0.036 s (0) for the modulation time, and 20.0 mV (-), 75.0 mV (+) and 47.5 mV (0) for the modulation amplitude.

The data obtained were analyzed using ANOVA. The proposed model was fitted to the following non-linear equation:

$$i_p = 0.0229 + 0.0008a_m - 0.9680t_m + 0.0021a_m^2 + 0.0095t_m^2 - 0.0141a_mt_m \quad (1)$$

where  $i_p$  is the predicted response and the coefficients are the adjusted parameters. This second order function is adequate to model the data because the lack of fit was not significant at the 95 % confidence level. In addition, the value of the coefficient of determination,  $r^2 = 0.986$ , indicates that most of the variability in the response is explained by the model. Consequently, taking into account that outliers were not detected and the residuals showed no clear pattern, the experimental results are successfully interpreted.

The ANOVA test indicated that at a confidence level of 95 %, the modulation time and the modulation amplitude were the significant factors ( $P < 0.05$ ), with an interaction between these variables. Moreover, the values of the coefficients in Eq. (1) indicate that the intensity of the reduction peak increases with increasing modulation amplitude and with decreasing modulation time.

The optimum values for the variables modulation time (0.012 s) and modulation amplitude (75.0 mV) were obtained by graphical analysis of the response surface graph (Fig. 3).

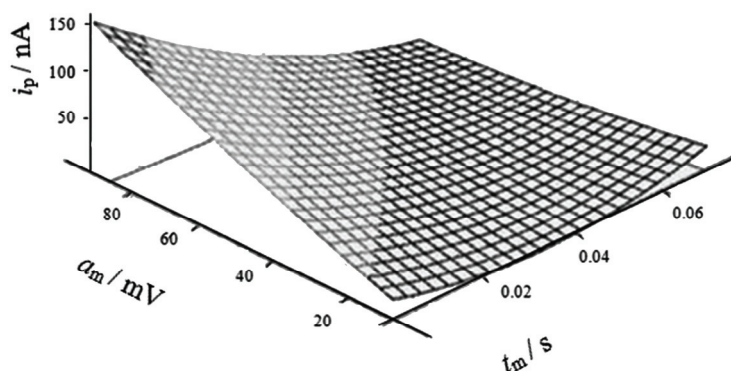


Fig. 3. Response surface generated by the central composite design for the optimization of the variables modulation amplitude and modulation time in the DPV analysis of DSAO.

#### Optimization of the instrumental variables in the DPV determination of HNAPO

The Taguchi methodology<sup>17</sup> was applied in order to check if the optimized design could also be applied to the determination of HNAPO. An orthogonal  $L_8$

matrix was used in order that the variables modulation amplitude, modulation time, potential step and interval time as well as the interaction between the two former factors could be evaluated. The values corresponding to the minimum and maximum levels were those previously selected for DSAO. The results (Fig. 4) showed that the modulation amplitude, modulation time and their interactions are the most influential factors. The ANOVA tests indicated that the modulation amplitude had the greatest influence (57.3 %) followed by the modulation time (13.6 %).

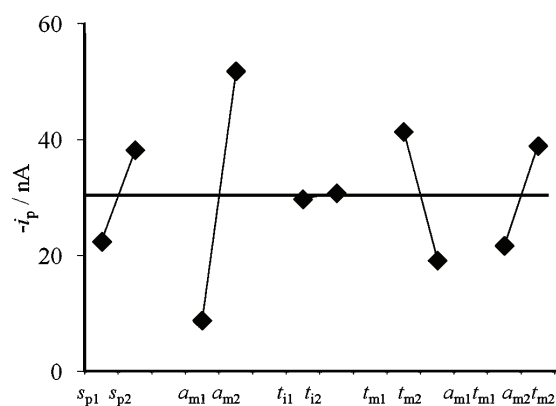


Fig. 4. Effect of the variables on the voltammetric peak intensity of hydro-alcoholic HNAPO solutions ( $0.82 \text{ mg L}^{-1}$ ) by applying the Taguchi methodology.

The results obtained showed that the optimum values for the significant factors, modulation amplitude and modulation time, are  $75.0 \text{ mV}$  and  $0.012 \text{ s}$ , respectively, whereas the maximum value of the potential step ( $10 \text{ mV}$ ) could be considered as the most appropriate, with the least influential factor, interval time, taking any value between  $0.1$  and  $0.4 \text{ s}$ .

Finally, confirmatory experiments were performed to verify that the predicted value for the response ( $i_p$ ) could be experimentally obtained. The theoretical response was obtained according to the following equation:

$$i_p = \bar{T} + (\bar{s}_{p2} - \bar{T}) + (\bar{a}_{m2} - \bar{T}) + (\bar{t}_{m1} - \bar{T}) + [(\bar{a}_{m2} \bar{t}_{m1} - \bar{T}) - (\bar{a}_{m2} - \bar{T}) - (\bar{t}_{m1} - \bar{T})] \quad (2)$$

where  $\bar{T}$  is the mean average of all the experimental results, and the values  $\bar{s}_{p2}$ ,  $\bar{a}_{m2}$  and  $\bar{t}_{m1}$  are the average responses corresponding to the experiments in which the different factors had acquired the level indicated in the subscript.

The theoretical current value obtained for a  $0.82 \text{ mg L}^{-1}$  HNAPO solution using the optimum combination of variables ( $\bar{s}_{p2} \bar{a}_{m2} \bar{t}_{m1}$ ) was  $-79.4 \text{ nA}$ , with  $-74.7 \text{ nA}$  being the experimental  $i_p$  value obtained at interval time values between  $0.1$  and  $0.4 \text{ s}$ , thus confirming the independence of the response on the interval time factor, and evidencing that the optimum combination of variables

previously obtained for the analysis of DSAO could also be used for the determination of HNAPO.

#### *Analysis of DSAO and HNAPO in commercial extractants*

For the determination of DSAO and HNAPO in hydro-alcoholic solutions, calibration curves of the standards (0.1 M KCl / 40 % methanol at pH 2.0) using the optimized method (interval time: 0.2 s, potential step: 10 mV, modulation time: 0.012 s and modulation amplitude: 75.0 mV) were constructed and are shown in Figs. 5 and 6, respectively.

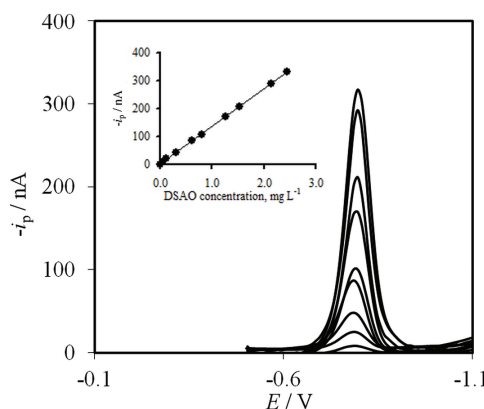


Fig. 5. DPV calibration curve of DSAO in 0.1 M KCl / 40 % methanol at pH 2.0.

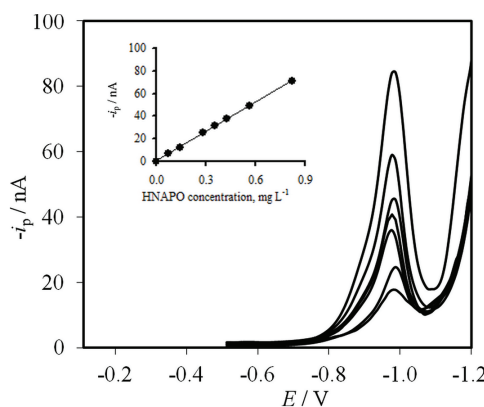


Fig. 6. DPV calibration curve of HNAPO in 0.1 M KCl / 40 % methanol at pH 2.0.

The statistical parameters of the calibration curves are summarized in Table I. The limits of detection and quantification were taken as 3 and 10 times the standard deviation of the regression lines, respectively. The intraday repeatability was checked in each case by analyzing three to five samples independently prepared according to the established procedure. The results, expressed as *RSD* / %, are also given in Table I.

TABLE I. Statistical parameters of the calibration curves for the determination of DSAO and HNAPO by DPV

Parameter	DSAO	HNAPO
Linear range, mg L <sup>-1</sup>	0.05–2.45	0.07–0.82
Slope $\pm s$ , nA L mg <sup>-1</sup>	133.98 $\pm$ 0.57	86.50 $\pm$ 0.76
Intercept $\pm s$ , nA	2.27 $\pm$ 0.71	0.55 $\pm$ 0.32
$r^2$	0.9999	0.9995
Limit of detection, mg L <sup>-1</sup>	0.034	0.019
Limit of quantification, mg L <sup>-1</sup>	0.113	0.064
Intraday repeatability, <i>RSD</i> / %	0.63 (0.17 mg L <sup>-1</sup> , $n = 3$ ) 1.92 (2.14 mg L <sup>-1</sup> , $n = 3$ )	2.47 (0.17 mg L <sup>-1</sup> , $n = 5$ ) 1.29 (0.57 mg L <sup>-1</sup> , $n = 5$ )

The developed DPV method was applied to determine DSAO in LIX 860, LIX 860-I and LIX 622 and HNAPO in LIX 84. All the solutions were prepared as described previously (40 % methanol, 0.1 M KCl at pH 2.0) and measured three times according to the optimized DPV conditions. The results are given in Table II.

TABLE II. Comparison of different methods for the determination of the percentages of DSAO and HNAPO in several commercial extractants

Analytical technique	Extractant	Compound	mass %	Ref.
HPLC-UV	LIX 860	DSAO	64.82 $\pm$ 0.96	12
GC-MS	LIX860	DSAO	66.6 $\pm$ 2.0	13
DPV	LIX 860	DSAO	65.7 $\pm$ 1.9	This work
DPV	LIX 860-I	DSAO	69.4 $\pm$ 1.9	This work
DPV	LIX 622	DSAO	75.0 $\pm$ 2.0	This work
DPV (platinum electrode)	LIX 84	HNAPO	49.8 $\pm$ 3.4	14
DPV	LIX 84	HNAPO	49.9 $\pm$ 1.2	This work

Samples of LIX 860 and LIX 84 had been previously analyzed by chromatographic (HPLC<sup>12</sup> and GC-MS<sup>13</sup>) and voltammetric (DPV<sup>14</sup>) methods, respectively as seen in Table II, and the results acceptably agreed with those obtained using the optimized voltammetric method proposed in this work.

#### CONCLUSIONS

The optimum combination of instrumental variables in the analysis of DSAO by differential pulse voltammetry was obtained by means of an experimental design methodology. Under these conditions, a well resolved reduction peak at –0.80 V was recorded. The optimized method was extended by using the Taguchi methodology to the analysis of HNAPO under the same experimental conditions by the same technique.

The differential pulse voltammetric method was successfully applied to the determination of DSAO and HNAPO in several commercial extractants. The results obtained from the developed method showed good agreement with pre-



viously reported HPLC-UV, GC-MS and electrochemical results. Moreover, this is the first time that DSAO was determined in LIX 860-I and in LIX622.

## ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ОДРЕЂИВАЊЕ 5-ДОДЕЦИЛСАЛИЦИЛАЛДОКСИМА И  
2'-ХИДРОКСИ-5'-НОНИЛАЦЕТОФЕНОН-ОКСИМА У КОМЕРЦИЈАЛНИМ  
ЕКСТРАКЦИОНИМ СРЕДСТВИМА

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Оптимизована је метода диференцијалне пулсне волтаметрије уз коришћење капљуће живине електроде (DME) за одређивање 5-додецилсалицилалдоксима у алкохолним растворима применом факторског и централног композитног дизајна. За одређивање 2'-хидрокси-5'-нонилацетофенон-оксима коришћена је методологија Taguchi дизајна са циљем проширења претходно оптимизоване методе. Метода је успешно примењена за одређивање 5-додецилсалицилалдоксима и 2'-хидрокси-5'-нонилацетофенон-оксима у узорцима комерцијалних екстракционих средстава, у концентрационим опсезима 0,05–2,45 и 0,07–0,82 mg L<sup>-1</sup>, редом, са границама детекције 0,034 и 0,019 mg L<sup>-1</sup>, редом.

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