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Automation of Voltammetric Measurements by Polarographic Analyser PAR 384B*

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A specific software package »ElectroAnalytical Research Software« (EARSOFT) for automation of voltammetric measurements using a polarographic analyser PAR 384B connected to a PC computer has been developed. The package enables successful adjustment of PAR 384B for systematic repetitive measurements using a PC. It is particularly advantageous for the experimental data analysis. The EARSOFT implements suitable procedures for automatic electro-analytical measurements such as a standard addition method and pseudopolarography, data processing routines (automatic and manual peak search analysis, baseline correction, polarographic / pseudopolarographic wave logarithmic analysis, linear regression, data smoothing, subtracting, editing, derivation and integration, *etc*.), as well as data graphic presentation sustaining an overlay up to 50 voltammetric curves (files). Determination of dissolved Cd, Pb and Cu concentrations in groundwater samples by a standard addition method is presented as an example. Determination of dissolved copper(II) species in a seawater sample using the pseudopolarographic approach exemplifies the possibilities of speciation of trace metals in natural water systems. These pseudopolarographic measurements show that copper(II) occurs mainly in the form of inert complexes (> 95%) in the analyzed natural seawater sample.

INTRODUCTION

During the last decades, microprocessor based electrochemical instruments have been developed to provide automated measurements using computer-controlled systems.[1–12] Performance of commercially available microprocesor-controlled instruments is fairly adequate, but obviously insufficient as far as automatic measurements with the corresponding data analysis are concerned. The advantages of computer-controlled systems are numerous. The data obtained can be stored in a digital format and subsequently transformed in a desired way. The raw data noise can be diminished by the application of digital filtering. Background correction can be easily implemented in a digital format, as well. A voltammetric / polarographic blank curve of the supporting electrolyte can be stored on the disk. This curve can be subtracted from the signal of the species to be measured in order to minimize the influence of the charging current and interferences from the supporting electrolyte. The actual voltammetric curve can be also corrected by subtraction of the virtuale obtained polynomial interpolated curve.

Computer-controlled measurement systems allow adjustments of various experimental conditions and automatic measurements using chosen procedures. Time-consuming measurements, such as pseudopolarographic measurements,[13] analysis of natural water samples using a standard addition method, different electrochemical measurements involving systematic changes of experimental parameters, *etc*. require automated measurements. Software packages or programs, which are a standard part of some instruments, offer the possibility of different data processing and graphic presentation.[2,4,5,10–12] Thus, the electrochemical measurements have become simpler and more convenient.

A »Windows-based« software package »ElectroAnalytical Research Software« (EARSOFT) used as connection between a PC and the polarographic analyser model PAR 384B is described. The benefits of automatic electrochemical measurements using methods such as pseudopolarography and a standard addition method are presented. The possibilities of several ways of data processing are illustrated, as well.

INSTRUMENT DESCRIPTION

The PAR 384B polarographic analyser is an instrument controlled by a microprocessor. It offers nine polarographic and voltammetric techniques: square-wave voltammetry (SWV), differential pulse polarography (DPP), normal pulse polarography (NPP), sampled dc polarography (SDC), square-wave stripping voltammetry (SWSV), differential pulse stripping voltammetry (DPSV), dc stripping (DCS), linear sweep voltammetry (LSV) and cyclic

staircase voltammetry (CSV). The operating software and computational capability include: (1) multi-point standards and calibration plots; (2) tangent fitted baseline; (3) background subtraction; (4) autoranging sensitivity; (5) automated timing sequences; (6) keystroke programming. Keystroke allows programming of an analysis sequence using the front-panel touch keys, which is then memorized by the PAR 384B and can be performed on request. The data of maximum nine curves can be stored in an internal memory with the possibilities of blank subtraction, peak location, and peak height determination from zero or from a tangent fitted to the curve. Calculation of an unknown concentration of electroactive species in the solution is possible for the standard addition method. A serial RS 232C port allows two-way communication between the PAR 384B and the host computer or a digital plotter or printer. The PAR 384B is also designed to control up to four different static mercury drop electrodes model PAR 303A at a time.

SOFTWARE DESCRIPTION

A Windows 95-based software package EARSOFT has been developed as a connection between a PC computer system and the PAR 384B polarographic analyser for different automatic electrochemical measurements (especially pseudopolarography), various data processing and graphical presentations. It is written in Borland Delphi 2.0* for the Windows 95 (32 bit version) environment. EARSOFT does not use any of the PAR 384B computational capabilities, for instance standard or calibration plots, blank subtraction, programmed measurements, peak search, *etc.*

The main window includes the program menu (Figure 1) consisting of the File option (the main options for the data and procedure handling: open, save, print, *etc.*), the Technique option (here one of the above mentioned PAR 384B techniques can be selected), the Method option (pseudopolarography or a standard addition method), the Settings option (settings of RS 232 serial port, transfer speed, rescale plot during playback, *etc.*), the Window option (common routines for windows handling) and the Help option (Help program and About form). The principal asset of the EARSOFT program is that it utilizes a PAR 384B polarographic analyser only for obtaining raw data with a specific technique. All methods, programmed measurements and data processing (*e.g.* standard addition method, automatic peak determination, blank subtraction, *etc.*) are entirely controlled by the EARSOFT package. Thus, the automation of measurements is enhanced, which significantly improves the performances of the original PAR 384B system. Using the appropriate technique offered by PAR 384B, and setting the appropriate timing and potentials by pressing the START button, the computer sends the necessary data to the PAR 384B to initiate the measurement. After the completion of measurement, the PAR 384B transmits the results (potentials and
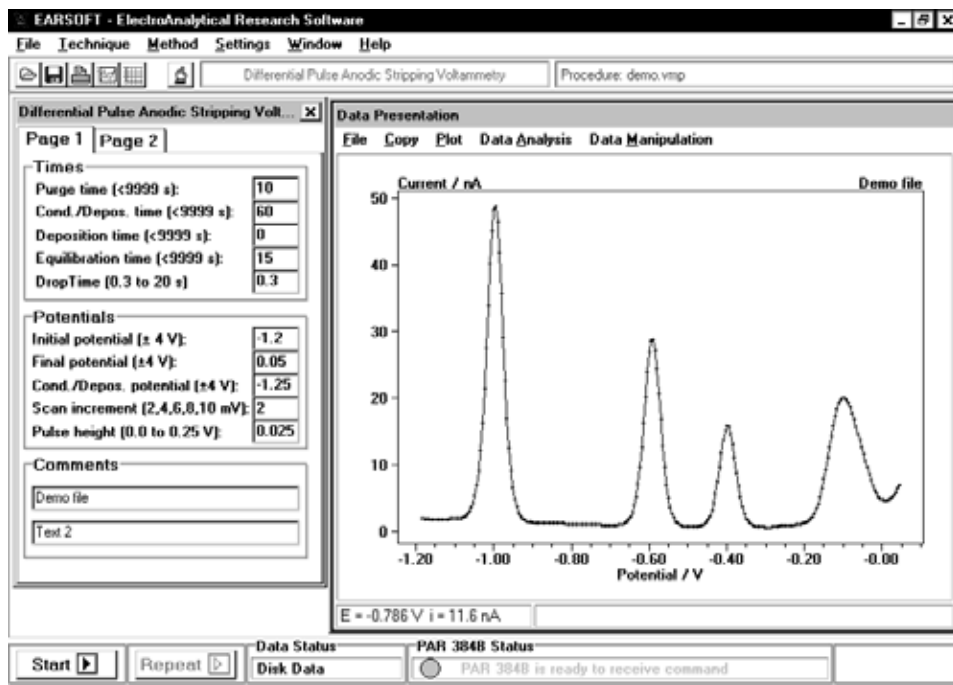
Figure 1. The main EARSOFT window with an active Procedure window and Data Presentation window on which the demo voltammetric curve is illustrated.

the corresponding currents) to the PC, and the data automatically appear on the graph in the Data Presentation window. After the whole measurement procedure is completed, it is possible to evaluate raw data.

Common routines for plot handling (automatic ranging, zooming, setting an active window of the data, input of the overlay data file, inserting text in the plot, setting axis range, setting graph properties) are incorporated into the Data Presentation menu under the option Plot (Figure 1). The Data Analysis option allows the following routines for data analysis: peak search, minimum and maximum search, linear regression and logarithmic analysis of polarographic/pseudopolarographic curves. The Peak Search option offers several methods for peak height determination: automatic peak search and determination of the peak potential and current height with or without tangent baseline, manual peak determination with a linear baseline, polynomial baseline (4th degree; an example in Figure 2), linear front baseline and linear rear baseline. The procedure for the Wave Log Analysis of DC polarograms, NP polarograms and pseudopolarograms consists of two steps: first, the limiting current (i_d) is calculated from the manually set base and the limiting current line which is necessary for the logarithm plot that appears

on the graph (Figure 3). Subsequently, the half-wave potential is determined and the reversibility of the process is estimated from the regression line obtained by selecting two points on the linear part of the corresponding logarithm plot (Figure 3). The Data Manipulation option includes the following routines: Smooth Data, Change All Points, Change Baseline, Subtract Disk File, Derivate, Integrate and View Data. Smoothings of raw data is performed using the Savitzky-Golay[14] method with the possibility of four data averaging levels (5, 9, 15 or 23 points). Raw data can be changed by adding, subtracting, multiplying and dividing potentials or currents by the corresponding values. A linear or a polynomial baseline correction (with a chosen degree of polynom) is also very useful, especially in the case of nonequal base currents prior to and after peak. All the changes of the raw data (work data) can be saved in the Data Presentation menu under option File (by command Save Work Data). It is also possible to copy a graphic presen-
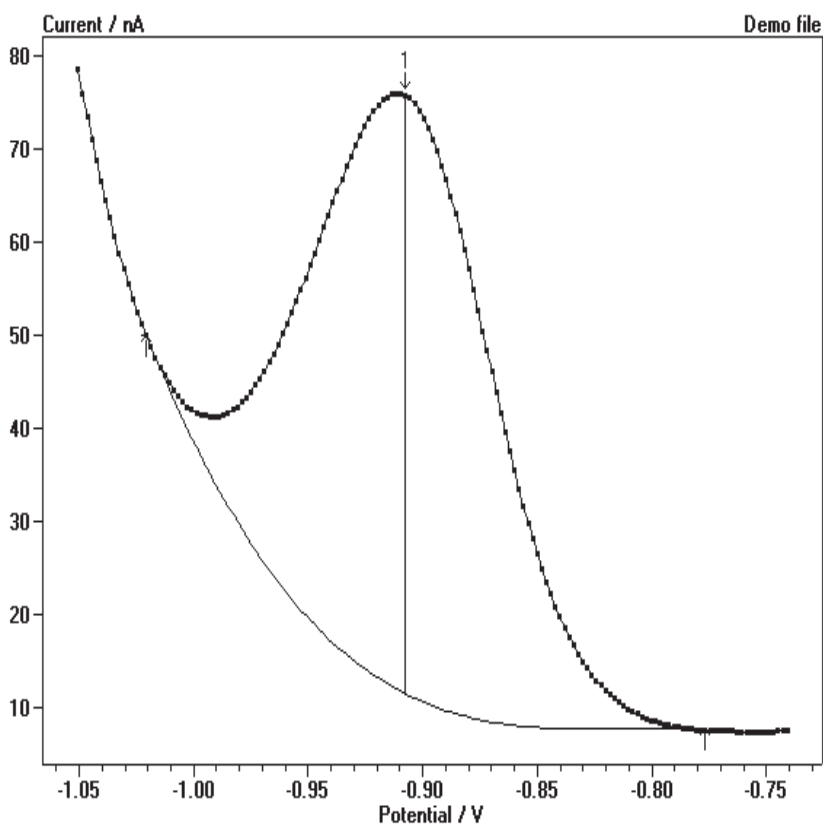

Figure 2. Data presentation window; as an example, peak current determination of Zn(II) (demo voltammetric curve) with the polynomial baseline is presented.
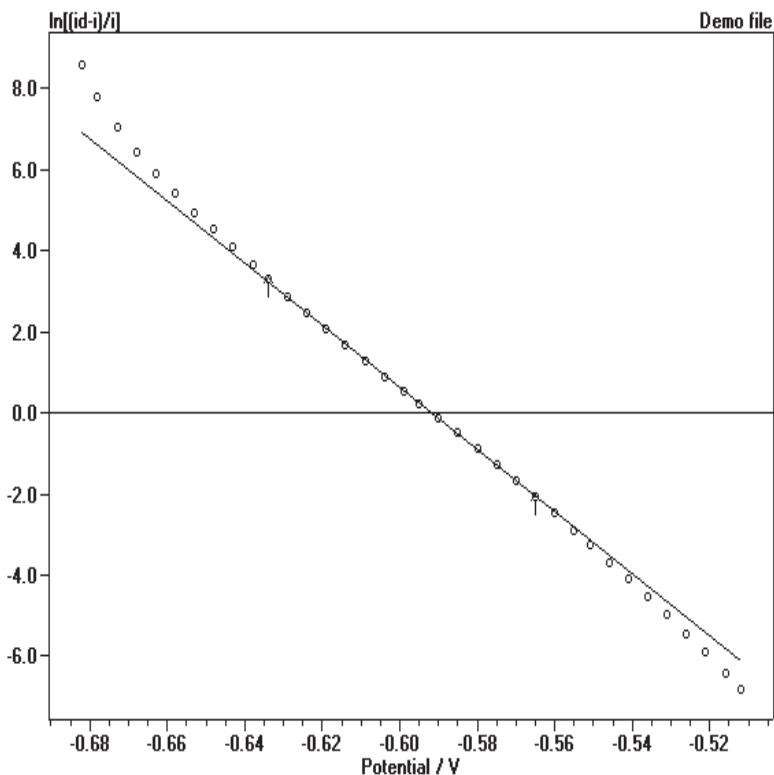
Figure 3. An example of logarithmic analyses on the demo polarographic curve with a manually selected linear part of the logarithmic plot.

tation into a clipboard or to save it as a BMP file. Once the procedure for running a PAR 384B is transmitted to the instrument, pseudopolarography or the standard addition method can be initialized.

Pseudopolarographic measurements can be performed for up to five different electroactive species (peaks) at the same time, with sufficiently separated peaks and distinguishable peak potentials (Figure 4). After completion of each step of the measurement procedure, the program automatically determines the location of the peak (their potentials with the corresponding currents) of all species and stores the data under separate files chosen prior to measurements. Each voltammetric curve is also stored under a specified file name and is available for further analysis. Similarly, for determination of unknown concentrations of the electroactive species using a standard addition method, the corresponding voltammetric curves, concentrations of the species added to the sample and the corresponding peak currents are stored in separate files.

Figure 4. An example of Pseudopolarographic window on which the parameters for two electroactive components are selected.

Minimum computer system requirements for the EARSOFT software package are a PC 486 with a 8 Mb RAM, 2 Mb free disk space and a Windows 95 operating system.

EXPERIMENTAL

Voltammetric measurements were performed using a new system consisting of a PAR 384B polarographic analyser and a PC (486 DX2-80 MHz/32 Mb RAM) with a new software package. A three-electrode system was applied. The working electrodes were a PAR 303A static mercury drop electrode (SMDE) assembly with a middle

drop-size and/or a preplated thin mercury film glassy carbon disk electrode (TMFGCDE) with the cell assembly described elsewhere.[15] The preplated TMFE ($\phi =$ 5 mm) was formed by electrolyzing the aqueous solution of 1×10^{-4} M $Hg(NO_3)_2$ and 3×10^{-2} M HNO_3 at the potential of -0.9 V during 5 minutes under hydrodynamic conditions (with 4000 rpm of turbine rotating speed). After that, the mercuric ions were washed off from the cell with the doubly distilled water and then the sample was introduced. A reference electrode was an Ag / AgCl / sat. NaCl and platinum wire was the counter electrode. The solutions were purged with an extra-pure nitrogen for 15 minutes prior to measurements; a nitrogen blanket was maintained thereafter. Seawater samples were collected in the Šibenik Bay (pH = 8.1×0.1, S = 32 ‰) and the groundwater samples were collected at the sediment depth of 40 m near the Sava River (Zagreb) and in the vicinity of a waste disposal landfill. Chemicals were either of »suprapur« grade: concentrated HNO_3 and $Hg(NO_3)_2$ (both Merck, Darmstadt), or of analytical-reagent grade: $Cd(NO_3)_2$, $Pb(NO_3)_2$ and $Cu(NO_3)_2$ (all Kemika, Zagreb).

RESULTS AND DISCUSSION

The analytical application of the system developed is shown by determination of the trace metal concentrations in the groundwater sample collected between the Sava River (Zagreb) and the waste disposal landfill – »Jakuševac« (at the sediment depth of 40 m). The groundwater sample was acidified to pH = 2.0 ± 0.1 with conc. HNO_3 immediately after sampling. In such a way, the »total« trace metal concentrations will be determined. Figure 5 illustrates a series of differential pulse anodic stripping voltamograms (DPASV) for cadmium(II), lead(II) and copper(II) obtained with PAR 303A electrode assemblies using the standard addition method. However, Figure 6 shows an example of the calibration curve for Pb(II) only. The total dissolved trace metal concentrations of Cd, Pb and Cu were calculated from the corresponding calibration curves: $(1.1 \pm 0.6) \times 10^{-10}$ M, $(6.2 \pm 0.6) \times 10^{-10}$ M and $(1.6 \pm 0.2) \times 10^{-8}$ M, respectively.

Pseudopolarographic determination of copper(II) species in seawater samples was carried out using a thin mercury film glassy carbon disk electrode (TMFGCDE). This is an example of the possibility of aplying the pseudopolarographic approach to the trace metal speciation in natural water systems. Figure 7 illustrates pseudopolarograms of copper in the seawater sample (pH = 8.1 ± 0.1) (curve 1) and with addition of 2.5×10^{-8} M Cu^{2+} (curve 2) and 5×10^{-8} M Cu^{2+} (curve 3), respectively. Each pseudopolarogram consists of 46 points (at a different accumulation potential). The duration of the whole measurements procedure for every pseudopolarogram was approximately 3.5 hour. For better comprehensibility, each pseudopolarogram was standardized to the initial value obtained at the accumulation potential of -1.5 V. No copper peak currents occurred on the first pseudopolarogram at accumulation potentials more positive than -0.6 V. This suggests
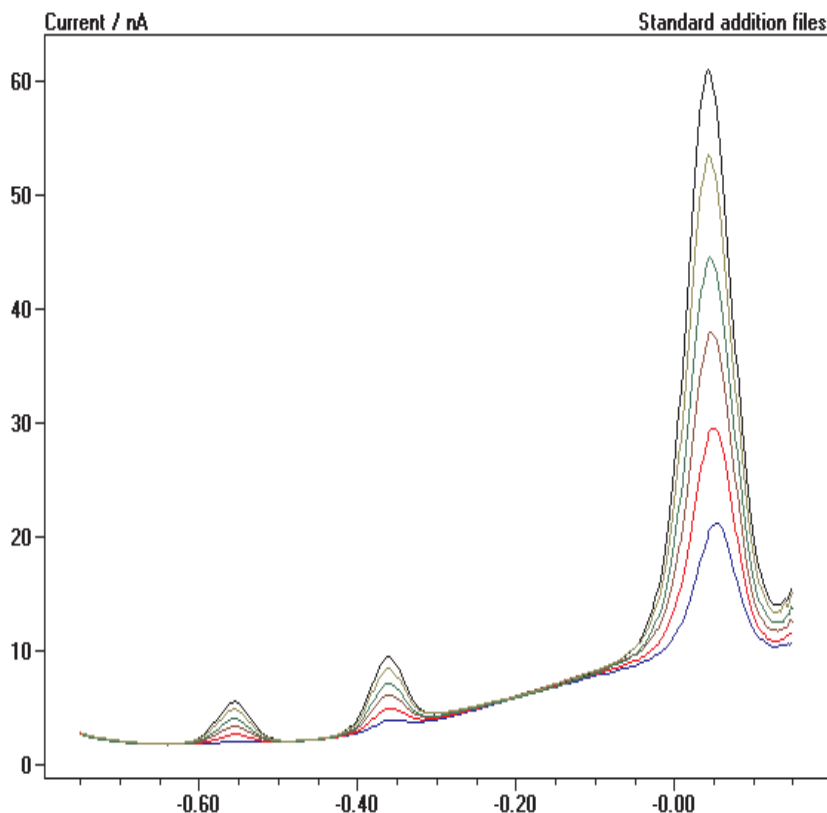
Figure 5. DPAS voltamograms (with growing concentrations of analytes) of the standard addition method for determination of Cd, Pb and Cu in the groundwater sample (collected at the sediment depth of 40 m near the Sava River (Zagreb); pH = 2.0 ± 0.1) obtained with SMDE PAR 303A electrode assembly; DPASV parameters: E_{dep} = –0.9 V, A = 0.025 V, t_{dep} = 300 s, t_{eq} = 30 s, t_{drop} = 0.3 s.

that the concentration of free copper and labile copper(II) species in the solution are below the detection limit under the given experimental conditions and that copper is practically completely bound to inert complexes (> 95%). The appearance of copper peak currents at potentials more negative than –0.6 V is probably due to the reduction of different inert copper(II) complexes. By addition of the ionic copper(II) to the solution, a wave of free and labile copper species appears at the potential of –0.43 V (Figure 7, curve 2). An increase of the peak currents at potentials more negative than –0.6 V was also registered on this pseudopolarogram. However, the ratio of the limiting current of the whole wave and the limiting current of the free and labile copper reduction wave is smaller. This ratio becomes more obvious by addition of 5×10^{-8} M Cu^{2+} (Figure 7, curve 3).
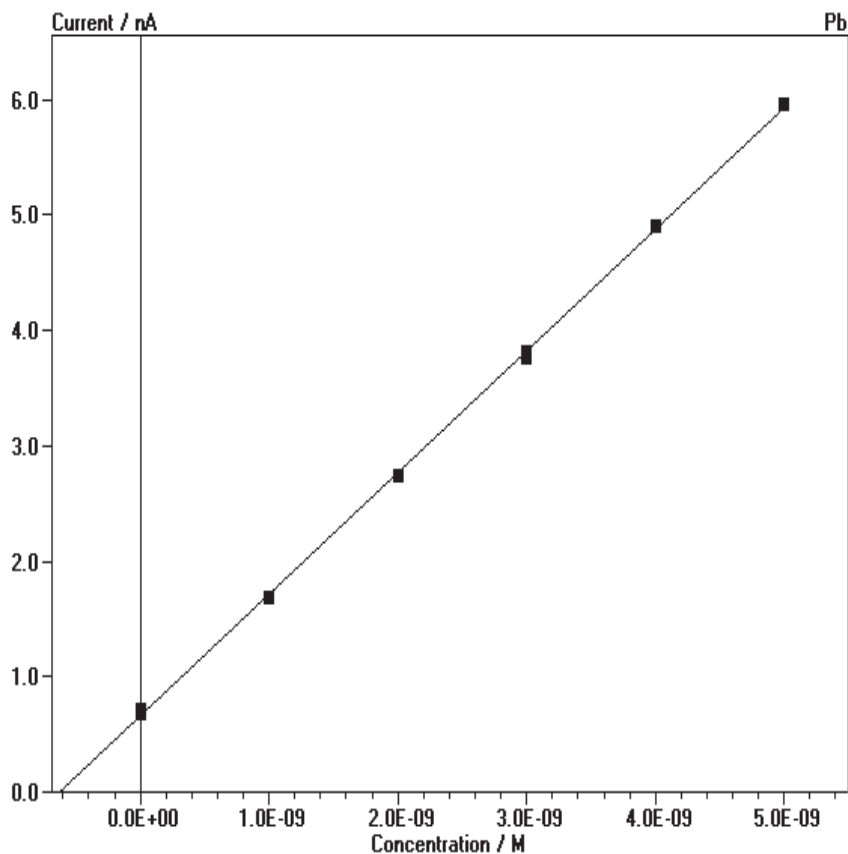
Figure 6. An example of the calibration curve (Pb) of the standard addition method for determination of Cd, Pb and Cu in the groundwater sample (pH = 2.0 ± 0.1); peak currents are determined from voltammetric curves on Figure 5.

The recorded pseudopolarograms of trace metals in natural water samples can be used for the estimation of the accumulation potential (where only the reductions of »free-labile« metal complexes occur). This is very important for determination of the metal complexing capacity.[16]

CONCLUSION

The measurement system consisting of a polarographic analyser PAR 384B and a personal computer using a new software package EARSOFT is particularly advantageous for automated data assessment. The system performs automatic routine analyses of dissolved trace metals easily and rapidly. The possibility of a long duration of automatic measurements (over-
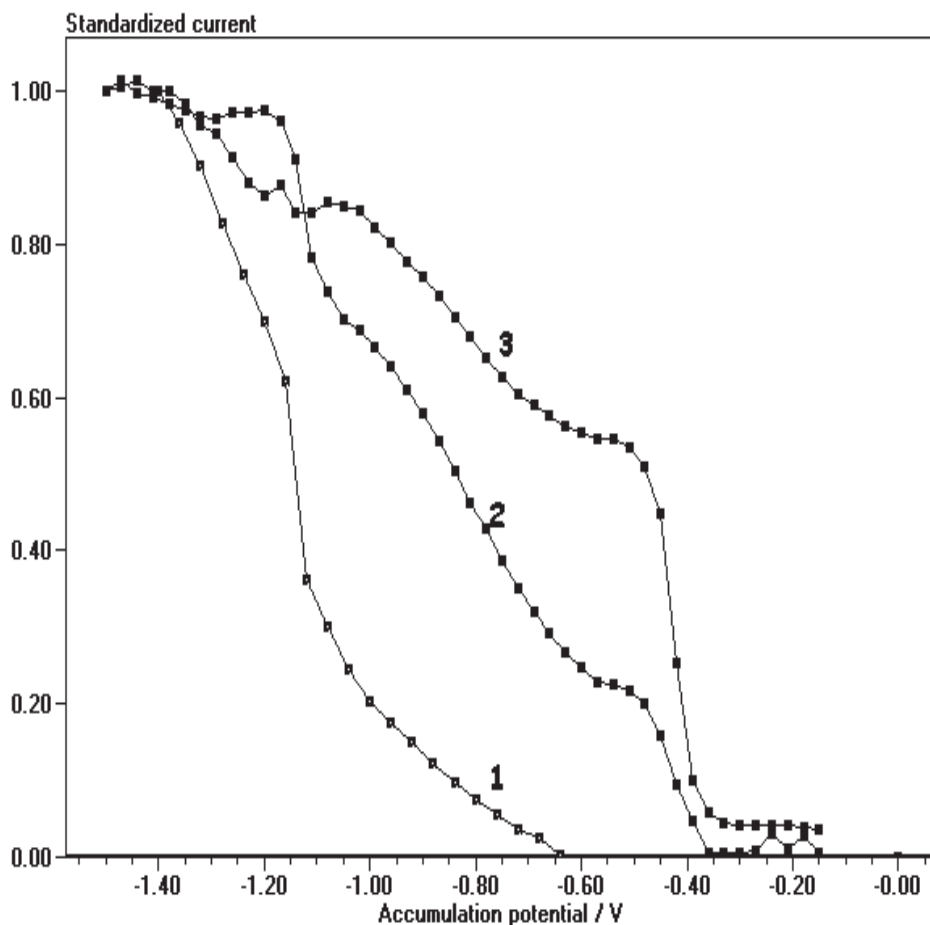
Figure 7. Pseudopolarograms of copper(II) obtained with TMFGCDE: (1) in seawater sample (collected in the Šibenik Bay; $S = 32$ ‰, pH = 8.1 ± 0.1); (2) by addition of 2.5×10^{-8} M Cu^{2+} and (3) by addition of 5×10^{-8} M Cu^{2+}. Pseudopolarograms are standardized to their initial values of peak currents (at $E = -1.5$ V); DPASV parameters: $E_i = -0.8$ V, $E_f = -0.1$ V, $A = 0.025$ V, $t_{dep} = 180$ s, $t_{eq} = 15$ s.

night or even for days, without an operator) is very useful for the methods utilizing repetitive measurements and a systematic change of one or two electrochemical parameters (such as pseudopolarography). Measurements performed using an automatic system provide more reliable and reproducible data (avoiding the possibility of personal errors). The EARSOFT is easy to handle and enables numerous routines for automatic and manual data analyses as well as graphic presentation.

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SAŽETAK

Automatizacija voltammetrijskih mjerenja polarografskim analizatorom PAR 384B

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Razvijen je specifični programski paket »ElectroAnalytical Research Software« (EARSOFT) za automatizaciju voltammetrijskih mjerenja instrumentom Polarographic Analyser PAR 384B povezanim s osobnim računalom. Uporabom računala, paket omogućuje zadovoljavajuću prilagodbu PAR 384B za sustavna ponavljana mjerenja. Posebno je pogodan za računalnu obradbu eksperimentalnih podataka. EARSOFT obuhvaća procedure za automatska elektroanalitička mjerenja kao što su metoda dodatka standarda i pseudopolarografija, pogodne rutine za obradbu podataka (automatsko i ručno određivanje visina vrha vala, promjena osnovne linije, logaritamska analiza polarografskih/pseudopolarografskih valova, linearna regresija, izglađivanje

podataka, odbijanje podataka iz slijepog pokusa, uređivanje podataka, derivacija i integracija podataka, itd.), kao i grafičko prikazivanje podataka (iscrtavanje do 50 različitih voltammetrijskih krivulja). Metoda dodatka standarda prikazana je na primjeru određivanja koncentracije Cd, Pb i Cu u uzorku podzemne vode. Kao primjer pseudopolarografskog pristupa određivanju fizičko-kemijskih vrsta tragova metala u prirodnim vodenim sustavima prikazano je određivanje kemijskih vrsta bakra(II) u uzorku morske vode. Ta pseudopolarografska mjerenja pokazuju da u analiziranom uzorku prirodne morske vode bakar(II) postoji uglavnom u obliku inertnih kompleksa (> 95%).