

VA_peak

A multipurpose and versatile VoltAmmetric Software Package for the Analytical Chemist

Version 2.109

Instruction Manual

Instruments supported :

- Amel 433 Multipolarograph
- Amel 2435 Potentiometric Stripping Analyzer
- PalmSens handheld Electrochemical Interface
- Automatic Syringe for STD additions

New facilities :

- Control of 1 to 3 electroanalytical instruments via serial or USB ports
- Power Interface for controlling external cells via Parallel port
- Import facility for Metrohm 757, Amel 433, Amel 2435, PalmSens and ASCII files.
- Up to 36 data memories, all configurable as Single Analyses, Standard Addition analysis and Cyclic Voltammetry analyses.
- Savitsky-Golay and Moving Median data filtering.
- Area or height quantitative calculations.
- Linear or Spline baselines
- Background subtraction

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1. Installation :

Hardware and Software requirements :

- OS : Windows95 to XP, all supported
- Required screen resolutions : 800x600 to 1280x800
Recommended resolution 1024x768
Set display characters to small (default Window option).
- One to three RS232 COM Ports
- One LPT parallel port (for the External Cell power controller)

File Installation :

1. Run the "Setup.exe" file.
2. Follow the instructions and choose the installation directory, generally "C:\Program Files" or "C:\Programmi"
3. Start the program by clicking on the "VA_peak" icon.
4. In the "VA_peak" subdirectory, you will also find the following files :
 - VA_peak Manual.pdf (this manual in Adobe Acrobat format)
 - the "Sampledatafiles" subdirectory (examples and data files).

Initial Instrumental Configuration :

The present instrumental configuration is displayed on the "Instrumental Configuration" window on top right of the screen. This configuration can be modified clicking on <Settings>, <Modify Settings> menu option. A new window will appear, allowing the user to select all the instrumental and software configuration:

- the three main instruments used for the voltammetric functions, the potentiometric (PSA/CCSA) function and for the auxiliary (Aux) options.
- the automatic syringe, and the type of controller for external cells.
- the initial directory for data saving and retrieving
- the options for automatic data recalculation during operations (AutoRecalc) and for displaying a diagnostic window. This option is only for expert users.
- the COM ports where all instruments are connected, and the volume of the automatic syringe.

Settings

Directory for DATA save E:\

Voltammetric Instrument PalmSens

Potentiometric(PSA) Instrument Amel2435

Auxiliary Instrument none

Autom.Syringe Connected to Amel2435

EXT Cell Controller PalmSens

AutoRecalc

Open Diagnostic Window

COM Port Instrument1 : Amel433 none

COM Port Instrument2 : Amel2435 COM3

COM Port Instrument3 : PalmSens COM3

COM Port Instrument4 : none none

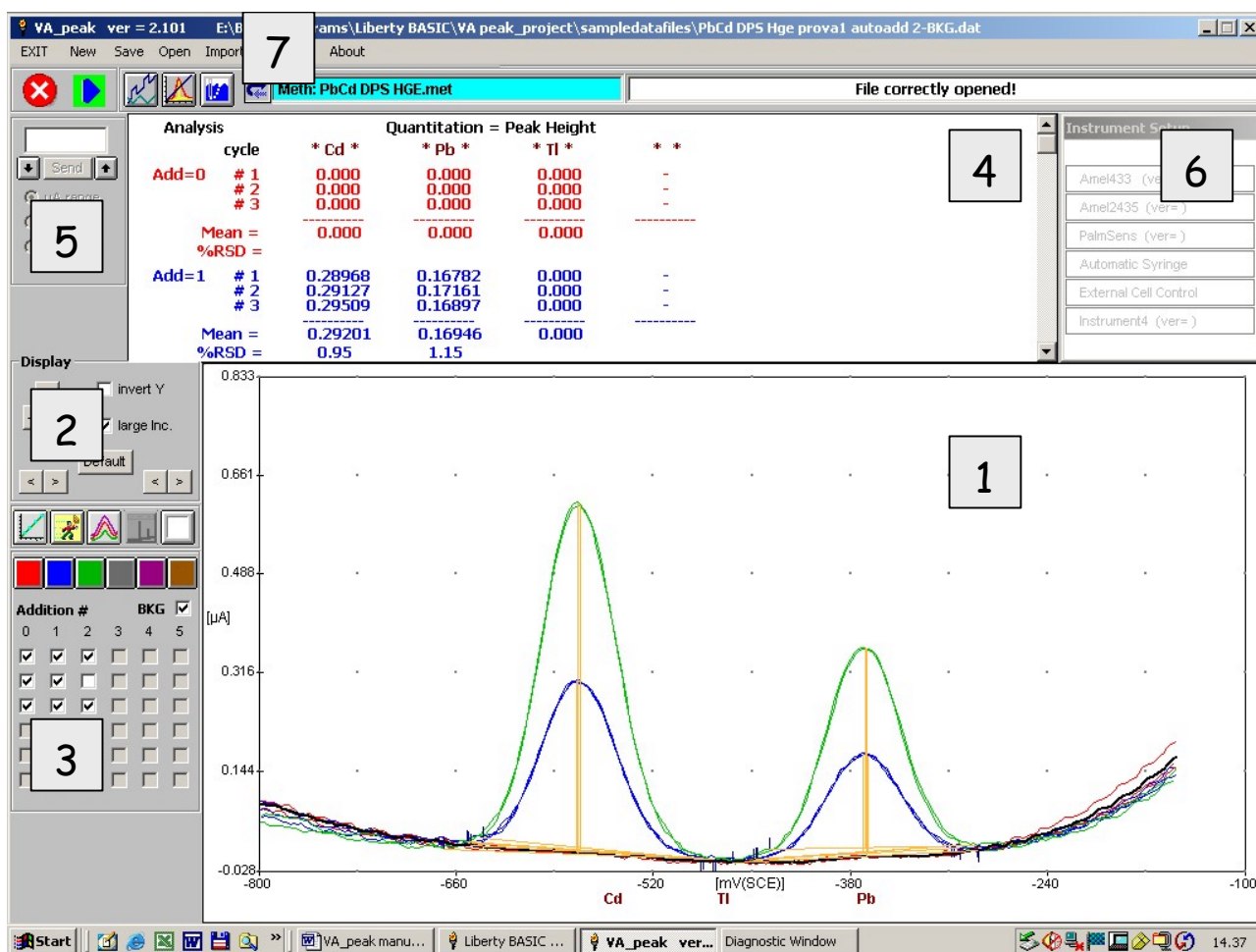
COM Port Instrument5 : none none

COM Port Instrument6 : none none

Autom.Syringe Volume (µL) 1000

Exit

2. Main Screen








General appearance of VA_peak main screen :

- 1. graphic window
- 2. display control area

Graph plot can be resized and shifted in Y and X directions with the buttons in the "Display" box on center left. Y axis can be inverted with the <Invert Y> button. The <Default> button is used to restore default settings.

Selection is made with following buttons :

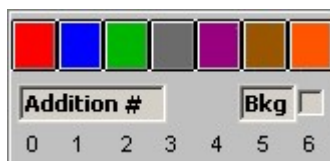
-  graph plot – data are shown after acquisition has finished
-  running graph – data are displayed during acquisition
-  least square calibration and quantitation graph
-  draw baselines and height/area – this button appears highlighted when manual redraw is required.
-  clear screen

- **3. data memories selection for visualization and/or quantitative results.**

Up to 36 or 42 (depending on software version) data memories are available, which can be arranged as three types of analytical experiments :

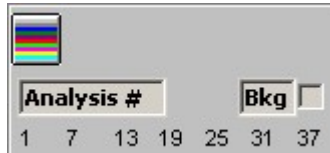
STD additions analysis.

up to 6 cycles of 6 additions, for a total of 7 analyses, may be chosen



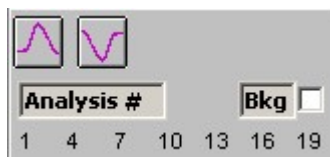
Single Analysis.

up to 42 single cycles may be selected.



Cyclic Voltammetry.

anodic and cathodic scans are separately processed and displayed, so up to 21 cycles are entered.



Each data memory can be selected or deselected by clicking on its checkbox :

- grayed-out empty memory
- white active memory – deselected
- checked active memory - selected

If data memory is deselected, it will be no more shown on screen, nor used in quantitative calculations. However, active memories can be re-selected at any time.

When background has been acquired, an enabled “Background” checkbox is displayed on the bottom, to allow background memory to be displayed on the graph screen as thick black line.

- **4. Text display area**

This window displays quantitative data, as height or area considering both peak or dc current voltammetric/ampereometric experiments, for up to 4 selectable elements.

- **5. Instrument control buttons for current range selection and offset correction.**

This option depends on the actual instrumental configuration :

- for Amel 433 instrument, current range and offset can be changed with <up> and <down> arrows and then sent to the instrument pressing the <Send> button.
- for PalmSens instrument, calibration of analog electronics is performed by pressing “Calibration” button. This operation must be done according to PalmSens’ manual instrument.

- **6. Instrument Configuration window**

This window is displayed by default on screen resolutions higher than 800x600 and it can be displayed or hidden via clicking on <Settings>; <Display Configuration>.

If instrument is not connected or is turned off, a warning message appears, and the instrument name becomes grayed-out. For example, on the window in the main screen at page 4, VA_peak software was started with all instruments turned off.

When the instrument is actually connected and the cell relay is ON to deliver current to the electrodes, the background of the instrument box changes from white to red.



- **7. Controls and Menus**

In the control line, 6 control buttons and 2 one-line text displays are shown :



Stop/Run buttons for data acquisition



Instrumental Parameters




Analytical Parameters



Degas and Deposition Window - only for data Acquisition

Small display

Cyan background; analytical parameters are cyclically displayed clicking on  button.

The following parameters can selected : Method; Analysis; Data Format; Electroanalytical function; Electrode type, Instruments, Analysis and Cycles

Large display

Shows all messages and data during all operations using different colors :

- white display – normal operations (file input-output, graphical representation, quantitation, etc.)
- yellow display – acquisition and analysis
- pink display – error conditions!

The Top Menu line displays the following choices :

- <EXIT> to end program and return to OS
- <New> starts a new analysis. User is prompted to save all data
- <Save> Analysis, Method and Report
- <Open> Analysis and Method
- <Import> for data import from other instrument files. Most instruments are supported, as well as different types of ASCII files.
- <Math> for mathematical operations on data files
- <Settings> for checking, setting or modifying instrumental configuration.
- <About> to obtain information on the software.

3. Graphic Windows

Three types of graphic windows can be selected and displayed :

- Graph Plot

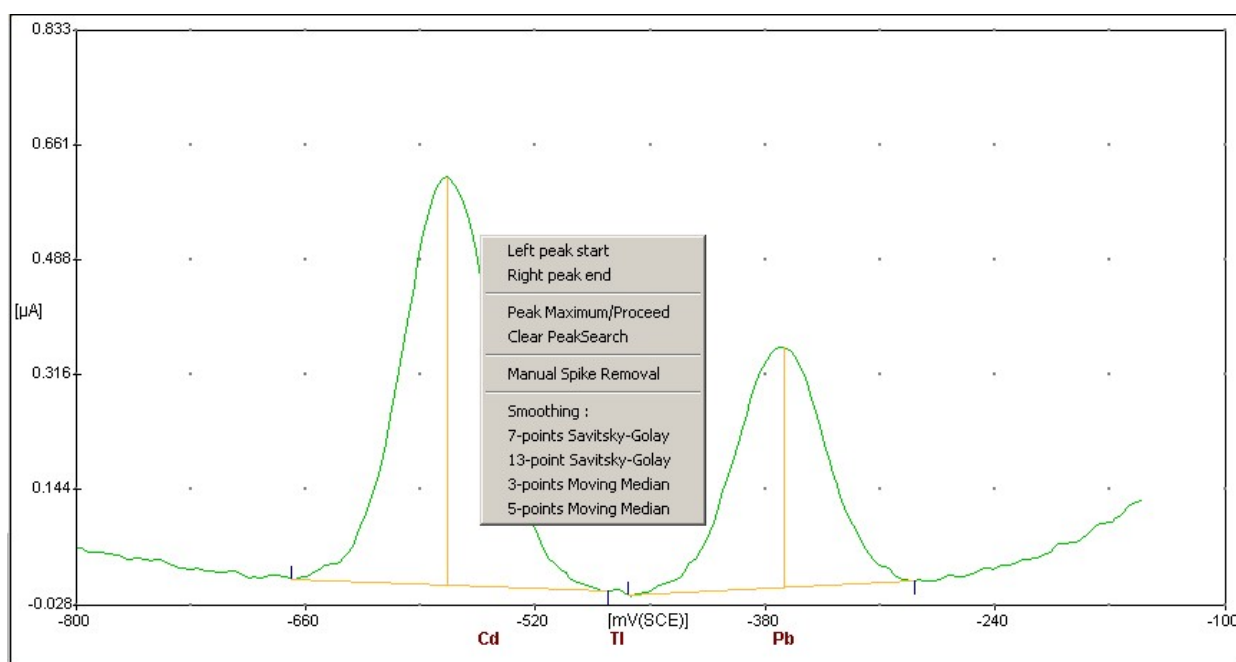
This window is characterized by a white background . All memories, if set, can be displayed on screen after acquisition, and resized on X and Y directions using buttons in "Display" box.

Different options may then be chosen via clicking left/right mouse buttons :

- RIGHT Mouse Button : **Data manipulation**

Two options are possible :

- i) when two or more memories are selected, the X,Y coordinates of any point on each curve can be read on the top display. Actually, no data manipulation is allowed in this case.
- ii) when only one memory is selected, the user can perform manual peak picking and baseline calculation, manual spike removal as well as data smoothing.



For smoothing, two options are possible :

- 7-points or 13-point convolution (Savitsky-Golay) functions using Gorry's method to avoid truncation at both ends of data set
- 3-points or 5-point Moving Median algorithm.

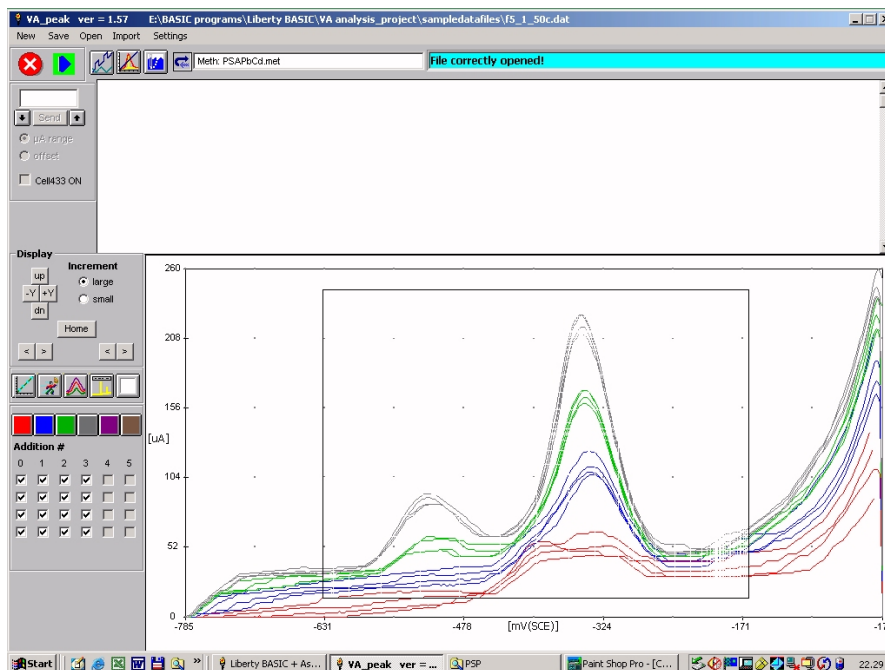
These algorithms have been reported in the literature (see References in Appendix 3) as best suited for voltammetric experiments; Savitsky-Golay convolution functions are ideal for high-frequency (noise) rejection, whereas moving median algorithm is best suited for automatic spike removal, e.g. for spikes caused by automatic scale change.

- LEFT mouse button : **Manual zooming**

Manual zooming is done as follows :

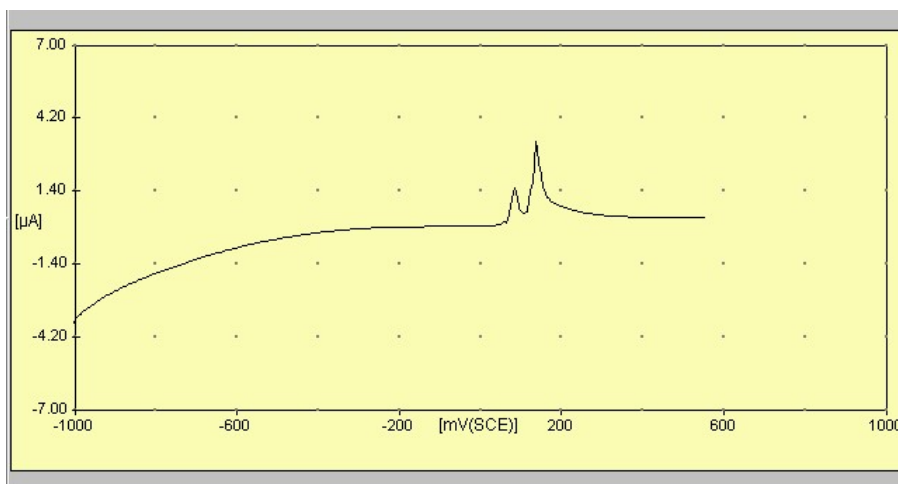
a box is selected when left mouse button is pressed, and then the selected region is redrawn upon releasing the button.

Initial (default) coordinates can be restored at any time with the <Default> button in the "Display" box at center left.

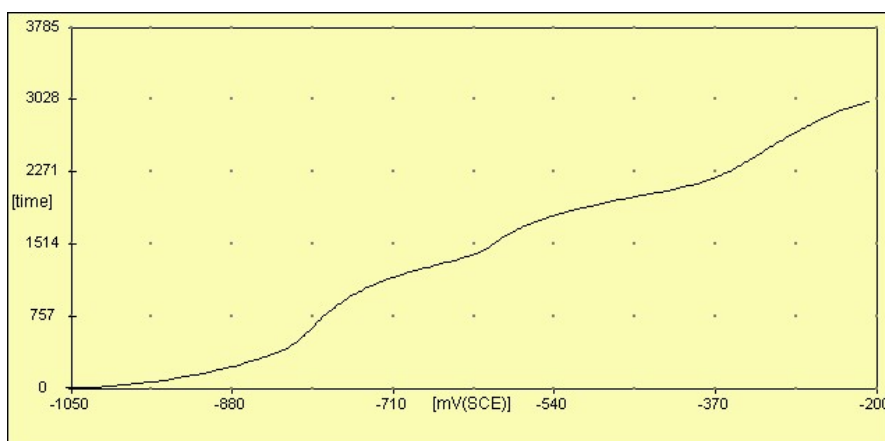


- Running graph

This window is shown on a yellow background, and is automatically selected upon data acquisition. With voltammetric functions, data are shown in real time during the scan; if scan rate is too fast for real-time display, data are automatically stored within internal memory, and transferred when acquisition is finished.

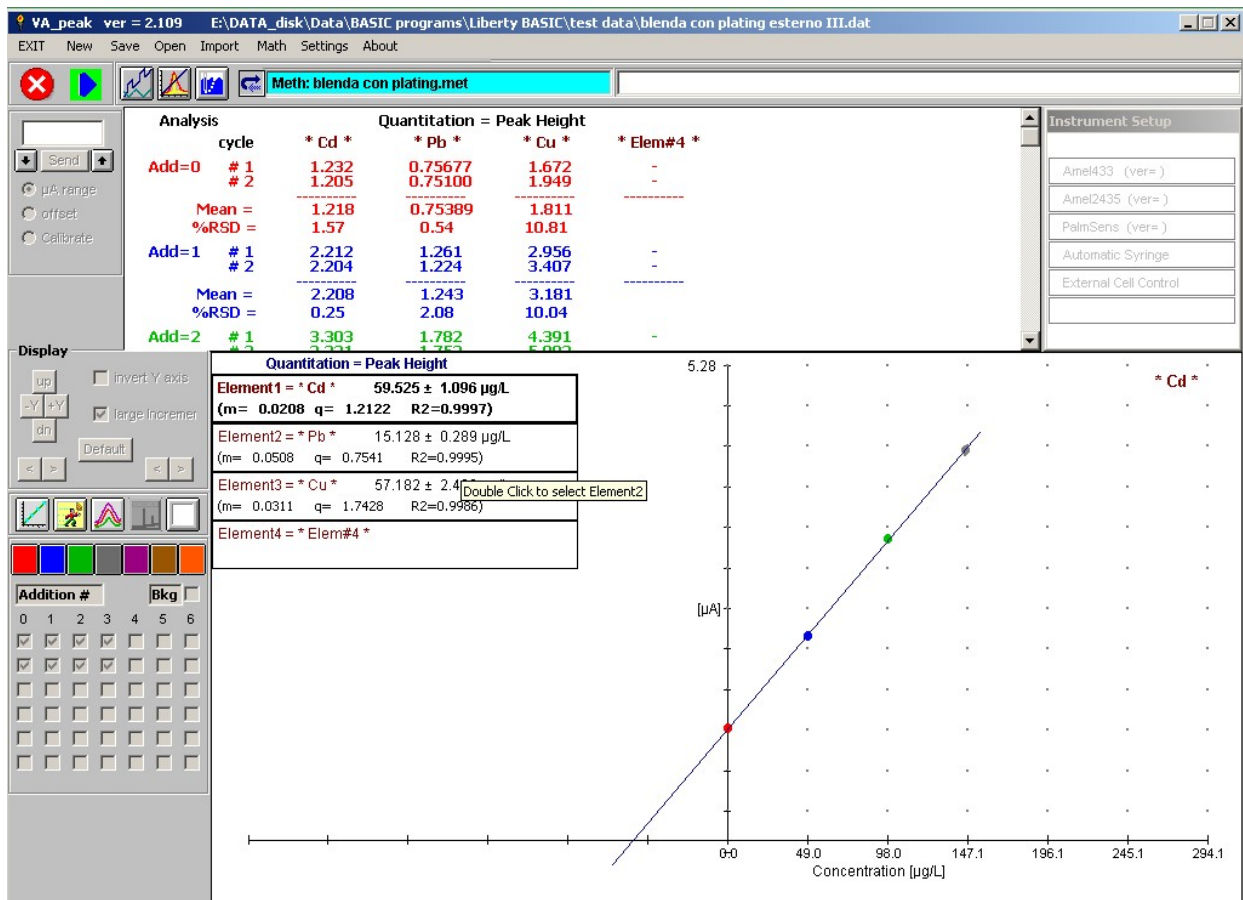


In PSA/CCSA, raw data, as time against voltage, are always displayed at the end of the acquisition step (generally lasting few second). First-derivative of raw data is then automatically calculated using a Savitzky-Golay, 9-point first-derivative smoothing algorithm, and displayed on the Graph plot. Raw and first-derivative data are shown on screen until the beginning of the next analysis cycle. At the end of each cycle, data are then rescaled and shown in the Graph plot.



- Least Square Calibration and Quantitation window

This window is used to display quantitative calculations via standard addition method using linear calibration model.



The choice of the element being displayed on calibration graph can be done in two ways, i) in the "Analytical parameters" window, by clicking the radiobutton on the right of the element selection menu, or ii) directly in the Quantitation window, by double clicking with left button on the element box on top left. In this way, the selected box is highlighted (as Cd in the example) and the name of the selected element is displayed in the top right position of the graph.

Quantitation may be done using peak heights (the default selection) or peak areas; area/height data are shown in text format on the top window for all four selectable elements.

Concentration of each of the four selectable elements is already corrected for sample dilution and shown together with best fit parameters, slope (m), intercept (q) and R^2 .

4. Parameters Windows

4.1 Instrumental Parameters window

The screenshot shows the 'Instrumental parameters' window with the following settings:

- ELECTRODE:** Drops: 3, Size(au): 15. Buttons: HDME 433, SOLID 433, SOLID 2435, EXT.
- PRETREATING:** Stirring Speed (rpm): On, Pretreating Time (sec): 60, Apply Condit.Potential: , Gas Purging: .
- BACKGROUND ACQUISITION:** Acquire!, Blank, Sample, No of Repetitions: 2.
- CONDITIONING:** Condit.Potential(mV): 0, Stirring Speed (rpm): On, Condit.Time (sec): 0.
- STRIPPING:** Stirring Speed (rpm): On, Current Range (µA): ±409.6, Depn.Potential (mV): -800, Depn. Time (sec): 60.
- ANALYSIS:** Lower Current range: ±100 nA, Higher Current range: ±100 µA, Initial Potential (mV): -800, Final Potential (mV): -100, Rest Time (s): 5, Smoothing: none, Max. AnalysisTime (s): 15, H/W Filter: none, Sampling Time (Auto): long, Stirring Speed (rpm): Off, Pulse Repetition (ms): 100, Step Potential (mV): 5, Pulse Time (ms): 40, Pulse Amplitude (mV): 25, Wave Period (ms): 100, Wave Increment (mV): 5. Summary: Number of Datapoints = 141, Scan Speed (mV/s) = 50.
- CLEANING:** Stirring Speed (rpm): On, Cleaning Time (sec): 0, CleaningPotential(mV): 0, Cell ON at End Cycle.

With present configuration, all voltammetric and stripping functions can be applied to each type of electrode configuration :

HDME 433	Hanging drop mercury electrode on Amel 433
SOLID 433	Solid electrode on Amel 433 cell
SOLID 2435	Solid electrode on Amel 2435 cell
EXT	External cell interfaced to the PC

When HDME 433 is selected, the number of mercury drops at the beginning of each analysis may be chosen, as well as their size (in arbitrary units). 3 (drops) and size 15 are default setting.

Electrochemical functions:

AD	Amperometric detection
PAD	Pulsed Amperometric detection
LS	Linear scan voltammetry
CYV	Cyclic voltammetry
StC	StairCase voltammetry or stripping
DP	Differential Pulse voltammetry or stripping
SqWav	Square Wave voltammetry or stripping

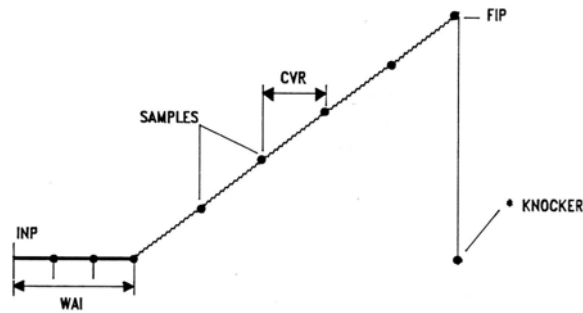
- <Potential Step> displays the value (in mV) of each potential increase in Staircase, Differential Pulse functions.
- <Wave Frequency> displays the frequency (in Hz) of square wave.
- Cleaning step :
 - Cleaning time : duration (in seconds) of Cleaning Step at the end of each voltammetric cycle. A Cleaning Time > 0 must be selected to allow Cleaning step to be performed.
 - Cell ON at end cycle : if checked, the cell remains ON with applied potential at the end of each cycle of analysis.

Please note that all analytical parameters are automatically checked, and if wrong parameters are entered (e.g. potential outside allowable range of -2000 to +2000 mV, or Initial_Potential = Final_Potential, or Sampling_Time > Pulse_Time, etc) a warning message is displayed on the upper textdisplay, changing background to pink!

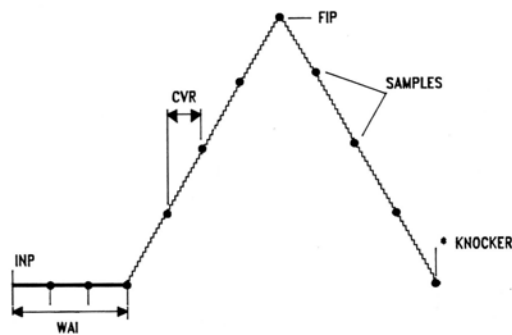
Full details on electroanalytical chemistry and electrochemical experiments may be found on many textbooks and references, some of them are listed on Appendix 2.

For a matter of information, few schematic details on most common voltammetric experiments are given here, as reported in the user manual of Amel 433 instrument :

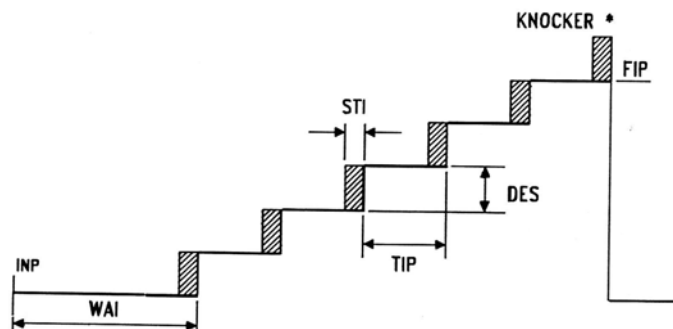
- Linear Scan voltammetry (LSV)



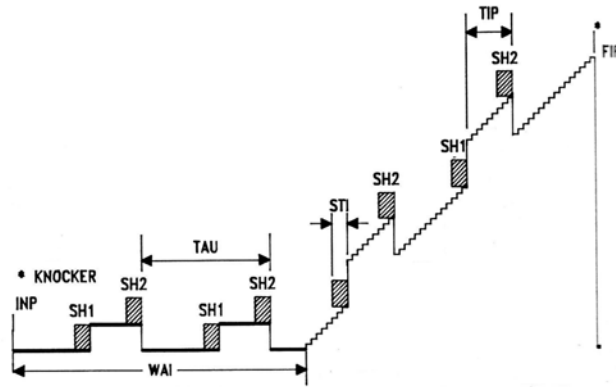
- Cyclic Voltammetry (CYV)



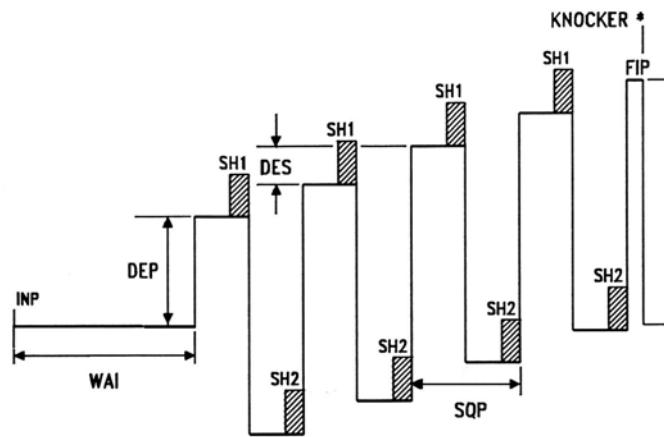
- Staircase Voltammetry (STC)



- Differential Pulse Voltammetry (DP)



-Square Wave Voltammetry (SqWav)



Scan parameters are then defined in the "Method Parameters" window as follows :

- | | |
|---|-------------------------|
| INP : Initial Potential | FIP : Final Potential |
| WAI : Rest Time | CVR : Sampling Interval |
| STI : Sampling Time | SH1,SH2 : Sampling Time |
| TIP : Step (or Pulse) Time | TAU : Pulse Repetition |
| DEP : HalfWave Amplitude | SQP : Wave Period |
| DES : Potential Step (in STC and DP) or Wave Increment (in SqWav) | |

4.2 Analytical Parameters Window

The screenshot shows the 'Analytical parameters' window with the following settings:

- Set Peak Parameters:**
 - Mode: peak, dc current
 - Element list: Cd (-550 mV, checked), Pb (-370 mV), Tl (-470 mV), and an empty slot.
 - min. pk_height: 0.05, % pk_threshold: lowest
 - pk_window (mV): 50, pk_width (mV): 100
 - Buttons: Auto, Recalc, PickPicking, Auto
- Set Analysis Parameters:**
 - Operator: CDossi
 - Description of the Experiment: autoadd experiment #1
 - Sample Volume (mL): 19.90, Electrolyte Volume (mL): 0.100, Added STD (μL): 100
 - STD Concentration (mg/L): Cd (2.000), Pb (5.000), Tl (1.000), and an empty slot (0.000)
 - Total Volume = 20.0, Dilution (Sample/TotalVolume) = 1/1.01
 - Analysis Type: Manual, Automatic
 - Single Analyses: Single Analyses, STD Additions
 - Cycles: 3, Additions: 2
 - AUTO Syringe additions
 - Stirring Time (sec): 0
 - Gas Purge
- Quantitation:** Area, Height, unit: μg/L
- Baseline Interpolation:** Linear, Spline, npoints: 6
- Background Subtraction:** Raw Data, Subtracted Data
- Exit button

All Peaks and Analytical parameters are entered here.

“Set Peak parameters”

This box is used to define automatic (or manual) peak picking routines.

Selection between peak or dc-current detection is first done.

The elements to be analyzed and corresponding peak max value, can be chosen from a selected list or manually entered.

Up to 4 elements (in peaks) or 1 element (in dc) can be automatically determined. Parameters are defined as follows :

- **min. pk_height** : peaks below this value (as area or height) are automatically discarded as noise
- **pk_window** : detection window (in mV) for peak recognition.
- **Pk_width** : full width (in mV) at half maximum (FWHM) of voltammetric peak.
- **% pk_threshold** : this parameter is used as threshold to distinguish analytical signal from noise; as default, <mid> is selected.
- **PeakPicking** : allows automatic or manual peak picking.
- **Redraw** : allows automatic or manual recalculations of baselines and quantitative results. It is normally set to Auto except when using slow computers.

“Set Analytical parameters”

This box allows the user to enter the operator name and the description of the experiment. Remind, in the “Description of the Experiment” box, wordwrap is automatic without requiring <Enter> key.

For Sample, Electrolyte and STD addition, the used volume is entered in the textboxes at the left. The total volume, calculated as (SampleVolume+ElectrolyteVolume), and sample dilution are automatically calculated and displayed.

The use of a multistandard solution for the 4 elements selected is now allowed (ver.2/101 and up).

"Analysis Type"

The user is allowed to define single or standard addition analyses.

- In STD additions, up to 6 cycles of 5 additions may be chosen, for a total of 36 data memories.
- In Single Analysis, up to 36 cycles may be selected. If Cyclic Voltammetry (CYV) experiment is selected, anodic and cathodic scans are separately processed and displayed, so up to 18 cycles are entered.
- Manual/Automatic button : if Automatic is selected, a new cycle is automatically started at the end of the previous one; in Manual, a info window appears after each cycle, prompting the operator to allow next cycle to be processed.
- Auto Syringe additions : this control is only enabled if automatic syringe is fitted in the instrument configuration. If selected, standard addition is automatically performed.
- After each addition, stirring and, if required, gas purging are activated, in order to allow mixing and removal of residual air introduced during STD addition.

"Quantitation"

This box allows the user to choose between height or area measurement for quantitative analysis, and the measuring unit.

"Baseline Interpolation"

- "Linear" : linear baselines are calculated and drawn between the left peak start and right peak end.
- "Spline" : cubic spline interpolation is calculated and drawn. The interpolation routine uses a number of points between 4 and 10, as chosen in "npoints" combobox, which are automatically selected by the software, half on the left side and half on the right side of each peak.

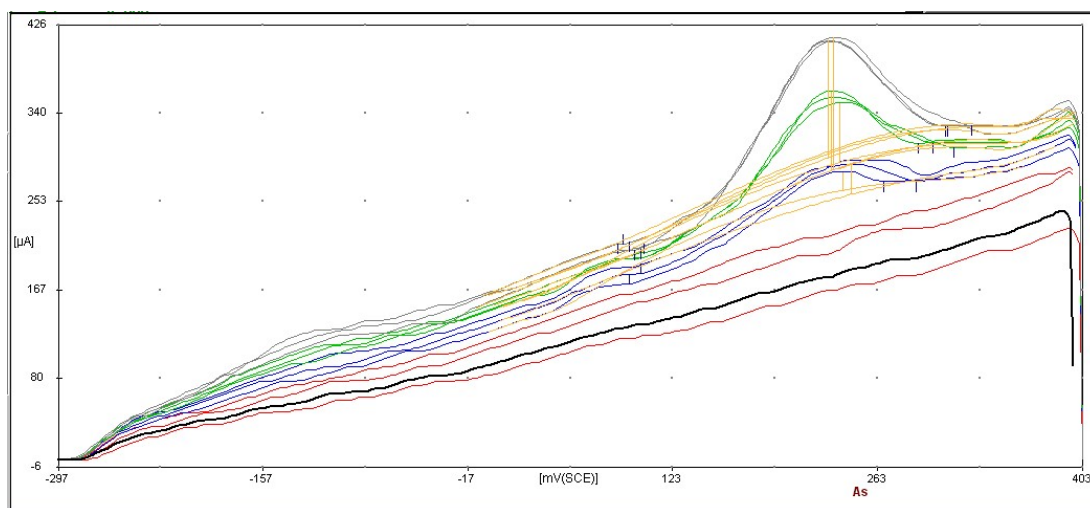
The goodness of spline interpolation may be optimized by varying the following parameters :

- "npoints", the numbers of points for interpolation
- "pk_width", the width of data interval chosen at the left and right sides, for interpolation
- "pk_threshold", for changing sensitivity to peak detection

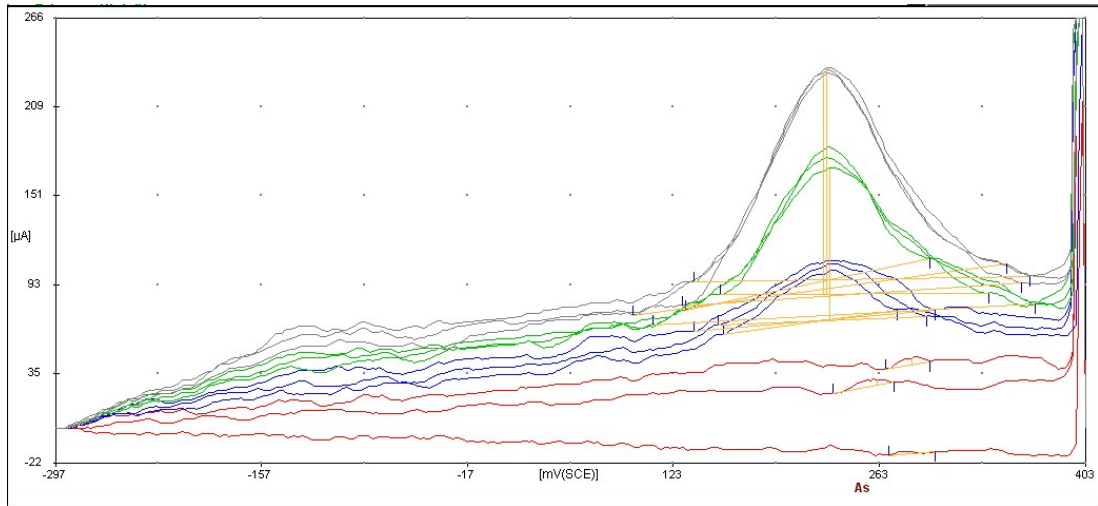
and by manually selecting the left peak start and the right end peak.

"Background Subtraction"

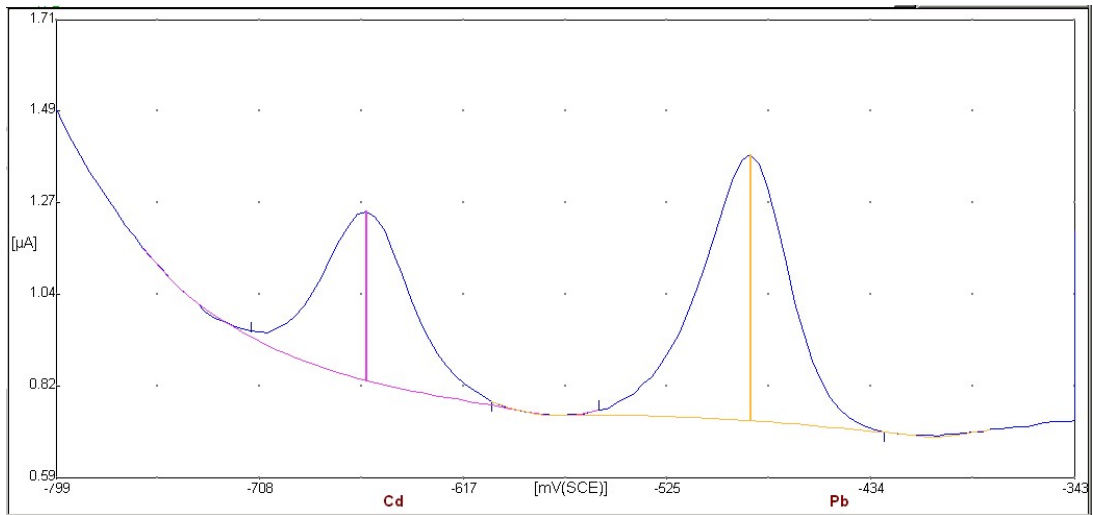
This box is used to select between Raw data or Background Subtracted data. This box is enabled only if background acquisition is selected and saved on file.



Raw data before background subtraction (CCSA analysis of As on gold film) with spline baselines



Same after background subtraction (in "Blank" mode) and linear baselines



Spline baseline on Cd and Pb analysis on Hg film.

How analysis is performed :

1. Initially, a pretreating step is done, as selected in the "PREATREATING" box. This step is used to bubble N₂ for removing any air or oxygen in the solution. Select "PurgingTime=0" to skip this step.
2. If selected, background is acquired and stored in memory. -
3. The analysis is now started, with a number of cycles and additions (number of analyses-1), as selected in the "Analytical Parameter" window
4. Prior of each cycle, a conditioning step can be selected, for removing any contamination left in the previous analysis and/or reconditioning the analytical film (e.g. mercury or bismuth). Select "Condit.Time=0" to skip this step.
5. In case of Stripping analysis, the deposition step is then performed
6. Data acquisition is now started. For voltammetric functions, visualization is done in real-time unless scan rate is too fast. In PSA, instead, the analytical signal is shown after data collection.
7. A cleaning step is then performed (if required) at the end of each cycle. Select "CleaningTime=0" to skip this step
8. Then, steps 4-7 are repeated until all cycles and analyses are completed. The user can stop the analysis at any time by clicking on "STOP" buttons, and waiting the main display to show a white color again, instead of the yellow color shown during analysis.
9. The operator is then advised to save analysis prior to do any other operation. REMIND: data are NOT saved automatically.

4.3 Purge/Deposition window



This window is used for manually performing (or checking) the following operations prior the analysis :

- activating stirring and/or gas purging
- purging/degassing solution in the cell
- film deposition
- electrode cleaning

Selection of the electrode and/or cell type must be previously done in the "Method parameters" window.

5. File Types

5.1 Open/Save/Report files

Three types of file, all of them in plain ASCII format, are created and used by the software :

Analysis file : .DAT extension

This file is used to save all analysis data (as space-separated x,y couples) with a heading containing all analysis information (date, time, operator, sample volume, standard addition etc...). Upon opening analysis file, the method file is automatically loaded. If the method file has been moved to a different directory, a file dialog window will appear, to prompt the user selecting the proper file.

Method file : .MET extension

This file is used to save all method parameters. Please, remind to save method file upon any change; this file is not automatically saved when saving analysis.

Report file : .TXT extension

This file can be generated, by operator choice, upon saving analysis file, and it contains all data regarding quantitative analysis (area/height values, sample information and final concentrations in sample for all selected elements).

Since all files are in plain ASCII format, they can be opened and visualized with any notepad or word processing software.

6. Appendixes

Appendix 1 :

Pinout of LPT port for EXT Cell controller.

d0 (pin #2) -> stirrer

d1 (pin #3) -> gas valve

d2 (pin #4) -> AUX functions

Busy (pin #11) -> set to GND EXT Cell controller connected

Ack (pin #10) -> set to 5V EXT Cell controller powered ON

Pinout of PalmSens DIO port for EXT Cell controller.

d0 -> stirrer

d1 -> gas valve

Appendix 2 : Selected literature

- Amel 433-A Technical and User's manual
- Amel 435/2435-A Technical and User's manual
- PalmSens User's manual.
- PalmSens PC User's manual
- P.Protti, Introduction to Modern Voltammetric and Polarographic Analysis Techniques, AMEL (Milano) – 2001 – (http://www.amelchem.com/download/items/voltammetry/manuals/eng/manual_eng.pdf)
- J.Wang, Analytical Electrochemistry, II Ed., Wiley-VCH – 2000.
- A.Savitzky and M.J.E. Golay, "Smoothing and differentiation of data by simplified Least Squares procedures", Anal. Chem., **39(8)** (1964) 1627-1639.
- P.A.Gorry, "General Least-Squares smoothing and differentiation by the convolution (Savitzky-Golay) method", Anal. Chem., **62**, (1990) 570-573.
- C.L.do Lago, V.F.Juliano and C.Kasceres, "Applying moving median digital filter to mass spectrometry and potentiometric titration", Anal.Chim.Acta, **310** (1995) 281-288.
- M.Jakubowska, R.Piech, T.Dzierwa, J.Wcislo and W.W.Kubiak, "The evaluation method of smoothing algorithms in voltammetry", Electroanalysis, **15(22)** (2003) 1729-1736.