APPLICATION OF PERSONAL COMPUTERS IN
THE ANALYTICAL LABORATORY—III
ASV ANALYSIS

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(Received 15 September 1986. Revised 8 February 1987. Accepted 21 February 1987)

Summary—Automatic operation and data-processing of ASV analysis is achieved by interfacing a
general-purpose polarograph to a personal computer. The software package, written in SUPER BASIC,
includes graphic routines that are used to display the voltamograms and calibration curve, and as an
interface with the operator. Data-processing can be done manually, interactively or automatically. In the
last of these modes, peak position and height are evaluated by first correcting for baseline drift and then
fitting the peaks to a Gaussian function. It is found that this procedure is relatively insensitive to noise.
The system is used routinely in the analysis of treated domestic wastewater and soils irrigated by effluents.
The flexibility of the programming and the feature of interactive work are important in this connection,
which calls for careful examination of peaks distorted by matrix interferences.

The application of inexpensive microprocessors and peripheral devices is revolutionizing the analytical
laboratory by automating many operational, control and computational tasks which hitherto have been
performed manually. Indeed, many commercially available analytical instruments are microprocessor-
based “smart machines”, which free the operator from the need to execute routine operations such as
graphical evaluation of peak heights in voltammetric analysis. This type of instrument is extremely useful
in the research and industrial laboratory when used for routine analysis of a large number of samples.
However, since these machines are usually “black boxes” to the user, in terms of knowledge of the
program(s) used, the use of microprocessor-based instrumentation could prove to be of no advantage to
the researcher. For example, assessment of interferences due to matrix and other effects could be
difficult or even impossible, if the instruments are not programmed to comment on the integrity of the
response.1 Careful data-evaluation and subsequent tuning of the data-processing algorithms is especially
important when large matrix effects are expected.

The need for more sophisticated data-evaluation and processing became apparent when we
approached the problem of analysis for heavy metals in domestic sewage waters by anodic stripping volta-
metry (ASV).2 The study of metal speciation and formation of organometallic complexes in these solu-
tions called for a careful examination of calibration plots obtained by the method of standard additions.

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For a full-scale range of ±2 V, as used here, the resolution is 0.5 mV, thought to be ample in the present application. The dual-slope type A/D converter is an integrating converter similar to the digitizer used earlier and has similar noise suppression characteristics. The main disadvantage of the present design of interface controller is the need for additional computer I/O lines to service the A/D converter. The additional I/O lines, as well as the original lines required to control the interface controller, were derived from a dedicated Peripheral Interface Adaptor (PIA), type 6526, that was connected to the main base of the personal computer used (Commodore model CMD 64). A different type of peripheral adaptor may be required if a different kind of personal computer is used.
HARDWARE AND SOFTWARE

The present: ASV instrumentation system (Fig. 2) comprises a CMD64 general-purpose personal computer, a 1514 diskette driver, an MPS801 line-printer (all from Commodore Business Machines, Inc.), the interface controller described above, an X–Y plotter (type 3086, Yew Co.), and a polarograph (E 1224) developed and built at the Department of Electrical and Computer Engineering, Ben-Gurion University. Design details of the polarograph have been described elsewhere. The instrument can be operated in the d.c. sweep, d.c. pulse, and differential pulse modes. The last mode was used in this study. The interface controller is used to perform the following tasks. (1) To sample the polarograph output voltage signal, which is proportional to the working electrode current. (2) To sample the working electrode potential. (3) To initialize the potential sweep. (4) To turn the magnetic stirrer on and off. (5) To actuate the solenoid valve used to control the flow of the purge gas (CO$_2$) through the sample.

It is also envisaged that the interface controller will eventually be used to control motor-driven burettes to perform automatic calibration by standard additions. Signal sampling is synchronized to the internal operation of the polarograph, in which turn is synchronized to the power-line frequency. The benefit of synchronization to the power-line frequency was discussed earlier.

The menu-driven software package developed for this application is organized in a number of basic blocks (Fig. 3): file management, polarograph control, automatic data-processing, manual data-processing, and input–output tasks. The program is written in SUPER BASIC, which includes high-level language graphic commands. These are used for plotting the voltamperograms, calibration curves, etc., on the monitor screen and the dot matrix printer.

The processing of the voltamperograms includes peak detection, baseline interpolation and peak-height determination. These can be performed either automatically or in an interactive mode. In the latter mode, which is akin to the approach described by others, the beginning, maximum and tail of each peak are marked by the operator by placing the cursor on corresponding points of the voltamperogram displayed on the monitor screen. Once these features are identified, the program will continue to process it. First, the baseline is restored by fitting a second-order polynomial to the data points on the two sides of the peak. The fitted baseline is then subtracted from the peak data-points to produce a zero baseline peak. The data-points around the peak are then processed for estimation of the peak value. Details of the algorithms used for this are given below.

In the automatic mode, peak detection is done by a subroutine which examines the derivative of the voltamperogram. It was found, however, that peak

![Flow diagram of supervisory program](image-url)

Fig. 3. Flow diagram of supervisory program.

marking could be unreliable if the digital differentiation was performed on the raw data, because of its inherent sensitivity to noise. We have therefore inserted digital filtering of the raw voltamperogram data before the peak identification procedure. The digital filter is similar to the one described earlier. Once the potentials of a peak’s main features are identified (start, maximum and end), the baseline fitting and peak-height algorithms are operated on the original (unfiltered) data to estimate the peak-height.

EXPERIMENTAL

Sampling

Soil and plant samples from the area of Beer Sheva, Israel, were analysed for Zn, Cd, Pb and Cu content. Samples of cultivated soils (from a depth of 30–40 cm) which had been irrigated with water from a local well, and leaves of plants grown on these soils, were collected in acid-washed glass dishes. In the laboratory the samples were dried at 70°C for 48 hr to remove moisture and 0.25-g portions of the dried samples were subjected to acid digestion (concentrated sulphuric acid at 400°C for 2 hr or until a clear solution was obtained) to remove organic compounds. After the digested samples had cooled to room temperature, the pH was adjusted to 4.5 and the volume to 100 ml with distilled and demineralized water (DDW), and the concentrations of Zn, Cd, Pb and Cu were determined by ASV. All reagents and chemicals used were of analytical
grade, and appropriate blanks were run for all chemicals used.

**ASV operating mode**

Differential pulse anodic stripping voltametry (DPASV) was used to determine the concentration of Zn$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ in samples from various sources. The test solution was placed in a 100-ml PTFE beaker fitted with a PTFE cover through which the electrodes and the tube carrying the oxygen-purging gas (CO$_2$) were inserted. The solution was stirred with a PTFE-coated stirring bar. A calomel electrode filled with saturated potassium chloride solution served as a reference electrode, and a coiled platinum wire was used as an auxiliary electrode. The working electrode was a hanging mercury drop electrode (HMDE, Metrohm type E410). The analysis consisted of the following steps: (a) plating the working electrode (WE) at −1400 mV for 120 sec in a stirred solution flushed with CO$_2$, (b) rest period, without stirring or flushing, for 30 sec at the deposition potential, (c) scanning from −1400 to +300 mV ($E_{app} = 50$ mV, $E_{ref} = 10$ mV, $T = 640$ msec) and recording the current on an X-Y plotter and/or saving the data on a diskette, (d) stripping the WE at +300 mV in stirred and flushed solution, (e) starting again from step (c). Steps (a)–(d) are controlled by the microcomputer. A fresh mercury drop was used for each plating/stripping cycle. Calibration was done by making standard additions of increasing concentrations of the cations to each sample.

**RESULTS AND DISCUSSION**

A typical voltamperogram as seen on the monitor screen and plotted on the dot matrix printer is depicted in Fig. 4(a). Examination of small details is facilitated by the zoom operation (Fig. 4, b, c) which enables the operator to investigate a small section of the voltamperogram by specifying the starting and end potentials of the section. Vertical scaling is done automatically. Following the automatic peak-identification procedure, all recognized peak shoulders and peak points are marked on the screen for inspection by the operator (Fig. 5). Another graphic feature is the presentation of a family of voltamperograms generated by the standard-addition procedure (Fig. 6). The resulting calibration data can also be graphed and, if required, recalculated after manual elimination of one or more points.

Proposed algorithms for baseline fitting and peak-height estimation were tested with experimental voltamperograms and a synthetic voltamperogram of the form:

\[ y = 10[\exp(-1.69 \times 10^{-1} x)] + 500[\exp(-0.001(x + 800)^2)] + GN[RND(TI) - 0.5] \]  

(1)

where the last term permits the addition of random noise [RND(TI)] at different levels (GN), and the base of the exponent is e.

The first question to explore was the influence of noise on the baseline fitting. It was found that the uncertainty of the fitted baseline was of the same order of magnitude as the added noise level, as intuitively expected. Another question to be investigated was the best form of the function to be used for peak fitting. Previous investigators suggested fitting a parabola to the peak data-points. Another possibility is to use a Gaussian function. Although more complex in form, the Gauss function can be converted into a second-order polynomial by a log transformation:

\[ y = A \exp\left[\frac{(x - x_0)^2}{2}\right] \]  

(2)

\[ \ln y = \ln A - \frac{(x - x_0)^2}{2} \]  

(3)

\[ \ln y = \ln A - \frac{x^2 + 2bx - x_0^2}{2} \]  

(4)

\[ \ln y = ax^2 + bx + c \]  

(5)

where \( a = -1/2 \); \( b = x_0 \); \( c = \ln A - x_0^2/2 \). Hence, by fitting equation (5) to the data, the coefficient a, b and c can be estimated and A, \( x_0 \) and \( x^2 \) derived. It was found, however, that direct application of the log transformation of equation (3) did not yield accurate results, owing to the finite resolution with which the calculations were done by the CMD 64 computer (which had a 9-digit mantissa and an exponent range...

![Graphical representation of results](image-url)
of ±38). The difficulty stems from the fact that the peak potential of some peaks (e.g., for Zn) is relatively large compared to the peak width. The accuracy of fit was improved markedly if a linear transformation of the form

\[ x'_i = x_i - x_0 \]  

(6)

preceded the curve fitting of equation (5). With this algorithm and a second-order polynomial fit we compared the Gaussian and parabolic fits for an experimental voltamperogram peak with added noise (Table 1). As the results of these tests seemed to indicate that a Gaussian fit was superior to a parabolic one, we adopted the former for implementation in the peak-height estimation routine.

The synthetic voltamperogram, equation (1), was used to test alternative procedures for processing the voltamperograms for peak-height estimation after baseline correction. Since the theoretical value of the synthetic peak height is 500 [equation (1), at \( x = -800 \)] deviations from this value are indicative of deficient algorithms, and lack of robustness in the presence of noise. The following six procedures were tested on the synthetic voltamperogram without added noise.

1. The signal was passed through the digital filter, the baseline was fitted, and the peak height estimated as the maximum distance between the restored base line and voltamperogram curve (calculated value 480.5).

![Graph 1: Display of peak features after automatic processing.](image)

![Graph 2: Voltamperogram family (sample as in Fig. 4) obtained after standard addition of (a) 0, (b) 10, (c) 20, (d) 40, (e) 60 ng/ml concentration of (1) Zn\(^{2+}\), (2) Ce\(^{3+}\), (3) Pb\(^{2+}\), (4) Cu\(^{2+}\).](image)

2. As for 1 but without passing the signal through a digital filter (calculated value 492.2).

3. Interactive mode without baseline fitting (estimated value 492.4).

4. Interactive work with baseline fitting (estimated value 490.9).

5. Baseline in fitting and Gauss fitting of peak (calculated value 495.7).

6. Same as 5 but after passing the signal through a digital filter (calculated value 483.7).

These results imply that: (a) the peak height is reduced by about 3% by use of the digital filter; (b) Gauss fitting improves the accuracy, presumably by smoothing the quantized data; (c) automatic peak-height processing can restore the peak value to within 1% of the true value.

The robustness of the algorithm in the presence of noise was tested by adding random noise to the synthetic voltamperogram and processing the data by the baseline restoration and Gauss fitting routines. Results for 2, 10 and 40% noise levels (relative to peak height) were 500.3 ± 0.07, 499.6 ± 5.6, 514.6 ± 23.6 respectively (mean ± 2 standard deviations; 10 deviations). The results seem to suggest that the proposed algorithms are highly effective, even in the presence of a relatively high noise level such as might

| Table 1. Comparison of (A) Gaussian and (B) parabolic fittings for a measured voltamperogram peak with added noise of 0.05 (RND -0.5) for three runs (a, b, c). |
|---|---|---|---|---|---|---|---|
| Fitting Peak | Original sample, \( l_p \) | \( l_p \) | \( l_p \) | \( l_p \) | \( l_p \) | \( l_p \) | Sample + noise |
| | | | | | | | |
| A | 1 | 0.51 | 0.569 | 110 | 0.500 | 96 | 0.508 | 98 | 0.526 | 101 |
| 2 | 0.113 | 0.095 | 84 | 0.139 | 123 | 0.147 | 136 | 0.127 | 112 |
| 3 | 0.391 | 0.373 | 95 | 0.402 | 103 | 0.395 | 101 | 0.390 | 107 |
| 4 | 0.400 | 0.420 | 105 | 0.434 | 109 | 0.412 | 103 | 0.422 | 105 |
| B | 1 | 0.508 | 0.549 | 108 | 0.566 | 111 | 0.499 | 98 | 0.538 | 106 |
| 2 | 0.111 | 0.155 | 140 | 0.163 | 147 | 0.134 | 108 | 0.151 | 136 |
| 3 | 0.362 | 0.316 | 87 | 0.332 | 92 | 0.425 | 117 | 0.358 | 96 |
| 4 | 0.390 | 0.430 | 110 | 0.445 | 114 | 0.429 | 110 | 0.435 | 112 |

*Deviations from noise-free value, %. 
Table 2. Comparison of calibration data obtained for (A) manual, (B) interactive, and (C) automatic data-processing modes for a sample of plant material; numbers in brackets are standard deviations (5 replicates)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Voltage, $mV$</th>
<th>Intercept on x-axis, ng/ml</th>
<th>Correlation coefficient</th>
<th>Slope of standard addition graph</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Zn</td>
<td>-900.0</td>
<td>-6.75</td>
<td>0.9953</td>
<td>20.3</td>
</tr>
<tr>
<td>Cu</td>
<td>+100.0</td>
<td>-10.32</td>
<td>0.9946</td>
<td>125.5</td>
</tr>
<tr>
<td>(B) Zn</td>
<td>-936.8</td>
<td>-6.36 (0.19)</td>
<td>1.0000</td>
<td>18.74 (0.03)</td>
</tr>
<tr>
<td>Cu</td>
<td>+28.7</td>
<td>-8.49 (0.64)</td>
<td>0.9742</td>
<td>118.7 (0.13)</td>
</tr>
<tr>
<td>(C) Zn</td>
<td>-935.6</td>
<td>-6.54 (0.19)</td>
<td>1.0000</td>
<td>18.46 (0.03)</td>
</tr>
<tr>
<td>Cu</td>
<td>+33.2</td>
<td>+20.31 (0.15)</td>
<td>0.9631</td>
<td>57.03 (0.15)</td>
</tr>
</tbody>
</table>

Fig. 7. Voltamperogram of the Cu$^{2+}$ peak after the standard addition of: (a) 0, (b) 10, (c) 30, (d) 50, (e) 70 ng/ml Cu$^{2+}$.

be encountered near the detection threshold of the instrument.

Manual, interactive and automatic data-processing were compared by applying them to one voltamperogram. The resulting peaks obtained for zinc by the three operational modes are in good agreement for the metal concentration and other parameters (Table 2). However, a large discrepancy was found between the manual and interactive modes on the one hand, and the automatic mode on the other, for the copper peak. As shown in Figs. 4–6 the zinc peak is sharp and regular but that for copper is very irregular. The copper peak changes shape when known amounts of copper are added (Fig. 7). In the voltamperogram for the original sample, only a shoulder is detected in the copper region, because of peak overlap [Fig. 4(c) and Fig. 7(a)]. On increasing the copper concentration by standard addition there is a gradual change in the signal shape and the shoulder for copper is converted into a detectable peak. The shoulder can be detected when the manual or interactive mode is used for data processing but not by the automatic mode, which would include it in the baseline correction. For the specific example shown here (Fig. 7), the signal for copper was detected as a separate peak only after addition of at least 30 ng of copper per ml. This explains the discrepancy with copper concentrations found by the different processing modes, and demonstrates the importance of the interactive data-processing option in addition to the automatic mode.

Acknowledgements—This study was financed by a grant from the European Economic Community and the Israeli National Council for Research and Development, Ministry of Science.

REFERENCES
