

## A Comparison of Qualitative and Quantitative Methods used to Define the Resolution of Two Overlapping Reversible Processes in Second and Fundamental Harmonic Alternating Current Voltammetry

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Different authors have reached different conclusions concerning the relative resolving power of the fundamental and second harmonic alternating current voltammetric (polarographic) techniques. In this paper, the different qualitative and quantitative methods used to define the resolution of two overlapping processes in alternating current voltammetry have been evaluated. With all qualitative definitions, resolution of the second harmonic method is confirmed to be marginally superior to the fundamental harmonic. However, quantitatively, the resolution achieved with either method is so similar that the relative order to resolving power reported has actually been determined by the definition of resolution used and subtle differences in the examples chosen to evaluate the resolution. Experimental data confirm that the similarities in the qualitative aspects of resolution are far more substantial than the differences.

### INTRODUCTION

Theoretical and practical aspects of second harmonic alternating current voltammetry (SHACV) or polarography (SHACP) have been presented in many papers.<sup>1-19</sup> The second harmonic methods are claimed to have some advantages over their fundamental harmonic voltammetric (FHACV) and polarographic (FHACP) analogues. For example, the charging current is minimal, so that at least for reversible processes, the signal to

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noise ratio, and therefore the detection limit, is superior. In the opinion of many investigators the SHAC methods also provide superior resolution.<sup>10,12,16-18,29-39</sup> For example, Garai and co-workers<sup>12,29</sup> calculated the admissible concentration ratio of the interfering and the determined elements for a reversible processes and concluded that the resolution of the SHACP technique was about two times higher than that of the FHACP. Sienkiewicz, using a different calculation method, stated that the resolution of the SHACP is 3-4 times higher than the fundamental one.<sup>16,18</sup> Contrary to these conclusions, when analyzing the theoretical shape of reversible SHAC curves, Bond concluded that the resolving powers of the SHACP and of FHACP were similar,<sup>20,40</sup> but noted that in certain senses the resolution of the fundamental harmonic technique may be considered to be even greater than that of higher harmonics.

One of the difficulties which has led to ambiguities concerning the relative order of resolution of the second and fundamental harmonic AC voltammetric methods is undoubtedly related to the different definitions of resolution used by various authors.<sup>20,21,25,40-42</sup> The aim of the present paper is to evaluate the resolution of the SHACP and SHACV for reversible processes on the basis of the criteria and procedures proposed earlier<sup>40,42-45</sup> and then to consider the importance of the definition with respect to the resolution relative to the fundamental harmonic techniques. This systematic method of data analysis is believed to rationalize discrepancies between conclusions reached in previous studies.

## EXPERIMENTAL

### *Apparatus and Reagents*

In experimental studies employing phase-selective AC techniques, a B analytical Systems Electrochemical Analyzer, Model BAS-100, was used with a EG&G Princeton Applied Research (PAR) Model 303A static mercury drop electrode (SMDE), a silver-silver chloride (3 M KCl) reference electrode and a platinum wire auxiliary electrode.

All chemicals used were of Analytical Reagent grade purity and distilled and deionised water was used throughout. Solutions were thermostated at (25±1) °C and deaerated with highly purified nitrogen for 8 minutes prior to performing the voltammetric experiments. A Cyber computer was used for the numerical calculations.

### DIFFERENT METHODS USED FOR CALCULATION OF RESOLUTION

The current-voltage relationship in phase-selective SHACP for a reversible process has been reported by Smith<sup>2</sup> in the following form:

$$I^{sh} = \frac{\sqrt{2} n^3 F^3 A C (\omega D)^{1/2} \Delta E^2 \sinh(\varphi)}{16 R^2 T^2 \cosh^3(\varphi)} \sinh(2\omega t - \frac{\pi}{4}) \quad (1)$$

where  $\varphi = \frac{nF}{2RT}(E - E_i)$  and other symbols have their conventional meaning or else they are defined in Appendix I or Figure 1.

This relationship is highly accurate for  $\Delta E \leq 16/n$  mV, although the deviation for  $\Delta E \leq 50$  mV is rather small.<sup>21</sup>

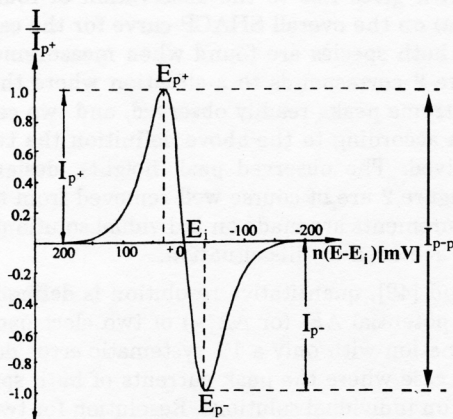


Figure 1. The theoretical shape for a reversible phase-selective second harmonic AC polarogram at 25 °C.

From equation (1) it follows that the second harmonic current is given by equation (2):

$$I^{sh} = K \frac{\text{tgh}(\varphi)}{\cosh^2(\varphi)} \tag{2}$$

where  $K = \frac{3\sqrt{3}}{2} I_{p+}$ .

Equation (2) also can be obtained by double differentiation of the equation for the reversible DC polarographic wave<sup>19</sup> and also describes the shape of the second harmonic AC voltammogram provided the AC time scale is much greater than the DC time scale, which requires that  $\Delta E \omega t \gg vt$ .<sup>21</sup> From equation (2) it follows that at 25 °C:

$$E_{p+} - E_i = 34.2/n \text{ mV}; E_i - E_{p-} = 34.2/n \text{ mV} \text{ and } E_{p+} - E_{p-} = 68.4/n \text{ mV}.$$

The SHACP curve resulting from two overlapping reversible processes designated as processes I and II can be expressed as follows:

$$I_2^{sh} = I_I^{sh} + I_{II}^{sh} = K_I \frac{\text{tgh}(\varphi_I)}{\cosh^2(\varphi_I)} + K_{II} \frac{\text{tgh}(\varphi_{II})}{\cosh^2(\varphi_{II})} \tag{3}$$

$$\text{where } \varphi_I = \frac{n_I F}{2RT} (E - E_i^I) \text{ and } \varphi_{II} = \frac{n_{II} F}{2RT} (E - E_i^{II}).$$

In reference [42], qualitative resolution in the SHAC method is defined to be the minimum difference in the reversible crossover potential  $\Delta E_i^I$  (or reversible  $\Delta E_{i/2}^I$ ) of two

electroactive species which gives rise to the observation of four distinct peaks (two maxima and two minima) on the overall SHACP curve for the case when equal values of the peak currents of both species are found when measurements are made on individual solutions. Figure 2 corresponds to a situation where the four distinct peaks can be observed (two extreme peaks readily observed, and two central peaks only just observed) and for which according to the above definition the two processes are said to be qualitatively resolved. The observed peak heights, designated  $(I_{p+}^I)_{\text{obs}}$ ,  $(I_{p+}^{II})_{\text{obs}}$ ,  $(I_{p-}^I)_{\text{obs}}$ , and  $(I_{p-}^{II})_{\text{obs}}$  in Figure 2 are of course well removed from the true values which are obtained when measurements are made on individual solutions so that quantitative resolution has not been achieved in this situation.

In references [40] and [42], quantitative resolution is defined as the difference in the reversible crossover potential  $\Delta E_i^r$  (or  $\Delta E_{i/2}^r$ ) of two electroactive species required to achieve their determination with only a 1% systematic error due to the overlapping of two processes for the case where the peak currents of both species are equal when measurements are made on individual solutions. Resolution for two overlapping reversible processes using this definition was calculated on the basis of equation 3. In principle, the current is proportional to concentration at all potentials. However, in this paper, resolution only has been considered from two kinds of current measurement:

1. In case of the species reduced at the more positive potential, the peak current of the positive maximum,  $I_{p+}^I$ , was measured, and in the case of the species reduced at the more negative potential, the peak current of the negative maximum  $I_{p-}^I$ , was measured.

2. The current values of both species are measured from the peak to peak values  $I_{p-p}^I$  and  $I_{p-p}^{II}$ , respectively.

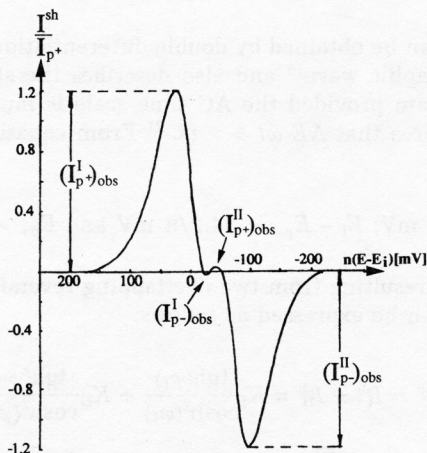


Figure 2. A theoretical phase-selective second harmonic AC polarogram showing an example where qualitative resolution has just been achieved (4 peaks observed as 2 maximum and 2 minima  $(I_{p-}^I)$  and  $(I_{p-}^{II})$ ;  $(I_{p+}^I)$  and  $(I_{p+}^{II})$ ) for two overlapping reversible processes when  $\Delta E_i = 70/n$  mV  $n_I = n_{II}$  and  $I_{p+}^I = I_{p+}^{II}$ , and  $I_{p-}^I = I_{p-}^{II}$  for the individual processes. Temperature = 25 °C.

The evaluation of the SHAC signal from peak-to-peak current measurements usually would be preferred in practice because of the inherent simplicity and lack of need to define the absolute values of the baseline. The results of theoretical calculations of the qualitative and quantitative resolution of SHAC method for different values of  $n$  and  $\Delta E_i^\dagger$  are shown in Tables I and II and compared with the resolution of FHACP, as calculated previously.<sup>42</sup>

In their paper,<sup>21</sup> Blustein and Bond calculated the theoretical admissible concentration ratio  $\alpha = (c_I/c_{II})$  of the interfering and the determined substances, which would permit the determination of the latter with 1% error for a given value  $\Delta E_i^\dagger$ . This approach defines the resolution in terms of concentration ratios. Resolution defined

TABLE I

Minimum differences at 25 °C (qualitative resolution) in  $\Delta E_i$  calculated to observe two separate SHACP peaks for each electroactive species when the peak current ratio  $Y = I_{p+}^{II} : I_{p+}^I = 1 : 1$  for pure solutions of each species. Results of calculation of qualitative resolution of FHACP as presented in reference [42] also are given.

Technique	$n_I$	$n_{II}$	$n_I$	$n_{II}$	$n_I$	$n_{II}$	$n_I$	$n_{II}$
		1	1	1	3	2	3	1
	2	2	3	1	3	2	2	1
	3	3						
SHACP $\Delta E_i$	68/n mV		32 mV		28 mV		44 mV	
FHACP $\Delta E_p$	68/n mV		46 mV		33 mV		57 mV	

TABLE II

Calculated values of  $\Delta E_i$  (mV) required in second harmonic AC polarography at 25 °C for the quantitative determination of two electroactive species with systematic errors equal to 1%, 2% or 5% under conditions when the current ratio  $Y = I_{p+}^{II} : I_{p+}^I = 1 : 1$  for pure solutions of each species. Results of calculations for fundamental harmonic AC voltammetry based on an equivalent definition also are given

Technique	Error	Separation required in potential for given Measurement Procedure <sup>(a)</sup>							
		1%		2%		5%		$I_{p-p}$	
		$n_I$	$n_{II}$	$I_{p+}$	$I_{p-}$	$I_{p+}$	$I_{p-}$		
SHACP ( $\Delta E_i$ , mV)	1	1						193/n (1%)	
	2	2	144/n	144/n	127/n	127/n	103/n	103/n	174/n (2%)
	3	3							149/n (5%)
FHACP ( $\Delta E_p$ , mV)	1	2	57	162	48	145	37	121	
	1	3	27	169	22	151	15	127	
	2	3	44	79	38	71	30	58	
	1	1							
	2	2	154/n	154/n	136/n	136/n	113/n	113/n	
	3	3							
FHACP ( $\Delta E_p$ , mV)	1	2	77	154	69	136	59	112	
	1	3	52	154	47	136	40	112	
	2	3	51	77	46	68	38	56	

<sup>a</sup> See text for details of measurement method.

in this way also depends on  $n_I$  and  $n_{II}$  as well as  $\Delta E_i^\dagger$  and provides another quantitative approach to the evaluation of resolution.<sup>40</sup> The data characterizing the resolution for the SH and FHACP techniques based on this alternative definition are given in Table III for an arbitrarily selected difference of  $\Delta E_i^\dagger = 100$  mV.

TABLE III

*Resolution in SHACP at 25 °C defined as the concentration ratio  $\alpha = c_{II}/c_I$  of the interfering (II) and determined (I) substances, which gives rise to overlap of the peak current of the determined substance at the 1% level when the difference in the crossover potentials  $\Delta E_i = 100$  mV. Results of calculations for the fundamental harmonic based on an equivalent definition also are given.*

$n_I$	$n_{II}$	$\alpha_{sh} = c_{II}/c_I$	$\alpha_{fh} = c_{II}/c_I$	$\alpha_{sh}/\alpha_{fh}$
1	1	0.18	0.13	1.4
1	2	4.1	1.5	2.7
1	3	220	33	6.6
2	1	0.77	0.50	1.5
2	2	8.7	6.0	1.5
2	3	240	130	1.8
3	1	2.1	1.1	1.8
3	2	19	13	1.4
3	3	420	300	1.4

## DISCUSSION

Using the definition of resolution developed in reference,<sup>42</sup> qualitative resolution for the SHACP technique is calculated to be superior than the FH technique by a few millivolts when  $n_I \neq n_{II}$  but equal when  $n_I = n_{II}$  (see Table I).

From data contained in Table II it can be seen that when  $n_I = n_{II}$ , quantitative resolution of the SHACP technique ( $\Delta E_i = 144/n$  mV), as defined in refs. [40] and [42], is marginally better than the resolution of the FHACP technique ( $\Delta E_p = 154/n$  mV), when using the method of measurement, in which only the values of  $I_{p+}^I$  and  $I_{p-}^{II}$  are taken into consideration. However, with this same criterion and for the cases where  $n_I \neq n_{II}$  ( $n_I = 1, n_{II} = 2$ ;  $n_I = 1, n_{II} = 3$ ;  $n_I = 12, n_{II} = 3$ ) quantitative resolution of the SHAC method is better than that of the FHACP technique only for the species which is reduced with the smaller number of electrons. For the species which is reduced with the greater number of electrons, the quantitative resolution of the SHACP technique is in fact marginally inferior than that for FH technique. This reversal of order illustrates how important the definition is in determining the relative order of the FH and SHAC methods. This point is further illustrated by noting that when the method of measuring the analytical signal from peak-to-peak values as proposed by Bond<sup>20</sup> is employed, the quantitative resolution of the second harmonic technique  $\Delta E_i = 193/n$  mV is obviously worse than the resolution of the FHAC technique  $\Delta E_p = 154/n$  mV for  $n_I = n_{II}$  (Table II).

When comparing the resolution by the tolerable concentration ratio method (Table III) the second harmonic method is always marginally superior to the fundamental harmonic, but again the value of  $n_I$  and  $n_{II}$  are very important in the calculated resolution. The different dependence of resolution on  $n_I$  and  $n_{II}$  is a direct result of the fact that  $I_p^{sh}$  depends on  $n^3$  (equation 1), whereas  $I_p^{fh}$  depends on  $n^2$ . All of the above theory

is based on the assumption of reversibility and absence of  $iR$  drop. The results therefore represent the most favourable conditions to achieve resolution, since irreversibility and uncompensated resistance lead to peak broadening.

The conclusions that the resolution in both the fundamental and second harmonic AC methods are very similar also is reached by consideration of experimental data for the reduction of mixtures of  $\text{In}^{3+}$  ( $n = 3$ ) and  $\text{Cd}^{2+}$  ( $n = 2$ ) in 1M HCl ( $\Delta E_{1/2}^r = -44$  mV) and 1 M NaBr, pH = 2.0 ( $\Delta E_{1/2}^r = 90$  mV). The voltammetric characteristics for reduction of both ions by DC, differential pulse and AC techniques are presented in Table IV. Data analysis leads to the conclusion that both the  $\text{Cd}^{2+}$  and  $\text{In}^{3+}$  ions are reduced reversibly or quasi-reversible in the investigated supporting electrolytes. Figure 3 shows data obtained for mixtures of  $\text{In}^{3+}$  and  $\text{Cd}^{2+}$  in the two electrolytes by DC polarography, FHACP, SHACP, differential pulse polarography (DPP) and cyclic voltammetry (CV) and it is clear that resolution in each of the methods examined is characterized by greater similarity than difference, although to the eye, qualitative aspects of resolution appear to be superior for the second harmonic AC method.

### CONCLUSIONS

A theoretical and experimental comparison of second and fundamental harmonic AC voltammetric techniques shows that the relative order of their power for quantitatively resolving overlapping reversible processes depends critically on the chosen resolution criterion as well as on the mode of measurement of the peak current and on the number of electrons involved in the overlapping electrode processes. That is, the techni-

TABLE IV  
Voltammetric Characteristics of  $\text{Cd}^{2+}$  and  $\text{In}^{3+}$  in 1 M HCl and 1 M NaBr at 25 °C  
(all data in mV)<sup>a</sup>

Ion	Supporting Electrolyte	DCP <sup>(b)</sup>		NPP <sup>(b)</sup>		DPP <sup>(b)</sup>			
		$-E_{1/2}$	$(E_{3/4}-E_{1/4})$	$-E_{1/2}$	$(E_{3/4}-E_{1/4})$	$\Delta E = -5$ mV	$\Delta E = -20$ mV	$\Delta E = -5$ mV	$\Delta E = -20$ mV
		$-E_p$	$W_{1/2}$	$-E_i$	$\Delta(E_{p+}-E_p)$	$-E_p$	$W_{1/2}$	$-E_p$	$W_{1/2}$
$\text{Cd}^{2+}$	1 M HCl	607	29.5	603	28	603	42.5	599	45.5
$\text{Cd}^{2+}$	1 M NaBr					616	42	608	44
$\text{In}^{3+}$	1 M HCl	564	19.5	562	20	560	30	556	33.5
$\text{In}^{3+}$	1 M NaBr					528	32	520	36
$\Delta E_{1/2}^{\text{Cd-In}}$	1 M HCl	43		41		43		44	
$\Delta E_{1/2}^{\text{Cd-In}}$	1 M NaBr					88		88	
Ion	Supporting Electrolyte	FHACP <sup>(b,c)</sup>		SHACP <sup>(c)</sup>		CV <sup>(d)</sup>			
		$\Delta E_{p-p} = 20$ mV	$\Delta E_{p-p} = 50$ mV	$-E_p^{\text{red}}$	$(E_p^{\text{ox}}-E_p^{\text{red}})$	$-E_p^{\text{red}}$	$(E_p^{\text{ox}}-E_p^{\text{red}})$	$-E_p^{\text{red}}$	$(E_p^{\text{ox}}-E_p^{\text{red}})$
$\text{Cd}^{2+}$	1 M HCl	605	42	601	41	605			28
$\text{Cd}^{2+}$	1 M NaBr	622	42	620	39	624			28
$\text{In}^{3+}$	1 M HCl	560	34	557	31	563			21
$\text{In}^{3+}$	1 M NaBr	532	31	530	31.5	534			18
$\Delta E_{1/2}^{\text{Cd-In}}$	1 M HCl	45		44				42	
$\Delta E_{1/2}^{\text{Cd-In}}$	1 M NaBr	90		90				90	

<sup>a</sup> Terms defined in Appendix I. <sup>b</sup> Drop time = 1 s. <sup>c</sup> Frequency = 50 Hz, drop time = 1.5 s.

<sup>d</sup> Scan rate = 100 mV s<sup>-1</sup>.

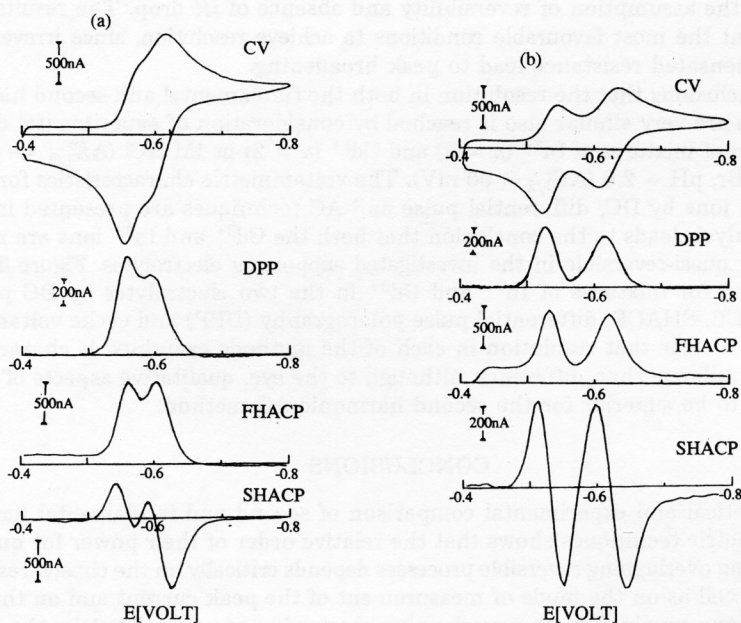


Figure 3. Experimental voltammograms (polarograms) obtained at 25 °C for mixtures of (a)  $3.5 \times 10^{-5}$  M  $\text{In}^{3+}$  and  $7 \times 10^{-5}$  M  $\text{Cd}^{2+}$  in 1 M HCl; (b)  $1.75 \times 10^{-5}$  M  $\text{In}^{3+}$  and  $3.5 \times 10^{-5}$  M  $\text{Cd}^{2+}$  in 1 M NaBr (pH = 2).

Experimental parameters. Cyclic voltammetry (CV): scan rate =  $100 \text{ mV s}^{-1}$ ; Differential pulse polarography (DPP): drop time = 1.0 s, pulse amplitude =  $-20 \text{ mV}$  FHACP and SHACP: frequency = 50 Hz, drop time = 1.5 s.  $\Delta E = 5 \text{ mV}$  (p-p).

ques actually have very similar resolving power and subtle changes in the definition of resolution may give rise to an apparent advantage of one method over the other. It is therefore not possible to unambiguously state whether the resolution of the second harmonic technique is superior to the fundamental harmonic or vice versa and this feature explains the apparent confusion in the literature on this matter. Since the similarity of resolution is much greater than the difference, resolution is unlikely to be a reason for preferring one technique over the other in many practical quantitative analytical applications when overlapping reversible processes are being considered. However, if one or both of the processes are irreversible, then the effectively different time scales of the different harmonics may be of crucial significance in achieving resolution.

## APPENDIX I

Definitions of notation used in the text, Tables and Figures.

$E$ : DC potential

$E_i$ : inflection or crossover potential, where the second harmonic alternating current equals zero. For a reversible processes  $E_i^r = E_{1/2}^r$  where superscript r when added to any parameter, implies that the value given is for a reversible process.



$\Delta E_i = E_i^{\text{II}} - E_i^{\text{I}}$ : the difference in crossover potentials of two electroactive species.

$E_{p+}, E_{p-}$ : potential corresponding to the maximum and minimum values of the second harmonic alternating current.

$I_{p+}, I_{p-}$ : maximum and minimum values of the second harmonic alternating current.

$I_{p-p} = I_{p+} + I_{p-}$ : value of peak-to-peak second harmonic alternating current.

$Y = I_{p+}^{\text{II}}/I_{p+}^{\text{I}}$ : maximum second harmonic alternating current ration of two electroactive species.

$\alpha = c_{\text{II}}/c_{\text{I}}$ : concentration ratio of two reversibly reduced species.

Other symbols have their conventional meaning.

DC, DCP: direct current or direct current polarography respectively.

AC: alternating current.

NPP: normal pulse polarography.

DPP: differential pulse polarography.

FHACP, FHACV: fundamental harmonic alternating current polarography or voltammetry respectively.

CV: cyclic voltammetry.

$E_{1/2}$ : half-wave potential.

$E_{1/2}^{\text{r}}$ : reversible half-wave potential.

$E_{3/4}, E_{1/4}$ : potentials at  $3/4 i_d$  and  $1/4 i_d$  respectively where  $i_d$  = diffusion controlled limiting current.

$W_{1/2}$ : width of wave at half peak height.

$E_p$  peak height

$E_p^{\text{red}}, E_p^{\text{ox}}$ : reduction and oxidation peak potentials respectively.

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## SAŽETAK

### Usporedba kvalitativnih i kvantitativnih metoda za ocjenu razlučivanja dvaju prekrivenih reverzibilnih procesa u voltametriji izmjeničnom strujom osnovnog i drugog harmonika

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Različiti autori došli su do različitih zaključaka u svezi s relativnom sposobnošću razdvajanja pomoću tehnika s osnovnim i drugim harmonikom u voltametriji (polarografiji) izmjeničnom strujom. U ovom radu usporedene su različite kvalitativne i kvantitativne metode koje se rabe za ocjenu razlučivanja dvaju prekrivenih procesa u voltametriji izmjeničnom strujom. Na temelju svih kvalitativnih definicija potvrđeno je da je metoda drugog harmonika nešto bolja od metode osnovnog harmonika. Kvantitativna razdvajanja postignuta bilo kojom od metoda toliko su slična da je relativni stupanj moći razlučivanja stvarno određen definicijom razdvajanja i finim razlikama u odabranim primjerima. Eksperimentalni podaci potvrđuju da su sličnosti u kvalitativnim aspektima razlučivanja daleko veće nego razlike.