

# Automatic polarographic elucidation of electrode mechanisms by means of a knowledge-based system

## Part 2. Staircase voltammetry, convolution voltammetry and chronocoulometry applied to simple mechanisms

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### Abstract

An improved expert system for the automatic elucidation of electrode reaction mechanisms is presented. The system is coupled to the electrochemical instrument, designs the experiment, controls it and collects the results automatically. The approximate logic concept is used to handle situations when inconsistent or conflicting information is obtained. Cyclic staircase voltammetry, chronocoulometry/chronoamperometry and convolution voltammetry are used at this stage of development. In the elucidation process, general information and characteristics of particular reaction steps are delivered, and are finally combined in an answer about the mechanism of the electrode reaction. The present set of rules allows full elucidation of ten simple mechanisms. For more complicated mechanisms, all stages of the elucidation except the final combination of all gathered knowledge, are output. The performance of the expert system was checked with four well-known electrochemical systems. In all cases, the answer about the reaction mechanisms was correct. The typical time for a full elucidation cycle was about 25 min.

*Keywords:* Coulometry, Voltammetry, Electrode reaction mechanisms; Expert system

Applications of artificial intelligence in the chemical laboratory have attracted wide attention (see, e.g. [1–9]). Examples are deductive expert systems [10,11] and neural networks [12–15], which have been applied successfully in numerous fields of analytical chemistry. Expert systems are useful in situations where routine work needs problem solving on the expert level, but a human expert is not available. Neural networks have proved their utility in cases when observed phenomena or processes are not well-defined or not exactly un-

derstood. A very promising class of inductive systems that heuristically create new reasoning rules, is still in the early stages of development.

For analytical chemistry, artificial intelligence is of interest because it offers possibilities for automation of non-standard or non-routine work. Moreover, it seems that applications of expert systems in more fundamental studies should be possible. In a previous paper [16], an expert system was described for elucidating electrochemical reaction mechanisms, which are of equal interest in analytical chemistry and fundamental electrochemistry. In the present paper, the possibilities of elucidation are extended and a new expert system capable of delivering much more information

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about the electrochemical system under study is presented.

There are two types of expert system. In the advisory (passive) type, queries are answered from information in the database and by using the reasoning rules; if the necessary information cannot be found or inferred, it is demanded from the operator. Such expert systems are relatively simple to build (see, e.g. [17]) and are generally applicable because it is irrelevant how the externally delivered information was obtained. Many expert systems used in the laboratory are of this type. The other type of expert system is coupled to the measuring instrument. The necessary experimental information is obtained directly and transferred to the expert system. The performance of these stand-alone active systems is much better; the system saves operator time and can work for long periods without human supervision. The disadvantage is that, although part of the experimental design can be done independently of the instrument by using appropriate rules, the system still has to meet some instrument-specific requirements.

The expert system described here is of the active type. Single steps in electrochemical work usually require little time, so that the expert system can be consulted often and a significant amount of time can be saved by direct transfer of data to the expert system. Moreover, electrochemical experiments are easy to automate and dedicated computer-controlled instruments are widely available now. The wider applicability of the expert system is achieved by using general electrochemical parameters to control the experiment and extracting the hardware-independent information from the data obtained.

The present expert system is run on an IBM PC-compatible computer. Other innovations are based on experience with the previously described system [16], which led to the two important observations. First, to increase the amount of information obtained from the expert system, more than one electrochemical technique is needed; cyclic techniques should be considered because they also deliver information about the properties of the reaction product. Secondly, polarographic experiments can be time-consuming; it would be

profitable to use another technique delivering the same (or similar) type of information in a shorter time. Consequently, cyclic voltammetry, chronocoulometry and convolution voltammetry were used for this work. Because of the memory limitations of the Apple-II computer, the availability of more advanced electrochemical instrumentation and the success of preliminary studies [18], both the computer system and programming language were changed.

In the form presented below, the expert system can fully elucidate a limited number of relatively simple mechanisms automatically. Even when full elucidation is impossible, the system yields a lot of information about the features of the electrochemical reactions. In such cases, the expert system, works as an intelligent instrument, delivering the initial characteristics of the system and leaving decisions about further investigations to the operator. It should be noted that, even then, the expert system follows the rules for the delivery of partial results and does not run experiments that are nonsensical on the basis of knowledge already collected. An additional attractive feature, common to most expert systems, is that the system can be extended by the introduction of new rules. Also, the performance of the expert system is usually better than that of the operator, particularly in terms of running experiments and producing evaluations. The set of rules in this expert system will be extended in the future, with respect to better extraction of the information available from the current set of techniques (improved efficiency of data exploitation) and by adding more electrochemical techniques to obtain different information. Additionally, the structure and function of the rules and expert-system shell will be optimized continuously during tests with new compounds.

#### SOFTWARE

Numerous changes have been made to the old expert system. The important changes concern the programming language: the reasoning part of the

system is currently implemented in PROLOG (SD-PROLOG version), a language designed for logic programming and particularly suitable for expert systems. However, because of its philosophy, PROLOG is not efficient in numerical calculations and cannot be used for low-level data manipulation, interactions with the operating system or hardware control. Therefore, parts of the system are programmed in C language (Microsoft C), which is excellent for these tasks, and possesses advanced features such as flexibility, high degree of standardization and portability. The problems of mixed-language programming can be overcome because of the Microsoft C interfaces to other languages and the SD-PROLOG built-in interface to C. Additionally, SD-PROLOG, like most PROLOG versions, is itself written in C, which facilitates mixed programming. In the expert system, modules coded in C are well-structured and perform well-defined tasks; they can be used as standard PROLOG predicates, so that drawbacks concerning program clarity are avoided. The low-level control of the experimental set-up and activities where time is crucial are done by assembler routines from the library of standard functions constituting part of the software of the measuring instrument

#### *Organization of the expert system*

The whole expert system can be functionally divided into the expert system shell, which is responsible for knowledge manipulation, the knowledge in the form of a set of rules and the initial facts, and the set of experiment modules. The experiment modules are stand-alone programs, each of which performs one complete electrochemical experiment (cyclic voltammetry, chronoamperometry, etc.) and delivers results (e.g., the positions and heights of voltammetric peaks). The advantage of this division is that the experimental modules can be developed, tested and even used outside the expert system. Moreover, it prevents problems with future computer memory deficiency when more techniques are introduced. Also, the software packages of many instruments quite often provide ready programs for running different experiments, so that eventual transfer of the expert

system to another measuring environment and connecting it with these programs would be greatly simplified.

*Expert system shell.* The use of different experimental techniques emphasizes the problem of receiving uncertain information. Results of different experiments can be inconsistent or even conflicting, and the expert system has to be able to handle such situations. A system based on Boolean true/false logic is not suitable for this purpose and approximate logic concepts must be applied. In the present system, uncertainty is represented in the form of so-called supporting pairs [19]: a supporting pair for the fact,  $(L, U)$ , consists of two probabilities:  $L = P(\text{true})$  and  $U = 1 - P(\text{false})$ . If there is no vagueness about the fact,  $L = U$ ; for an uncertain fact,  $L \neq U$  and the difference between these two numbers can serve as a measure of uncertainty. The value  $L$  can be considered as the lowest possible support for the facts, while  $U$  as a highest possible one. The mean value,  $(L + U)/2$ , can be used to compare the support for different facts or to rank them on priority lists.

Similarly, a supporting pair can be assigned to rules, where it acts as a weighting factor and can represent how clearly the conclusion of the rule is linked to its antecedents. The mechanism of propagation of supporting pairs and uncertainties through conjunctions and disjunctions of facts and through rules has been described [19].

The usual representation of facts in the form of an associative triplet  $\langle \text{object} \rangle \langle \text{attribute} \rangle \langle \text{value} \rangle$  (e.g.,  $\langle \text{grass} \rangle \langle \text{colour} \rangle \langle \text{green} \rangle$ ) has also been changed to the form  $\langle \text{condition} \rangle \langle \text{value} \rangle \langle \text{supporting pair} \rangle$  (e.g.,  $\langle \text{colour of grass at night} \rangle \langle \text{black} \rangle \langle 40\% \dots 90\% \rangle$ ).

The whole expert system shell consists of three subunits: inference engine, explanation facility and utilities. The knowledge database, an essential part of the expert system, already exists as part of the PROLOG language and need not to be programmed; database management, searching and matching are also left to PROLOG. Of the remaining subunits, the inference engine and explanation facilities are programmed totally in PROLOG, while the utilities (extended calculational support, some experimental data processing,

additional knowledge manipulation, statistics) are implemented in both PROLOG and C language.

#### Experimental modules

For the present version of the expert system, three electrochemical techniques were selected: cyclic staircase voltammetry, double-step chronocoulometry and convolution voltammetry. This selection was based on the fact that information obtained from these techniques is complementary. Staircase voltammetry is a popular and relatively easy way of studying electrode mechanisms; it is much faster than the previously used polarography [16], allows greater variation of the kinetic parameter (scan rate comparing to the drop time), and has a well-developed theoretical basis. In the cyclic version, it also gives valuable information about the behaviour of the primary reaction product. Its main disadvantage is the overlapping of signals (peaks) in the case of complex voltammograms. Chronocoulometry is a very simple but powerful method for studying the flux of the electroactive substance across the electrode surface, and is well suited for distinguishing between different types of control of the overall process (semi-infinite linear diffusion, adsorption, kinetic control, etc.). The cyclic version (double-

potential-step chronocoulometry) which is used here also gives some characteristics of the reaction products.

Convolution voltammetry (semidifferential voltammetry in this case) is an interesting technique because resolution is enhanced compared to cyclic voltammetry. In the expert system presented, semidifferential voltammetry is used for the detection of severely overlapping peaks and peaks overlapping with the wave from decomposition of the supporting electrolyte, i.e., to detect situations where the real number of separate signals differs from the number of peaks/waves obtained in simple voltammetry. This application certainly does not exhaust the possibilities of this technique but rather uses the features attractive for the expert system in its current stage of development. It is doubtful if convolution voltammetry should be considered as a separate technique, because it actually uses data obtained from cyclic voltammetry, but the features of the deconvoluted signals differ very much from the original ones and so it will be treated here as a separate technique. Semidifferentiation of data is done by using Grünwald's definition and one of three algorithms: G0, G1 or G2 [20,21].

Each technique is implemented in the form of a

TABLE 1  
Input and output data of the experiment control routines

Technique	Input parameters	Output parameters <sup>a</sup>
Staircase voltammetry	Scan rate	Numbers of peaks in all branches
	No of branches	All peak parameters
	Start potential	
	Turn potential	
	No. of replications	
Convolutive voltammetry	Scan rate	Numbers of peaks in all branches
	Instance of differintegration	All peak parameters
	Algorithm of differintegration <sup>b</sup>	
Chronocoulometry (CC)	Technique (CC or CA)	$Q$ vs $t^{1/2}$ intercepts
Chronoamperometry (CA)	No of steps	$Q$ vs $t^{1/2}$ slopes
	List of step potentials	Linearity probability <sup>c</sup>
	List of step times	Underlinearity probability <sup>c</sup>
	Sampling interval	Overlinearity probability <sup>c</sup>
	Delay time <sup>d</sup>	
	No of replications	

<sup>a</sup> The peak parameters are the positions and values of the peak maximum, inflection points and limits. <sup>b</sup> The G0, G1 or G2 algorithm [20,21]. <sup>c</sup> These terms are explained in the section on the characteristics of separate signals <sup>d</sup> Time between potential pulse and first measured charge/current

separate, stand-alone program. Input of experimental parameters and output of measurements are achieved by exchanging description and report files between the expert system and programs (modules) for experiments (eventual interactive input/output may be possible). The input and output information is summarized in Table 1. As can be seen, the pertinent experiment modules offer more possibilities and deliver more information than is currently used by the expert system (multi-scan voltammetry, multistep chronocoulometry/chronoamperometry, different convolution functions, etc.). This information will be used in future extensions.

All experiment control modules are written in C language with limited use of assembler routines from the instrument software package. These routines produce A/D and D/A conversions, combined conversions and timing control. Semi-differential voltammetry is operated by using data-files created by the module for cyclic voltammetry.

*Set of rules and initial facts.* The variable part of the expert system is the set of rules which depends on the particular problem to be solved. In the expert system described, rules are represented in the PROLOG form rule (*conclusion, supporting pair, antecedents*), where antecedents are interconnected by the <and>, <or> and <not> operators. The simple antecedent can be just a fact from the database or the name of the routine producing some specific action. The design of the experiment and the experiment itself are done by such "fact" routines. At the start of a run with the expert

system, a few facts containing basic information have to be delivered. These facts are listed in Table 2.

#### THEORY FOR ELUCIDATION OF ELECTRODE REACTIONS

The general approach to the elucidation of electrode reaction mechanisms presented here is based on a classification method. Each step in the reasoning process results in a piece of information which explains a specific feature of the system and is useful in the subsequent reasoning of the expert system or the analysis beyond it. The first step deals with the general electrochemical properties of the compound investigated: the system is assigned to one of several classes of complexity based on the number of peaks. In the next step, the relationships among oxidation and reduction signals are found and in the third step, the overall reaction, expressed as the net charge passing the electrode in the oxidation-reduction cycle, is studied. After this general characterization, the most complete independent characteristics of all signals are sought, and finally all pieces of information are combined in order to give an answer about the overall mechanism of the reactions at the electrode.

##### *Classes of complexity*

The classes of complexity (further referred to as system types) are defined in Table 3. They are based on the numbers of peaks in the cathodic and anodic branches of the cyclic voltammogram and allow simple (one-step) and complex (multi-step) processes to be distinguished. They can also detect or indicate totally irreversible steps in the reaction at the electrode (the entries are a symmetric one-signal and asymmetric multi-signal), as well as indicate possible errors in the measurements or in the initial data (the entries in Table 3 are electrochemically inactive or contradictory).

*Detection of hidden signals.* To obtain valid results in the previous step, one must be sure that all the signals that exist have been found. Some of them might not be recognized because of overlap with other signals or with the background current

TABLE 2

List of initial data to be delivered to the expert system before a run

Most positive potential
Most negative potential
Minimal scan rate <sup>a</sup>
Maximal scan rate <sup>a</sup>
Number of electrons involved
Number of replicate measurements
Sampling interval <sup>b</sup>
Delay time <sup>b</sup>

<sup>a</sup> Parameter for cyclic voltammetry <sup>b</sup> Parameter for chronocoulometry

TABLE 3

Criteria for assigning the system under study to a particular class of complexity (system type)

System type	F <sup>a</sup>	B <sup>b</sup>	F + B
Electrochemically inactive	0	0	-
Symmetric one-signal	1	1	-
Asymmetric one-signal	1	0	-
Possibly one-signal	≤ 2	≤ 2	> 2
Symmetric multi-signal	> 1	> 1	> 4
Asymmetric multi-signal	> 2	0	-
Contradictory	0	> 0	-

<sup>a</sup> Number of signals in the forward branch of the voltammogram. <sup>b</sup> Number of signals in the backward branch

at the ends of the potential range; two closely placed voltammetric peaks may overlap to form one peak or peaks close to the edges of the potential window may be visible only as small inflections on the background current rise of may be totally indistinguishable. In both situations, semi-differential voltammetry (e.g. [22]) can be used. Semiderivative voltammograms contain peaks that are much sharper and so are better separated; and peaks normally hidden in the background current rise may become visible [23].

The chemical system is tested for the presence of hidden signals by comparing the numbers and positions of voltammetric and semiderivative peaks. Any difference provides evidence for hidden signal(s); otherwise the voltammogram is considered to be free of hidden signals. This test operates as an exclusive Boolean test where support of (0, 0) or (1, 1) is assigned to the appropriate hypothesis.

*Oxidation-reduction relationships.* In the case of complex mechanisms, information concerning the relationships between different oxidation and reduction signals is very valuable. These relationships are studied by recording a series of voltammograms and examining the variation of the numbers of signals in the forward and reverse branches. Peaks in the reverse branch peaks are then related to the appropriate forward peaks. For a single-step mechanism (symmetric one-signal in Table 3), it is of course assumed that there is a clear relationship between the two signals.

*Net reaction.* As already mentioned, the net reaction in the oxidation-reduction cycle is studied

by measuring the maximal and net charge through the electrode during the cycle. When the net charge is less than half the maximal charge passed, the expert system considers this as confirmation of the hypothesis that there is no net reaction; otherwise the alternative hypothesis is accepted. This test is arbitrary in character and will later be replaced by a more flexible test.

*Characteristics of separate signals.* In the present version of rules, the search for the independent characteristics of each signal is conducted by investigating the variation of the peak potential ( $E_p$ ) with the logarithm of the scan rate ( $\nu$ ) and by studying factors controlling the diffusion of the electroactive substance to the electrode surface.

Nicholson and Shain [24] published a set of criteria for the elucidation of single-step mechanisms based on the  $\partial E_p / \partial \ln \nu$  dependence. These criteria are applied here to the particular steps of the reaction in a multi-step mechanism. Because of this extension, these criteria may not always be valid, therefore the term *suggestion for mechanism* is used instead of *mechanism* in the context of the separate-signal characteristics. Criteria are based on tests of the sign of  $\partial E_p / \partial \ln \nu$  values and their variation with scan rate. The supporting pair is created by using the output of statistical tests based on analysis of variance (ANOVA) for the trend and the *t*-test and ANOVA for the sign. The assignment of the suggestions for mechanism for the different dependences of  $\partial E_p / \partial \ln \nu$  on scan rate is summarized in Table 4.

The factors controlling the diffusion of the electroactive substance (further referred to as control of the process) were determined by using double-step chronocoulometry. From Fick's laws, the chronocoulometric charge ( $Q$ ) passing the electrode should increase linearly with time  $t^{1/2}$  if the substance reaches the electrode by semi-infinite linear diffusion. When the electroactive compound is produced in a chemical reaction, the charge should increase more quickly than  $t^{1/2}$ . A similar situation occurs for spherical diffusion, when  $Q$  vs.  $t^{1/2}$  plots also deviate from linearity. Another effect is observed, however, when the electroactive compound arrives at the electrode by limited diffusion. It can be expected that the charge will increase more slowly than  $t^{1/2}$ , owing to de-

TABLE 4

Criteria for suggestions for mechanisms of single signals [24]

Suggestion for the step mechanism	Symbol of signal mechanism	$\partial E_p/\partial \ln v$ value	$\partial E_p/\partial \ln v$ vs. $v$ trend
Fast electron transfer	E	0	Const = 0, (and not) increasing, (and not) decreasing
Slow electron transfer	Es	$-RT/2nF$	Const = $-RT/2nF$ , (and not) increasing, (and not) decreasing
Chemical reaction before fast electron transfer	CE	$\geq 0$	Increasing, (and not) constant, (and not) decreasing
Chemical reaction before slow electron transfer	CEs	$\leq 0$	Increasing, (and not) constant, (and not) decreasing
Electron transfer before reversible chemical reaction	ECr	$\leq 0$	Increasing, (and not) constant, (and not) decreasing
Electron transfer before irreversible chemical reaction	ECi	$\leq 0$	Increasing, (and not) constant, (and not) decreasing
Fast electron transfer with catalytic regeneration of substrate	ErCat	$\geq 0$	(not) constant
Irreversible electron transfer with catalytic regeneration of substrate	EiCat	$\neq 0$	(not) constant

pletion of the diffusion zone and the  $Q$  vs.  $t^{1/2}$  plot will again be nonlinear, but the deviation will be of the opposite type. When a  $Q$  vs.  $t^{1/2}$  plot is drawn and the data are tested for deviations from linearity, probabilities (and consequently supporting pairs) can be assigned to the hypotheses that there are positive and negative deviations from the expected model. Positive deviations (overlinearity) mean that the data fit a polynomial model  $a_0 + a_1 t^{1/2} + a_2 (t^{1/2})^2$  better than a linear  $a_0 + a_1 t^{1/2}$  model, and the signs of the  $a_1$  and  $a_2$  coefficient are the same ( $t > 0$ ). In the case of negative deviation (underlinearity), the signs of the  $a_1$  and  $a_2$  coefficients are different.

Appropriate criteria for decisions on diffusion control are collected in Table 5. It should be noted

that, at the present stage of development, infinite spherical diffusion and kinetic control are indistinguishable.

#### Elucidation of the overall mechanism

At the stage of combining all information concerning system type, hidden signals, step interconnections, net reaction and separate-signal characteristics, some limitations were imposed. Only a few mechanisms can be elucidated fully with the current set of rules. Elucidation is not yet possible when there is more than one signal in one branch or when hidden signals are found. In these cases, the expert system ends the reasoning with the system mechanism *unknown*, but all previously described partial information is available.

The set of mechanisms consists of ten systems covering simple electron transfer, transfer followed or preceded by simple chemical steps and two mechanisms with catalytic regeneration of the electroactive compound. Criteria for the elucidation are collected in Table 6. In some rules, the control of the process for the backward signal was allowed to be semiinfinite linear diffusion (1) or limited diffusion (2). This was done because it was

TABLE 5

Criteria for the factor controlling the diffusion of the electroactive substance to the electrode surface (control of the process)

Process control	$\partial Q/\partial (t^{1/2})$ vs $t^{1/2}$
(1) Semi-infinite linear diffusion	Constant
(2) Limited diffusion	Decrease (underlinearity)
(3) Spherical diffusion or kinetic control	Increase (overlinearity)

TABLE 6

Criteria for elucidation of the overall mechanism for a system at an electrode

System mechanism	Symbol	System type <sup>a,b</sup>	Flow control <sup>c</sup>	Suggestion <sup>d</sup>	Net reaction <sup>b</sup>
Fast electron transfer	Er	Symmetric one-signal	F: (1) B: (1) <or> (2)	F E B E	No
Slow electron transfer	Es	Symmetric one-signal	F (1) B (1) <or> (2)	F: Es B: Es	No
Irreversible electron transfer	Ei	Asymmetric one-signal	F (1)	F: Es	Yes
Chemical reaction before fast electron transfer	CEr	Symmetric one-signal	F (3) B (1) <or> (2)	F: CE	No
Chemical reaction before slow electron transfer	CEs	Symmetric one-signal	F (3) B (1) <or> (2)	F CEs	No
Chemical reaction before irreversible electron transfer	CEi	Asymmetric one-signal	F (3)	F CEs	Yes
Electron transfer before reversible chemical reaction	ECr	Symmetric one-signal	F: (1) B: (3)	F ECr	No
Electron transfer before irreversible chemical reaction	ECi	Asymmetric one-signal	F (1)	F ECi	No
Fast electron transfer with catalytic substrate regeneration	ErCat	Symmetric one-signal	F (3) B (3) <or> (1)	F: ErCat	Yes
Irreversible electron transfer with catalytic substrate regeneration	EiCat	Asymmetric one-signal	F (3)	F EiCat	Yes

<sup>a</sup> See Table 3; there are no hidden signals. <sup>b</sup> Facts with support obtained in Boolean tests, thus (0.0, 0.0) or (1.0, 1.0) only. <sup>c</sup> See Table 5 for explanation of (1)–(3). <sup>d</sup> Suggestion for the signal mechanism (Table 4).

expected that, for small mercury electrodes and the time scale of experiments, deviations from linear diffusion would be significant.

## EXPERIMENTAL

The functioning and performance of the expert system were checked with four electrochemical systems which involve different reactions at the electrode. All are well-known systems so that full elucidation could be checked. The systems were Cd<sup>2+</sup>/Cd(Hg) in KCl, Zn<sup>2+</sup>/Zn(Hg) in KCl, Fe(III)/Fe(II) in oxalate solution and Fe(III)/Fe(II) in oxalate solution with hydrogen peroxide present.

Solutions (0.1 M) of Cd<sup>2+</sup> and Zn<sup>2+</sup> were prepared from cadmium sulphate (Merck, Suprapur) and zinc sulphate (Fluka, p.a.), respectively. In the experiments with iron(III), a standard solution of Fe(NO<sub>3</sub>)<sub>3</sub> (1 g l<sup>-1</sup> Fe<sup>3+</sup>; Merck) was used with 0.025 M oxalic acid/0.25 M sodium oxalate (Merck). Approximately 0.1 M hydrogen peroxide

was prepared from a 35% solution (Merck); 1 M KCl was used (Merck, Suprapur). All substances were dissolved in deionized water (Millipore Q-II). Oxygen was expelled with polarographic-grade nitrogen (Hoekloos).

For the experiments, a fully computer-controlled Autolab-100 electrochemical system (Eco Chemie, Utrecht) was connected to a Metrohm 663-VA static mercury drop electrode; an Ag/AgCl electrode (3 M KCl; Metrohm) was used as reference in all experiments. The Autolab-100 was controlled by an Olivetti M24 personal computer (IBM PC/XT-compatible), which was also used to run the expert system.

For each of the investigated systems, different ranges were examined for the voltammetric scan rate. The range for Cd<sup>2+</sup> was 0.1–2.0 V s<sup>-1</sup>, for Zn<sup>2+</sup> 0.1–3.0 V s<sup>-1</sup>, for Fe(III) 0.1–1.2 V s<sup>-1</sup>, and for Fe(III) in the presence of hydrogen peroxide 0.25–2.25 V s<sup>-1</sup>. For all chronocoulometric experiments, the timing of the measurements was identical: 1-s preconditioning at a potential where no reaction occurs at the electrode, followed by

two potential steps of 400 ms each. The charge sampling interval was 6.1 ms and there was a 10-ms delay time before the first sampling. During the conditioning period, the drift of the integrator was measured for later correction of the results.

Each experiment was repeated four times and the results were averaged.

## RESULTS AND DISCUSSION

The results of the reasoning process for all four investigated systems are collected in Tables 7–10; all the facts established by the expert system and their supporting pairs are included. Each table contains the set of results for sub-classifications (system type, suggestion for step mechanism, etc.)

TABLE 7

Results of the expert system run for  $\text{Cd}^{2+}$  ( $3.2 \times 10^{-4} \text{M}$ ) in KCl

(The Table collects all facts established by the expert system together with their supporting pairs)

SYSTEM TYPE <sup>a</sup>	CONTROL OF THE PROCESS <sup>b</sup>
symmetric one-signal 1 0, 1 0	Forward peak
other 0 0, 0 0	semi-infinite linear diff 0 726, 0.726
	other 0.0, 0 0
SUGGESTION FOR STEP MECHANISM <sup>c</sup>	Backward peak: limited diffusion 0 969, 0 969 semi-infinite linear diff 0.031, 0 031
Forward peak E 0.047, 0 060	other 0 0, 0.0
Es 0 025, 0 81	HIDDEN SIGNALS
other 0.0, 0 0	No hidden signals 1 0, 1 0
Backward peak E 0.231, 0 344	NET REACTION
Es 0 017, 0.159	No net reaction 1 0, 1 0
other 0.0, 0 0	
OVERALL SYSTEM MECHANISM <sup>d,e</sup>	
Er 0 519, 1 0	
Es 0 020, 0 622	
other 0 0, 0 0	
Most probable mechanism: Er	
Total run time ca. 24 min	

<sup>a</sup> From Table 3 <sup>b</sup> From Table 5 <sup>c</sup> From Table 4 <sup>d</sup> From Table 6. <sup>e</sup> Support normalized to the highest value obtained, which is taken as 1

TABLE 8

Results of the expert system run for  $\text{Zn}^{2+}$  ( $2.0 \times 10^{-4} \text{M}$ ) in KCl

(The Table collects all facts established by the expert system together with their supporting pairs)

SYSTEM TYPE <sup>a</sup>	CONTROL OF THE PROCESS <sup>b</sup>
symmetric one-signal 1.0, 1.0	Forward peak
other 0.0, 0.0	Semi-infinite linear diff 0 651, 0.651
	other 0 0, 0 0
SUGGESTION FOR STEP MECHANISM <sup>c,e</sup>	Backward peak: limited diffusion 0.994, 0 994 semi-infinite linear diff 0 006, 0.006
Forward peak: Es 0.002, 0.002	other 0 0, 0 0
Es 0.002, 0.002	HIDDEN SIGNALS
E $10^{-4}$ , $10^{-4}$	No hidden signals 1.0, 1 0
other 0 0, 0.0	NET REACTION
Backward peak: Es 1.0, 1 0	No net reaction 1 0, 1 0
E $< 10^{-6}$ , $< 10^{-6}$	
other 0 0, 0 0	
OVERALL SYSTEM MECHANISM <sup>d,e</sup>	
Es 1 0, 1 0	
Er $10^{-8}$ , $10^{-8}$	
other 0.0, 0 0	
Most probable mechanism Es	
Total run time ca 21 min	

<sup>a–e</sup> See footnotes to Table 7

and the final decision about the mechanism of the electrode reaction. In all cases, the expert system was able to find the correct reaction mechanism. As can be seen, in almost all classifications, the highest support was assigned to the correct fact; because of the restriction on the potential range, only the  $\text{Fe(III)} \rightleftharpoons \text{Fe(II)}$  process was recorded, which produced the decision that the system type is symmetric one-signal in the case of iron(III) with hydrogen peroxide in oxalate medium. The only exception was for control of the process; for the re-oxidation signal, limited diffusion was always found to be the most probable. The reason for this is that for the small mercury drops (and time scale), curvature of the electrode led to deformation of the chronocoulometric plots, which were interpreted as limited diffusion in case of iron(III). This indicates that better criteria must be devel-

TABLE 9

Results of the expert system run for Fe(III) in oxalate medium (Conditions: concentration  $1.79 \times 10^{-4}$  M Fe(III) in 0.025 M  $\text{H}_2\text{C}_2\text{O}_4$  0.025 M  $\text{Na}_2\text{C}_2\text{O}_4$ . The table collects all facts established by the expert system together with their supporting pairs)

SYSTEM TYPE <sup>a</sup>	CONTROL OF THE PROCESS <sup>b</sup>
symmetric one-signal 1.0, 1.0	Forward peak
other 0.0, 0.0	semi-infinite linear diff 0.668, 0.668 other 0.0, 0.0
SUGGESTION FOR STEP MECHANISM <sup>c</sup>	Backward peak limited diffusion 0.993, 0.993 semi-infinite linear diff. 0.007, 0.007 other 0.0, 0.0
Forward peak: E 0.019, 0.019 Es $5 \times 10^{-6}$ , $5 \times 10^{-6}$ other 0.0, 0.0	
Backward peak E 0.072, 0.072 Es $4 \times 10^{-5}$ , $4 \times 10^{-5}$ , other 0.0, 0.0	HIDDEN SIGNALS No hidden signals 1.0, 1.0
OVERALL SYSTEM MECHANISM <sup>d,e</sup>	NET REACTION No net reaction 1.0, 1.0
Er 1.0, 1.0 Es $2 \times 10^{-7}$ , $2 \times 10^{-7}$ other 0.0, 0.0	
Most probable mechanism Er	
Total run time 22.5 min	

<sup>a-e</sup> See footnotes to Table 7.

oped for distinguishing between different types of diffusion.

The final result of the reasoning process, the decision about the most probable reaction mechanism, is based on relative support, i.e., the supporting pairs normalized to the highest probability obtained. The reason for this is that some of the supporting pairs assigned in sub-classifications (especially those in the statistical trend tests) were small and their conjunction led to very small supporting pairs. Because the main interest was in comparing the support for different hypotheses, the more informative relative probabilities were used. The low support mentioned for the trend test is caused mainly by the use of a limited number of data points and by the noise in the experimental data. Improvement would require more experiments or an increased number of repli-

cations at the expense, however, of the total run time. The results obtained suggest that this is not necessary for getting the right answer about the mechanism of these simple electrode reaction.

Tests with  $\text{Cd}^{2+}$  and with Fe(III)/Fe(II) in oxalate medium (in both systems, the reductions are reversible but the products are dissolved in mercury and solution, respectively) were made in order to check the ability of the expert system to decide about the phase in which the product of the reaction is present. However, such discrimination was not possible with the present set of rules and the reasoning results were the same for both systems.

TABLE 10

Results of the expert system run for Fe(III) +  $\text{H}_2\text{O}_2$  in oxalate medium (Conditions:  $1.79 \times 10^{-4}$  M Fe(III) and  $8 \times 10^{-4}$  M  $\text{H}_2\text{O}_2$  in 0.025 M  $\text{H}_2\text{C}_2\text{O}_4$  0.025 M  $\text{Na}_2\text{C}_2\text{O}_4$ . The most negative potential was such that hydrogen peroxide was not reduced. The table collects all facts established by the expert system together with their supporting pairs)

SYSTEM TYPE <sup>a</sup>	CONTROL OF THE PROCESS <sup>b</sup>
symmetric one-signal 1.0, 1.0	Forward peak
other 0.0, 0.0	kinetic or spherical diff 0.876, 0.876
SUGGESTION FOR STEP MECHANISM <sup>c</sup>	semi-infinite linear diff. 0.124, 0.124 other 0.0, 0.0
Forward peak ErCat 0.072, 0.746 E 0.051, 0.051 Es 0.051, 0.051 CE 0.049, 0.49 other 0.0, 0.0	Backward peak limited diffusion 0.999, 0.999 semi-infinite linear diff. 0.001, 0.001 other 0.0, 0.0
Backward peak: E 0.002, 0.002 Es 0.001, 0.001 other 0.0, 0.0	HIDDEN SIGNALS No hidden signals 1.0, 1.0
OVERALL SYSTEM MECHANISM <sup>d,e</sup>	NET REACTION No net reaction 0.0, 0.0
ErCat 1.0, 1.0 other 0.0, 0.0	
Most probable mechanism ErCat	
Total run time: ca 25 min	

<sup>a-e</sup> See footnotes to Table 7

One of the attractive features of the presented expert system is its speed. For the compounds studied the total elucidation time varied from about 21 to 25 min, depending on the range of scan rates used in the experiments. This is a significant improvement compared to the previous expert system which needed approximately 8 h.

Future development of this expert system will involve the incorporation of more complicated mechanisms, improvement of existing tests and optimization of the structure and functioning of the expert system shell and the set of rules. Most probably, more electrochemical techniques will also be used.

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