

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
5 (1999)

**POSSIBILITIES OF THE PA-3 POLAROGRAPHIC
ANALYSER INTERFACED TO A PERSONAL
COMPUTER IN VOLTAMMETRIC ANALYSIS**

Radovan METELKA^a, Michal STRELEC^b, Ivan ŠVANCARA^{a1},
František DUŠEK^b and Karel VYTRÁS^a

^aDepartment of Analytical Chemistry,

^bDepartment of Process Control and Computer Techniques,
University of Pardubice, CZ-532 10 Pardubice

Received October 29, 1999

Acquiring of the experimental data from PA-3 polarographic analyser and their treatment by personal computer was performed using commercially available AD/DA converter and a software developed on basis of Visual Basic 3.0 developing environment. Only minimal hardware arrangements to PA-3 are necessary when requiring no special technical skill. Analyser's output to XY recorder is connected to the input of AD/DA converter and digitised data are transferred to the computer using its serial port. Further processing of the data is handled by software "Polarograf" which is able to acquire, plot and manage experimental data and capable of exporting them in a readable form for Excel or other software. Functionality of the system was verified using several model voltammetric systems measured with carbon paste electrodes. The same principle of interfacing can be

¹ To whom correspondence should be addressed.

applied with only small changes practically to all analogue electroanalytical instrumentation.

Introduction

Instrumentation in the electroanalytical chemistry, like in other analytical areas, has passed through a stormy growth. Sequential technical discoveries and their applying to the analytical instrumentation put aside generations of former arrangements and made possible to fulfil at that time non-performable analytical requirements. A fast progress in electronics enabled achieving of very low detection limits (e.g. in stripping analysis), reducing the dimensions of whole analytical device and resulting in development of self-operating analysers.

In the first fifty years of history of voltammetry, the above-mentioned evolution process was characterised by several fundamental changes, which allowed one to improve the analytical instrumentation. Several examples shown on classical Heyrovský's direct current polarography are given in the following points [1]:

- use of electric circuit based on the Wheaston bridge principle for measuring the resistance of the cell and for correction of the ohmic drop,
- use of automated stepless change in polarisation potential,
- automated registration of polarographic currents,
- recording of polarographic waves by mechanical recorders of X-t and of X-Y type,
- introducing of the three-electrode configuration for reducing the ohmic drop,
- improvement of the ohmic drop compensation by using a feedback circuit,
- automated compensation of charging current and the other residual currents,
- registration of polarographic and polarisation curves in differential mode.

Development of electronics in the last half-century has facilitated the introducing of new voltammetric methods to practise; for example, alternate current-, square wave- and differential pulse voltammetry with the aid of circuitry capable to monitor very rapid electrode processes. Accession of operating amplifiers and integrated circuits in the period of 1950 – 1970 participated then in the revival of voltammetric techniques as such.

Electroanalytical instrumentation was further enriched by exploiting highly integrated circuits and modern computers. The so-called artificial intelligence, to-make-decision devices and expert systems were going to the fore as well as applications of new statistical methods.

Several perspectives of construction of computer-controlled electroanalytical instrumentation were evolved according to the development of electronics and computers. One way is to use general data-acquiring device or a card with adding the voltammetric accessories into, typical examples being a potentiostat, the I/E

converter, electrode stand, etc. [1,3–6]. Such modular arrangement was used a number of years ago but its main principle is still persistent and often used in today's instrumentation [7].

Another way of construction utilises the integration of all necessary parts to the only one device. Miniaturisation of electronic components has permitted the production of portable analysers for field analysis, which can be powered by batteries or even "all-in-one" card plugged into expanding slot of a computer. Electrode stands are usually designed as a separate compartment of the instrument; in some cases, however, being its integral part [8–10]. For practical reasons, it is worth to adapt older electrochemical instrumentation to computerised devices, depending on the type of apparatus. Some of formerly manufactured analysers could communicate with a computer *via* special interface, but, normally, such devices did not offer similar possibilities. Thus, the only way is to interface them to a computer *via* a suitable analog-to-digital converter [1,11–14].

This work deals with such a type of adaptation and presents some results obtained by analysing model systems using stripping voltammetry with carbon paste electrodes.

Experimental

Apparatus

All experiments were performed using a PA-3 polarographic analyser (Laboratorní přístroje, Prague, the Czech Republic) with SMDE 1 electrode stand (Laboratorní přístroje, Prague, the Czech Republic) adapted for measurements with carbon paste electrodes. The CTRL-51 AD/DA converter (UTIA ČSAV, Prague, the Czech Republic) used for digitising of the experimental data provide 10 bits of resolution in ranges of 0 – 10 V and 0 – 5 V for 12 input channels with the minimum sample interval of 10 msec. Output channels were not used. A converter was connected to analyser's output to XY recorder and linked to computer's serial port COM2. Relay circuit was mounted inside the polarograph and connected to START button, thus achieving semiautomatic start of measurements and a small jack type connector was installed on backside of PA-3 providing the connection to converter. Details about wiring are given in table below

PA-3 analyser	AD/DA converter
X axis	channel 1
Y axis	channel 2

Voltage ranges of both used input channels of converter were adjusted at ± 2.5 V to

meet the range of analyser's output to XY recorder and to exploit the whole sampling range. The analyser and converter were assembled together with an ordinary computer with 486 processor and 8 MB of RAM; all being connected into one plug only for minimising the interference.

Software

For acquiring, plotting and evaluating of voltammetric data, the software called "Polarograf" was developed. At the time of developing the software, the Visual Basic version 3.0 was chosen for its simplicity in programming for "Windows 3.x" operating system. Since the PA-3 analyser does not offer any capabilities to be connected to a computer, semiautomatic mode was used to perform voltammetric measurements. All parameters for analysis must be set on instrument before measuring, only the start and the end of analysis is synchronised. The main features of developed software are listed below and are evident also from the scheme in Fig. 1:

- input of PA-3 set-up parameters for a given type of measurement,
- semiautomatic start and stop of analysis synchronised with PA-3 analyser,
- registration of up to 20 measurements in one experiment with displaying run of measurements,
- displaying of one or several selected measurements and change of their position (shift, overlay),
- evaluation of selected measurement, i.e. setting the baseline, calculating the peak potential, the peak area or a peak width in its half height,
- storing and managing of data files of up to 20 experiments (copy, move, delete),
- exporting to a format readable for Excel or another related program,
- printing of experimental curves on a printer installed in Windows.

Electrodes

According to a previously recommended procedure [15,16], carbon paste electrodes (CPES) were prepared by thoroughly mixing 0.5 g of graphite powder CR-5 (Tesla Lanškroun, the Czech Republic) with 0.2 ml of the corresponding pasting liquid using a pestle and mortar. Tricresyl phosphate (TCP, Fluka, Germany), Uvasol paraffin oil (Uv, Fluka, Germany) and Lukooil MV-15500 silicon oil (SO, Lučební závody Kolín, the Czech Republic) were used as pasting liquids. All the carbon pastes were packed into piston-like electrode holders. Self-made Pt-plate serving as auxiliary electrode and an Ag/AgCl (1 M KCl) electrode as the reference completed the cell. Stirring was performed by Teflon-coated magnetic bar at ca 300 rpm.

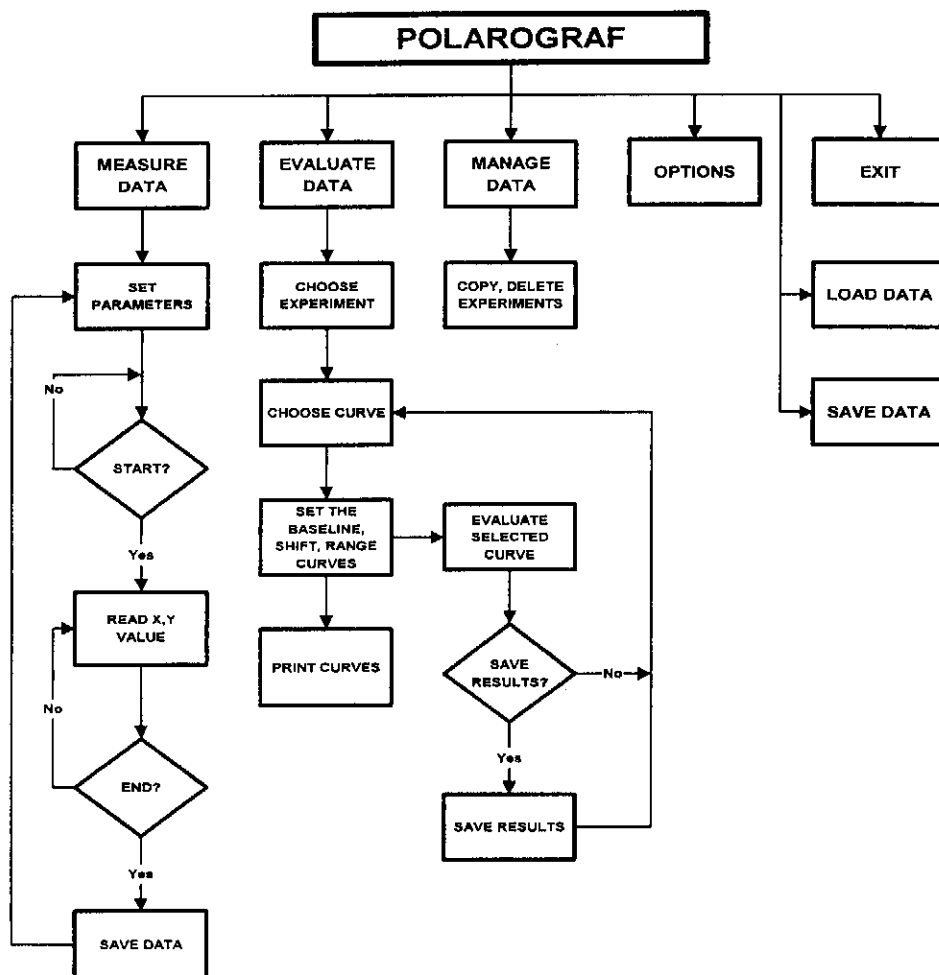


Fig.1 Schematic flowchart of POLAROGRAF program

Chemicals

All the chemicals used were of analytical grade and purchased from Lachema (Brno, the Czech Republic) unless stated otherwise. Stock solutions for the preparation of the supporting electrolytes were made 1 mol l^{-1} in concentration. Standard solutions of analytes and test chemicals prepared in a concentration of 0.1 or 0.01 M were diluted immediately prior to use.

Results and Discussion

Anodic Stripping Voltammetry at Mercury Film-Plated Carbon Paste Electrodes

Determination of numerous heavy metals can easily be done utilising the carbon paste electrodes plated with a mercury film. During the accumulation time, the mercury film deposited onto the surface of a CPE is formed from the Hg(II) ions spiked in the solution to be analysed. Metals deposited are reduced at the electrode forming instantaneously amalgam with mercury. Then, amalgam is reoxidised ("stripped off") to the solution by imposition of potential scan, giving rise to voltammetric signals [17].

These processes are the fundamentals of numerous classical stripping methods and their voltammetrical characteristics are very well known, including relatively difficult theoretical background of measurements in a differential pulse mode. The shape and magnitude of anodic peaks is unambiguously defined for numerous metals in dependence on their valence, affinity to amalgamation (i.e., the measure of reversibility), the supporting medium used and, naturally, on the concentration. Literature also describes numerous phenomena, relations and trends explaining under which circumstances the peaks can be overlapped, defor-

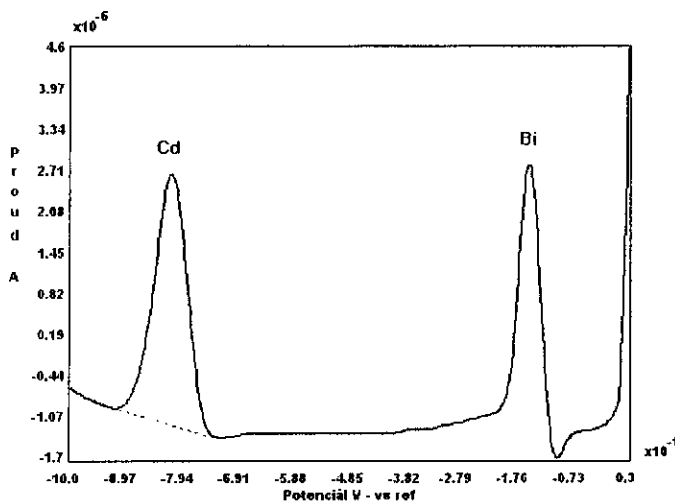


Fig. 2 Differential pulse anodic stripping voltammetry of Cd(II) and Bi(III) at mercury film-plated C/SO carbon paste electrode. Experimental conditions: supporting electrolyte, 0.1 M HCl + 1×10^{-5} M Hg^{2+} ; $c(\text{Cd}^{2+}) = 2 \times 10^{-6}$ mol l $^{-1}$; $c(\text{Bi}^{3+}) = 1 \times 10^{-6}$ mol l $^{-1}$; accumulation potential, $E_{ACC} = -1.0$ V vs Ag/AgCl; accumulation time, $t_{ACC} = 30$ s; equilibration time, $t_{EQ} = 15$ s; initial potential, $I_{INIT} = -0.1$ V; final potential, $I_{FIN} = +0.5$ V, scan rate, $\nu = 20$ mV s $^{-1}$; pulse height, $\Delta E = 50$ mV

med, lowered or even completely eliminated. All these aspects indicate clearly why stripping voltammetric analysis at a mercury electrode has been chosen for demonstrative measurements in the present work.

Two combinations of mixtures of heavy metals were chosen to obtain the corresponding responses recorded with the instrumental configuration tested. Based on previous experience [15–17], carbon paste-based electrode was selected as a support for a mercury film, in this case that containing silicone oil. Figure 2 provides a picture of typical voltammograms for Cd(II) and Bi(III), Fig. 3 shows the same for Tl(I) and Cu(II). As seen, the individual peaks are well-developed, resolved, and can easily be evaluated even in a simplified way as the peak heights. However, the voltammetric curves also reveal some disturbances originating from the device that seem to be caused by not very well tuned linkage of all the apparatus as indicated by "derivative behaviour" on fast variations of the signal.

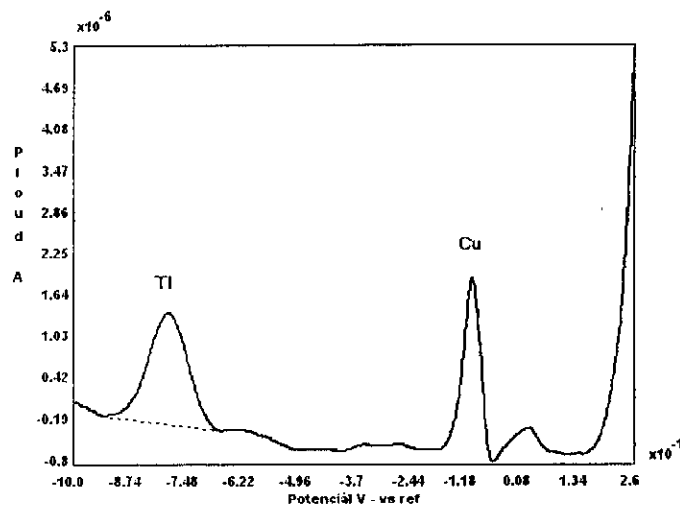


Fig. 3 Differential pulse anodic stripping voltammetry of Tl(I) and Cu(II) at mercury film-plated C/SO carbon paste electrode. Experimental conditions: 0.1 M acetate buffer + 1×10^{-5} M Hg^{2+} ; $c(\text{Tl}^+)$ and $c(\text{Cu}^{2+}) = 2 \times 10^{-6}$ M; $E_{ACC} = -1.0$ V vs Ag/AgCl; $t_{ACC} = 30$ s; $t_{EQ} = 15$ s; $I_{INIT} = -0.1$ V; $I_{FIN} = +0.5$ V; $\nu = 20$ mV s $^{-1}$; $\Delta E = 50$ mV

Adsorptive Stripping Voltammetry of Nickel

Bivalent nickel is preconcentrated onto the electrode surface *via* physico-chemical forces as the dimethylglyoximate complex, whose cathodic reduction can then be recorded voltammetrically. At a CPE, the signal of Ni is superimposed on increasing wave of hydrogen evolution at potentials beyond -1.0 V vs SCE [18]. In addition,

the whole base-line is usually distorted in consequence of reduction of oxygen dissolved in the paste.

The example has been chosen due to the fact that this system comprises two responses completely different in nature and hence even differing also in the peak shape. Firstly, it is a peak of Ni representing a typical response for non-electrolytic desorptive process [15], which is indicated by its characteristic sharpness. On the other hand, a broad plateau-like response for oxygen is an evidence of complicated electrolytic transformation; in this case, two-step reduction of oxygen *via* peroxide. Owing to this flat response, the evaluation of the signal of interest, i.e., Ni-peak, can be quite difficult, requiring usually an effective subtraction of the base-line deformed by unwanted (but unavoidable) background of oxygen [18].

In this test, Uvasol oil-containing CPE was used. Both voltammograms in Fig. 4 illustrate the above-stated specifics; the upper curve indicating also the way of computing the peak height. Wave of oxygen can also be noticed; nevertheless, for rather high concentration range chosen, its disturbing effect is not yet so pronounced.

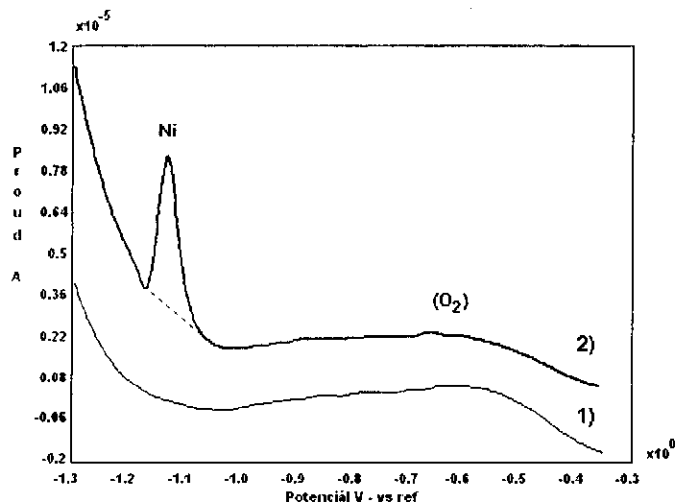


Fig. 4 Adsorptive stripping voltammetry of Ni(II) at C/Uv carbon paste electrode: 1) base-line, 2) addition of 5×10^{-6} M Ni(II); Experimental conditions: DPCSV; $0.5 \text{ M NH}_4\text{Cl} + 0.05 \text{ M triethanolamine} + 1 \times 10^{-4} \text{ M dimethylglyoxime}$; $E_{ACC} = -0.3 \text{ V}$; $t_{ACC} = 30 \text{ s}$; $t_{RQ} = 15 \text{ s}$; $I_{INIT} = -0.3 \text{ V}$; $I_{FIN} = -1.4 \text{ V}$; $\nu = 20 \text{ mV s}^{-1}$; $\Delta E = -50 \text{ mV}$

Stripping Voltammetry of Iodide Utilising Preconcentration Based on Ion-Pair Formation

Iodide as voluminous anion forms readily ion-pairs with protonated lipophilic tricresylphosphate which can be used directly as a liquid binder in the paste [19]. The ion-pairs formed are accumulated onto the carbon paste bulk *via* their extraction and, under a sufficiently positive potential, instantaneously oxidised to elementary iodine. This electroactive substance is subsequently reduced back to iodide during cathodic voltammetric scan [19].

The ion-pair forming system is worth to allow one to demonstrate herein another type of voltammetric responses. Slow diffusive re-extraction of species from the electrode interior during voltammetric reduction gives rise to a characteristic, very wide signal which has to be always evaluated as peak area [19,20]. Furthermore, due to a highly saline medium analysed, the electrode base-line is again considerably deformed, which may make difficult the evaluation of the peak of interest.

In Fig. 5, the voltammogram below depict a typically broad response for iodide. The measurement suffers from a noise implying some oscillation superimposed on the baseline of parabolic shape. The reason can be inadequate non-synchronisation of the sampling frequency with the voltage frequency. As found, this interference negatively affects measurements solely at a higher sensitivity of the

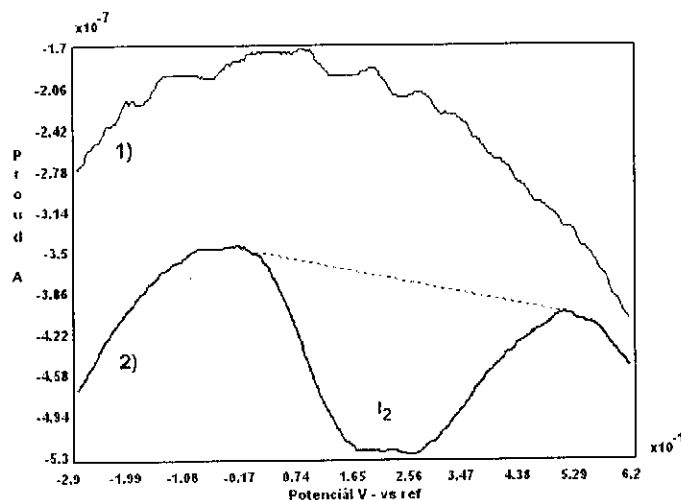


Fig. 5 Differential pulse stripping voltammetry of iodide utilising the ion-pair formation at tricresyl phosphate-based carbon paste electrode: 1) base-line, 2) addition of $5 \times 10^{-6} \text{ M I}^-$; DPCSV; $E_{ACC} = +0.7 \text{ V}$; $t_{ACC} = 60 \text{ s}$; $t_{EQ} = 15 \text{ s}$; $I_{INIT} = -0.7 \text{ V}$; $I_{FIN} = -0.3 \text{ V}$; $v = 20 \text{ mV s}^{-1}$; $\Delta E = -50 \text{ mV}$

apparatus; nevertheless, it will be necessary to find a way to eliminate or, at least, minimise this undesirable noise.

Somewhat cut-off response for iodide which seemingly indicates overloaded device and, therefore, wrongly performed measurement is due to the aforementioned re-diffusion process. As ascertained recently, the complicated pathway of the analyte through and out of the carbon paste bulk often results in such unusually shaped signals [19,20]. These peaks may exhibit various shoulders and waves at the foot or badly developed tops, the latter being also seen in the figure (the peak is not cut off regularly).

Conclusion

The aim of this article was to demonstrate the possibility of interfacing of the PA-3 polarographic analyser to a personal computer *via* AD/DA converter, which enables one to exploit more effectively such a set-up in the present day's electroanalysis. The functionality of the system was verified on selected model voltammetric systems using different types of carbon paste electrodes. It has been shown that this combination provides parameters comparable to those offered by a similar device employing classical PAR 174 A instrument which has been used successfully for several years [11].

Some results indicate that attention should further be focused on the optimum linkage of the individual parts of the apparatus as it may introduce some noise to the analog-to-digital data conversion and their transfer to computer. Also, it seems to be helpful to develop a new control software by using suitable "visual" software development kits. This would significantly simplify the whole proposal of the interface when achieving a shortening of time for its realisation and, at the same, improving the set-up as such.

The results presented also suggest that a device comprising an older — but still satisfactorily operating — analyser, from today's point of view less powerful computer, cheap interface as well as friendly-to-use software may still offer good performance, for example, as an instrument for tutorial purposes.

Acknowledgements

A financial support from the Grant Agency of the Czech Republic (Projects No. 203/98/P086, 203/99/0044) is gratefully acknowledged.

References

1. Bond A.M., Švestka M.: *Collect. Czech. Chem. Commun.* **58**, 2769 (1993).
2. Barek J.: *Pokroky v diferenčně pulsní polarografii a voltametrii organických látek*, in *Nové směry v analytické chemii* (J. Zýka, Ed.), Vol. 5, SNTL, Praha 1988.
3. Thomsen K.N., Skov H.J., Dam M.E.R.: *Anal. Chim. Acta* **293**, 1 (1994).
4. Ivanov Yu.A., Grigorev S.V., Moshkin V.V., Merzha A.N., Khustenko L.A., Makatrova A.I.: *Zh. Anal. Khim.* **49**, 961 (1994).
5. Liao B.Y., Young M.S., Wang C.Y.: *Rev. Sci. Instrum.* **65**, 1679 (1994).
6. Stein J.A., Fitch A.: *Anal. Chem.* **67**, 1322 (1995).
7. Eco Chemie B.V.: <http://www.ecochemie.nl>
8. Desmond D. Lane B., Alderman J., Hall G., Alvarez-Icaza M., Garde A., Ryan J., Barry L., Svehla G., Arrigan D.W.M., Schniffer L.: *Sens. Actuators B* **34**, 466 (1996).
9. Metrohm Ltd.: <http://www.metrohm.com>
10. Polaro-Sensors Ltd.: <http://www.polarsen.cz>
11. Kalcher K., Jorde C.: *Comput. Chem.* **10**, 201 (1986).
12. Kalcher K., Greschonig H., Jorde C., Leitner A.: *Comput. Chem.* **12**, 43 (1988).
13. Tait R.J., Bond A.M., Finin B.C., Reed B.L.: *Collect. Czech. Chem. Commun.* **56**, 192 (1991).
14. Kounaves S.P., Lu D.D.: *Comput. Chem.* **16**, 29 (1992).
15. Švancara I., Vytřas K.: *Chem. Listy* **88**, 138 (1994).
16. Kalcher K., Cai X., Kölbl G., Švancara I., Vytřas K.: *Sb. Věd. Prací, Vys. Škola Chem. Technol. Pardubice* **57**, 5 (1995).
17. Švancara I., Pravda M., Hvizdalová M., Vytřas K., Kalcher K.: *Electroanalysis* **6**, 663 (1994).
18. Renger F., Švancara I., Šuška M.: *Sb. Věd. Prací, Vys. Škola Chem. Technol. Pardubice* **56**, 5 (1995).
19. Konvalina K., Švancara I., Vytřas K., Kalcher K.: *Sci. Pap. Univ. Pardubice Ser. A* **3**, 153 (1997).
20. Švancara I., Čermáková I., Gössler W., Kalcher K., Vytřas K.: *Sci. Pap. Univ. Pardubice*, in press.