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Demo version:

The Demo version of *CACYVO 2.0* without data acquisition and without file import abilities is freeware and may be distributed freely.

Full version: (The demo version is transferred into the full version with the registration code)

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Table of Contents

1 Introduction

The **C**omputer **A**ssisted **CY**clic **VO**ltammetry software, *CACYVO*, runs under *Windows* and manages CV-representation, evaluation and interpretation including so far unknown features as:

· specific import filters for PAR 270/250 (ASCII and binary format), Metrohm VESUV files, and Autolab GPES;
· a general import filter for any two column representation of current/potential values;
· software -assisted peak value evaluation, *i.e.* i_p, E_p, Q;
· mechanistic analysis on single CV's using different models, e.g. E_{irrev}, E_{rev}-C_{irrev}, E_{rev}-C_{cat};
· graphic correlation of peak values from a series of CV's with experimental parameters, e.g. i_p vs $v^{0.5}$, E_p vs log{additive};
· spreadsheet representation of the CV data points including editing options;
· filter, zoom and add or subtract a constant current or voltage value;
· add- and subtract entire CV's from each other;
· normalization of CV's with respect to electrode surface, scan rate (n) or $n^{0.5}$;
· multiple CV representation in two and three dimensions, using different experimental parameters as the third axis, *e.g. v*, log{additive}, temperature;
· different representation options, *e.g.* axes, boxes with ticks in or out;
· direct export of any representation into other *Windows* programs, *e.g.* Word, Corel Draw, *via* clipboard (copy - shift insert)
· help assistance for all activity

In combination with the A/D-converter board 800/3 from Microstar (not included), and interfaced with a function generator and a potentiostat, *CACYVO* can also be used for CV data acquisition in the range of 0.02 to 500 V/s. The current *CACYVO* version communicates well with the function generator AMEL 568. Any other programmer can be used, provided that it generates a trigger output. However, in such a case data acquisition is less comfortable. [a] *CACYVO* acquisition options includes:
· single and multiple scan data acquisition;
· continuous scan data acquisition;

[a] Future versions of *CACYVO* will take advantage of the A/D and D/A abilities of the Microstar 800/3 board.

CACYVO **may be of interest for you:**

1. If you are equipped with any of the following digital CV data acquisition instruments and software:
   PAR 270 (and compatibles)
   Metrohm VESUV
   Autolab General Purpose Electrochemical System GPES
   You will continue to use your equipment for data acquisition, but you can import the CV's stored on a DOS-disc into *CACYVO* using the specific import filter to evaluate, interpret and represent them under the *Windows* environment.
   Read chapter 2 and 3 of the manual and refer to chapter 7 for specific questions.

2. If you use **any other digital CV data acquisition instrument**, that stores CV's on a DOS disc in a two column representation of current and potential, you can import the data directly into *CACYVO* using the general import filter to evaluate, interpret and represent them under the *Windows* environment.
Read chapter 2 and 3 of the manual and refer to chapter 7 for specific questions.

3. If you use the **AMEL 568** programmer possibly in combination with the **AMEL 553** potentiostat, we recommend to purchase the A/D conversion board 800/3 from Microstar. *CACYVO* will develop its full power, i.e. control of data acquisition and evaluation, interpretation and representation of the results under the *Windows* environment.
Read chapter 2, 3, 4 and 6 of the manual and refer to chapter 7 for specific questions.

4. If you use any other analog function generator with a trigger output and potentiostat such as PAR 173/175, we recommend you to purchase the A/D conversion board 800/3 from Microstar. Data acquisition with *CACYVO* is then possible - however with less comfort then in case 3. Full power in evaluation, interpretation and representation of the results under the *Windows* environment is available.
Read chapter 2, 3, 5 and 6 of the manual and refer to chapter 7 for specific questions.

5. If you have a potentiostat with a modulation input, but **no fast function generator**, wait for the next version of *CACYVO*. It will make use of the function generator build-in on the Microstar 800/3 A/D D/A conversion board. Inform the authors about your interest in the new version of *CACYVO*.

2 Installation of *CACYVO*

1. Insert the floppy in your drive
2. From *Program Manager* choose *File, Execute* then enter "a:setup.exe" and press <Enter> or double click "setup.exe" from *File Manager*.
3. The setup program asks for the destination path. Press <Enter> if you agree.
4. The program will be installed and a group with the program icon and the help file icon will be added to the Program Manager.

After installation double click the *CACYVO* symbol.

CACYVO installation copyies also the Microstar A/D converter dynamic link library (dapio.dll) intothe *Windows* system directory.

Known problems:

Sometimes the installation program interrupts the installation and an error message is displayed:

"Warning - can not copy file a:\ddeml.dl_ since the destination file is already in use"

You then have to move the file ddeml.dll in the windows\system directory into a different directory and restart the setup program. After installation you can move the original ddeml.dll file back into the windows\system directory.

or later:

"commdlg.dll is in use. Please close all applications and re-attempt setup"

Do the same thing as shown above with the file "commdlg.dll" which is also in the windows\ system directory.

These two problems should be solved when you read this document.

3 Representation, evaluation and interpretation of cyclic voltammograms

4 Representation of CV's

5 Representation of a single CV

1. Load a CV from disc (or produce one by acquisition, see chapter 6, and go to step 2)
   choose *open CV* from the main menu *File*;
   choose the **drive**, the **directory**, the **type of file** and the **file name** in the box.

2. If the CV is noisy,
   either chose *Filters, CV-Filters, Golay Sawitzki*.
   If it is not noisy go to step 3.

3. From the *Display / 2-dim settings* menu disable **Display peak evaluation** to suppress the display of evaluated peak values.

4. From the *Display / 2-dim settings* menu choose
   · **i-direction** and **E-direction**
   · **Font** and **Font size**
   · **axes position** and **grid** option
   · **ticks/line/caption settings**
     Check your settings in the *Display / 2-dim settings* with the **OK**-button.
   These settings will be stored if you quit the program and will be active when you start *CACYVO* next time.

5. If you want to normalize the current, choose *v* or *v*$^{0.5}$, and/or **surf. w.e.** (for current densities) from the menu *Display i-normalization*.

<div align="center">

μ §
Fig. 1
a voltammogram before filtering

μ §
Fig. 2
same voltammogram as in Fig. 1 after filtering

</div>

6 2-dim representation of a series of CV's

Load the first CV of a series according to steps 1-5 in 3.1.1
6. Select *Overlay* from the main menu *File* and choose the **drive**, the **directory**, the **type of file** and the **file name** in the box.
7. For an offset representation without common i-axis select *Shift CV* in the main menu *Edit*

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Fig. 3
Series of overlaid CV's prepared in *CACYVO* and copied directly into Word (using the grid option, a larger font size and line thickness for representationn purpose).

Fig. 4
Same series of overlaid CV's as in Fig. 3 prepared with *CACYVO* using $v^{0.5}$ normalization and inverted axes.

Fig. 5
Series of three overlaid CV's has been prepared in *CACYVO* using the *shift current* option. They were copied to the clipboard and inserted into *Corel Draw*. Molecular formula were drawn in *Chem Window*, the character size of the potential axis was adjusted and the current axis was replaced by a current scale indicator.

7 2-dim representation of a series of partial CV's

Load and overlay the CV's according to steps 1-5 in 3.1.1 and step 6 in 3.1.2; use the *Shift CV* option (step 7), if necessary:
8. Select *Data Cursor* in the *Edit* menu and define the limits of the partial CV.
9. Enable *Partial CV* in the *Edit* menu.

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Fig. 6
series of overlaid partial CV's
prepared in *CACYVO* using the shift
CV option

8 3-dim representation of CV's

Load and overlay the CV's according to steps 1-5 in 3.1.1 and step 6 in 3.1.2;
10.   Select *3-dim Parameters* in the *Display* menu and define the z-axis settings.
11.   Enable *Show 3-D* on in the *Display* menu.

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Fig. 7
series of overlaid CV's in 3-dimensional
representation. The z-axis unit is log[additive].
(cobalt-corrinoid system, additive = n-Butyliodide)

9 Evaluation of cyclic voltammograms

1. Load a CV from disc (or produce one by acquisition, see chapter 6, and go to step 2)
2. If the CV is noisy, either chose *Filters, CV-Filters, Golay Sawitzki* or disable *peak auto detect* in the menu *Analysis*. If it is not noisy go to step 3
3. Enable **Display peak evaluation** in the *Display / 2-dim settings* / **line styles/colors** menu.
4. Choose *Ep, ip Evaluation* in the menu *Analysis*, set the tangent and then the peak current according to the bottom line instructions. Finish the evaluation of the first peak (tangent <u>and</u> peak) before proceeding to the next peak. If you are interested in the faradayic charge under the CV trace for surface confined, electroactive species, choose *Q-Evaluation* in the menu *Analysis*, set the tangent and then the limits of integration according to the bottom line instructions. If you want to correct any evaluation, chose *Delete Evaluation* in the *Analysis* menu. All evaluations of the current CV will be lost and you have to start again from zero with evaluation.
5. Choose **Assign Peaks** in order to link the cathodic and anodic waves of a simple redox couple. Such an assignment is compulsory for the subsequent determination of E^o (reversible couple), of k^o_s (heterogeneous e.t. rate constant, quasi reversible couple), or of k (first or second order chemical rate constant, E_{rev}-C_{irrev}).

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Fig. 8
CV with **Display peak evaluation**
enabled (axes edited in *Word*).

10 Interpretation of cyclic voltammograms

Single CV's:

If steps 3.1.1-5 have been executed on a single CV, choose *Single CV mechanism* in the menu *Analysis* and decide for one of the models to be applied. *CACAVO* 2.0 includes the following 5 mechanistic models and will calculate the corresponding parameters:

- E_{rev}: $\quad\quad\quad\quad$ E°, n, D
- E_{q-rev}: $\quad\quad\quad\quad$ E°, k°
- E_{irrev}: $\quad\quad\quad\quad$ k°, a, D
- E_{rev}-C_{irrev}: $\quad\quad\quad$ k_f, $k_{2.\,order}$
- E_{rev}-$C_{cat.}$: $\quad\quad\quad$ k_{cat}

Note: It's up to the operator to choose the appropriate model according to the criteria discussed in the original literature and presented in a simplified version in the **Single CV mechanism Help File**. Application of the wrong model forces *CACYVO* to produce wrong results without notification.

Fig. 9 and 10
Screen prints of evaluated CV and corresponding
E_{rev} - C_{irrev} mechanism evaluation (reversible).

Series of CV's:

Interpretation of a series of CV's in *CACYVO* is based on the influence of a single experimental parameter (e.g. scan rate, temperature, time) on an electrochemical observable (e.g. i_p, E_p). The corresponding dependence is plotted in a x-y graph; for its interpretation the operator is refereed to the literature [1].

1. *Overlay* (see section 8.2) a series of evaluated CV's (see section 3.1.1-5) with one experimental parameter changing.
2. Choose Analyze series of CV's from the main menu Analysis.
3. Choose observable (current, potential or charge (**y-axis settings**, **Variable**)) and select the wave
4. Choose the changing experimental parameter (**x-axes settings**, **Variable**) and select the **scale** (linear or logarithmic).
5. Choose **graph** and **actualize graph** to see the graphic representation.
6. Choose again **grid** and edit the column **display** in order to eliminate a data point
7. Choose **show linear fit** for a best fit.

Fig. 11
Currents (y-axis) plotted against $v^{0.5}$ (x-axis) and corrresponding linear regression. The (0,0) point is not a experimental value, it was manually added to the spreadsheet.

Fig. 12
Evaluation of the 3-dim example in Fig. 7

11 How to use *CACYVO* in combination with the AMEL 568 programmer and the Microstar DAP 800/3 A/D-Converter

CACYVO has been originally written for the DAP 1200/4 A/D converter board from Microstar. The more recent DAP 800/3 is also supported by our software. We recommend to purchase the DAP 800/3 from:

Microstar Laboratories^{TM}
2265 116th Avenue N.E.
Bellevue, WA 98004
USA
Sales & Customer support: (206) 453-2345
Finance & Administration: (206) 453-9489
Fax: (206) 453-3199

The DAP 800/3 is an A/D and D/A converter. The latter option is not used by the current *CACYVO* version 2.0. However, future *CACYVO* versions will make use of the D/A abilities of DAP 800/3, i.e. the excitation signal will be generated on board.

12 DAP-Jumper settings for the DAP 800/3

The range of the A/D-Conversion has to be set from -5Volts to +5Volts. Make sure, that the jumper J9 on your board is correctly set (page 37 Hardware Manual). The factory configuration is bipolar (-5V to +5V) so you usually don't need to change any jumpers.
Connect the DAP, the AMEL 568 and the PC as shown below:

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A scheme of the RS 232 cable is shown in the technical reference at the end of this document.

13 How to use *CACYVO* in combination with other electrochemical hardware and Microstar DAP-A/D converters (e.g. series 800 and 1200)

14 DAP-Jumper settings

The range of the A/D-Conversion has to be set from -5Volts to +5Volts. Make sure, that the jumpers on your board are correctly set (read your DAP-Manuals for more information).

15 DAP-tuning with *CACYVO*

If you use a different DAP board you have to enter an A/D conversion rate in the *Preferences* (Field "DAP Performance") dialog box (Menu Acquisition). A table with the DAP-boards and the corresponding values is shown in the technical reference. Tune your card as indicated after the table

Note:
If you don't use the AMEL 568 you have to enter the potentials and scan rate settings in the *function generator* dialog box (Menu Acquisition). Your function generator must be equipped with a trigger.
Connect the DAP, the function generator and the PC as showed in the following illustration:

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16 How to acquire data

Using the AMEL 568
1. Define experimental parameters in the *experimental conditions* dialog box (optional) and excitation signal (compulsory) in the *function generator* dialog box (Menu Acquisition)
2. Adjust the current scale of the potentiostat (it has to fit that of the *function generator* dialog box)
3. Press <F9> or click *Data Acquisition* (Menu Acquisition)
4. Switch purging off, switch the cell on
5. Press <Enter> or click the "OK" button ®
   · data transfer to the function generator
   · trigger sent to A/D-converter, excitation and acquisition starts
   · A/D-converter data are displayed on the screen

Using a custom function generator
1. Define experimental parameters in the *experimental conditions* dialog box (optional) and excitation signal (compulsory) in the *function generator* dialog box (Menu Acquisition)
2. Define the potentials and the scan rate on your function generator
3. Adjust the current scale of the potentiostat (it has to fit that of the *function generator* dialog box)
4. Press <F9> or click *Data Acquisition* (Menu Acquisition)
5. Switch purging off, switch the cell on
6. Press <Enter> or click the "OK" button ®
   · trigger sent to A/D-converter, excitation and acquisition starts
   · A/D-converter data are displayed on the screen

Important Note:
Sometimes, the DAP-A/D board is not addressed by the computer.
We have observed the following problem with the DAP 1200/4:
DapView (DV.EXE) could not be started from the *Windows* environment if *Windows* was loaded by the autoexec.bat file (error message: DAP communication could not be established).
® start DV.EXE form c:\dap before starting *Windows*.

17 Detailed description of the *CACYVO* menus

After starting *CACYVO*, the *main menu* appears with a menu bar and several buttons on the top of the screen.

The status bar:

The status bar at the bottom contains the actual mouse coordinates and a drop down box with the actual CV number and its scan rate, and an information field.

The different menus are explained on the following pages.

Important
When *CACYVO* is started, the symbol "*Graphics Server* " appears on the bottom of your screen. Do not close this application as *CACYVO* needs it for exchanging graphics via the clipboard.

18 Menu File:

19 Open CV (Menu File)

Loads a CV from disc. If you have not saved the current CV, it will be lost.

Shortcut
<Ctrl> + <O> or "open file" button in the button bar .
  "open file" button

_____
Dialog Box Options

File Name
    Select the file you want to open. Either type the name of the file or select it from the list.

Drives
    Select the drive in which the file you want to open is stored.

Directories
    Select the directory in which the file you want to open is stored.

List of file types
    Select the type of file (BIN, CVW or CVD) you want to open.

Related topics:
Overlay CV
Save CV (as)
Import CV

20 Overlay CV (Menu File)

Loads a CV file onto yet displayed CV(s). Overlaid CV's can not only be saved a in single files.

Shortcut
<Ctrl> + <V> or "overlay file" button in the button bar .
  "overlay file" button

3-dimensional representations are possible from overlaid CV's. The Add/subtract option is only available if two CV's are overlaid.

_____
Dialog Box Options

File Name
    Select the file you want to overlay. Either type the name of the file or select it from the list.

Drives
    Select the drive in which the file you want to overlay is stored.

Directories
Select the directory in which the file you want to overlay is stored.

List of file types
Select the type of file (BIN, CVW or CVD) you want to overlay.

Related topics:
Open CV
Add/subtract CV

21 Delete CV (Menu File)

Deletes one CV from memory. Enter the number of the CV you want to be deleted in the input box. The option is only available, if more than one CV is loaded. Any modifications and evaluations made and not stored will be lost.

Related topics:
Overlay CV

22 Save CV (Menu File)

Saves the current CV under the name displayed in the title bar. Only a single CV can be saved per file. Having more than one CV loaded, you have to specify it in the drop down box at the bottom of the main window before saving.
If a CV has been imported you will be asked for a new filename.
If you are altering an existing CV but you do not want to overwrite the original version use the command "save as".

Shortcut
<Ctrl> + <S> or "save file" button in the button bar .
  "save file" button

The CV is saved together with the following settings/parameters:

- CV filtered? ® true or false
- experimental conditions
- kinetic analysis (only one analysis per CV!)
- evaluated peak currents and peak integrals

You can check or change these values with any text editor (e.g. notepad)

Related topics
Save CV as

23 Save CV as (Menu File)

Saves an acquired CV, a new version of an existing CV or an imported CV.

Shortcut
<Ctrl> + <A>

_____

Dialog Box Options

File Name
> Type a name for the new file. You may overwrite an existing file by selecting its name from the list.
> The filename can contain up to eight characters and precedes the three character extension. ASCII files saved from *CACYVO* have the extension "cvd", binary files "bin".

Drives
> Select the drive in which you want the file stored.

Directories
> Select the directory in which you want the files stored.

List Files of Type
> Select the type of file to be saved, either binary or text. Text files can be read and edited by text editors.

free disc space on drive [kB]

> It informs you about the free space on your actual drive. When it is less than 20kB the numbers will turn red and flash. It is suggested to change the floppy disc or to remove files from the hard disc.

used disc space on drive [%]

This status bar informs you about the available place on the actual drive.

Related Topics:
Save CV

24 Import CV (Menu File)

Allows you to import CV's from
> • PAR (e.g. Model 270)
> • Metrohm VESUV
> • ECO (Autolab)

Shortcut
<Ctrl> + <I>

_____
Dialog Box Options

File Name
   Type the name of the file you want to import, or select it from the list. To list a different type of file, choose the type from the file type box.

Directories
   Select the directory in which the file you want to import is stored.

Drives
   Select the drive in which the file you want to open is stored.

List Files of Type
   - PAR, Princeton Applied Research: these files commonly have the extension "dat" (The program recognizes binary and ASCII files)
   - Metrohm files (VESUV), these files commonly have the extension ".cv"
   - Autolab files with the extension ".icv"
   - ASCII (*.*): any extension is possible.

For overlaying CV's from imported files you first have to save them in *CACYVO*-format.

Importing ASCII:
Select the file you want to import. You will then be asked how the E and i-values are stored, the conversion factors for i and E as well as for the row sequence of E and i.

Related topics:
Export CV
Overlay CV

25 Export CV (Menu File)

The option creates an ASCII-file of the current CV in memory (E- and i-values) or a HPGL file of all loaded CV's (including i_p, E_p-evaluations).

The HPGL -Format (*.plt or *.hgl) is a vector graphic format used for plotters.

26 Print CV (Menu File)

Shortcut
<Ctrl> + <P> or "Print button" in the button bar .
  "Print button"

Prints the current screen contents on your default printer in **landscape orientation** (see *Printer*

Setup).

27 Printer Setup (Menu File)

Use this command to select the printer and printer options you want to use to print your drawing.
_____
Dialog Box Options

Printer
> Selects the default printer or a printer listed in the box under **Specific Printer**.
> Only installed printers appear in the list. You install printers through the *Windows* Control Panel.

Orientation
> The command has no affect on printing in *CACYVO* (*CACYVO* always prints in landscape).

Paper
> Selects the paper size and source. Click on the arrows on the right of the Size and Source boxes to see a list of options you can choose.

Options
> Displays a dialog box where you can choose default options for the printer you select.

28 Exit (Menu File)

Ends the current *CACYVO* session.

Shortcuts
<Alt> + <F4> or <Ctrl> + <X>.

Caution: any changes since the last saving will be lost!

The next time you run *CACYVO*, the program will use the same settings as in the last session, i.e.:

• Window size and origin.
• All settings in Display ® 2-Dim settings.
• Function generator setup (Potentials, current amplification, scan rate).
• RS 232 settings and DAP-settings.
• Maximal Number of points to acquire.

29 Menu Edit

30 Zoom (Menu Edit)

Zooms a portion of the screen.

Shortcut
<Ctrl> + <Z> or "zoom" button in the button bar .
  "zoom" button

Click with the left mouse button on an edge of the region to zoom. Draw the mouse to the opposite corner of the rectangle to define the zoomed region and click.

On the right and lower side of the window two scroll bars appear. You can scroll through the CV by clicking the arrows on the scroll bar, by clicking on the scroll bar itself or by dragging the scroll bar square.

Related Topic
Normal size

31 Normal Size (Menu Edit)

Displays the CV's in the memory in the original size.

Shortcut
<Ctrl> + <N> or "normal size" button in the button bar .
  "normal size" button

Use this button also to redraw the CV's if they are not properly displayed.

Related topic
Zoom

32 Data Cursor (Menu Edit)

A cursor is placed on the first point of the CV (the first CV in case of overlaid CV's). The coordinates are displayed in the button bar. It can be moved along the data points of the CV.

velocity of the cursor:

Slow:
    press <¬> or <®> key
Intermediate:
    press <Shift> and <¬> or <®> key simultaneously.
Fast:

press <Ctrl>, <Shift> and <¬> or <®> key simultaneously.

Jump to next CV (in case of overlaid CV's):
    press <> key
Jump to previous CV (in case of overlaid CV's):
    press <¯> key

Use cursor for marking and cut a part of a CV
    1. Move the cursor to the first limit.
    2. Press the space bar.
    3. Move the cursor to the second limit. The selected partial CV is displayed in a different color.
    4. Press the space bar

You can display the whole CV again by disabling *Partial CV* in the "Edit" menu.
When you overlay a CV while "Partial CV" is active, the *Partial CV*-option is deactivated.

Related topic
Partial CV

33 Partial CV (Menu Edit)

This option is only available if you have set two limits on a CV. You can toggle between *Partial CV* and full CV by clicking the *Partial CV* option.

Related topic
Data Cursor

34 Shift CV (Menu Edit)

This option lets you shift the latest loaded CV horizontally and/or vertically.

It is used to display several CV's on a single screen with the "reference i" option (Menu "2-dimensional options").

35 Add/subtract CV (Menu Edit)

This option is only available if **two** CV's are loaded. Both CV's must have the same scan rate, number of points and potential limits.
You have the following options:

CV Nr 1 - CV Nr 2
This will subtract each current value of CV number 2 (the latest loaded CV) from the corresponding value of CV number 1 (the prior loaded CV).

CV Nr 1 + CV Nr 2
This will add each current value of CV number 2 to the corresponding value of CV number 1.

36 Copy to clipboard (Menu Edit)

Shortcut
<Ctrl> + <Ins>.

This option lets you copy the graphic to clipboard and insert it in any *Windows* application that supports graphics, such as *Word for Windows, Corel Draw, Write* etc.
In *Word* and *Corel Draw* the graphic is copied as *Windows* metafile, in *Write* it is copied as bitmap
.
You can edit the graphics in *Corel Draw* (after "ungrouping") or in *Word* (double click the graphic).

Known bugs
Grid lines are not displayed properly in *Corel Draw*. However, you can define the shape of the grid lines as follows:
Ungroup the graph in *Corel Draw* then select the appropriate line type for the grid lines.
Mark the grid lines and click "apply" in the line combo box of *Corel Draw*.
CACYVO may copy the graph not properly to Clipboard, e.g. only the axis are displayed when you insert the graphic in *Word* or *Corel Draw*. This is a bug of *Graphics Server*.
In this case you have to exit from *CACYVO* and start it again. If that doesn't help, exit *Windows* and restart it.

Related topic
Save graphic

37 Save graphic (Menu Edit)

The option lets you save all loaded CV's in the metafile format. Many other *Windows* applications recognize this format, e.g.*Word* for *Windows*, *Corel Draw*.

Known bug
CACYVO may copy the graph not properly to Clipboard, e.g. only the axis are displayed when you insert the graphic in *Word* or *Corel Draw*. This is a bug of *Graphics Server*.
In this case you have to exit from *CACYVO* and start it again. If that doesn't help, exit *Windows* and restart it.

Related topic
Copy to clipboard

38 Menu Acquisition

39 Function generator (Menu Acquisition)

This option lets you program the function generator.

Shortcut
<Ctrl> + <F> or "function generator" button in the button bar .
  "function generator" button

Note:
If you have an AMEL 568, connected with a serial cable (RS232) to the computer, the program programs the function generator.
Even with a manually set function generator you have to define the function generator settings here, in order the program knows how the set the A/D converter.
_____
Dialog Box Options

Potentials (1-14)
  Enter the starting potential, the switching potential(s) and the final potential in Volts. You can enter up to 14 and at least two potentials.

Scan rate
  Enter the scan rate. Integer values from 1 to 1024 are accepted. You can toggle between "V/s" and "mV/s". The DAP 800/3 can handle scan rates from 20mV/s up to 500V/s..

Current amplification
  Enter the current amplification (1 Volt corresponds to xx Ampères). You can toggle between "A", "mA" , "mA" and "nA". If the current amplification is too low the program indicates that after acquisition.

Initial / Final delay
  Enter the equilibration (closed circuit) time for the experiment. Integer values from 1 to 1024 are allowed (no decimal values). You can toggle between "min", "sec", "msec" and "msec". For continuos acquisition a low value of 20ms is recommended.

OK
  Closes the function generator window.

continuos scans...
  Shows an additional dialog box option for the specification of the continuos acquisition. Continuos acquisition is possible from few minutes to several hours. You can define how many CV you like to store on disc (a few up to several hundreds).

_____
Additional Dialog Box Options

target path

Lets you select the target path of the continuos acquisition files in the directory list below.

drives (HDD only)

Lets you select the target drive of the continuos acquisition files in the drive list below. Only the hard disc is allowed for continuos acquisition.

reset

resets the "#cycles" and "save every" value to "1"

autosave parameters

filename (4 lett.)

Lets you enter the common filename of the files. Only 4 letters are allowed. The program adds the second part of the filename as a number from 0001 to 9999.

#cycles

Lets you enter the number of cycles the function generator has to do. Depending on the computer you are using and the scan rate the program may not count all CV's executed by AMEL.

#save every

Lets you determine how many CV's you want to save during acquisition. The program saves the first and then every x-th file (x in this box).

available/needed place [kB]

Shows the needed and available place for the continuos acquisition experiment on your hard disc. If the needed place is larger than the available place, it turns from green to red. It is recommended to reduce #cycles and/or to increase #save every.

Continuos scans limitations:

The continuos scans option was tested with an 486-DX2/66 PC and an DAP 800/3 A/D-board. With this equipment a maximum scan rate of 200mV/s is suggested. Higher scan rates may cause data loss.

Note:

CACYVO disables the *Windows* screen saver during data acquisition to prevent information loss. Third party screen savers should be disabled manually.

40 Experimental conditions (Menu Acquisition)

Shortcut

<Ctrl> + <E> or "Experimental conditions" button in the button bar .
  "Experimental conditions" button

Lets you define the experimental (chemical) conditions related to the actual CV. Date and time is updated by the program.

Abbreviations:

w.e.	working electrode (string)
surf. w.e. [cm^2]	surface of the working electrode (num. var.)

r.e.	reference electrode (num. var).
r.e. vs NHE [V]	reference electrode as compared to NHE (num.var.)
a.e.	auxiliary electrode (string)
elyt	electrolyte (string)
[elyt][mol/l]	concentration of the electrolyte in mol/liter (num. var.)
elact.sp.	name of the electroactive species (string)
[elact.sp.][mol/l]	concentration of the electroactive species (num. var.)
surf. confined	surface confined or homogenous (string, "h" or "s")
temp [°C]	Temperature (num. var.)

(num. var. = numeric variable)

41 Preferences (Menu Acquisition)

_____

Dialog box options

Serial Port:
    Define the settings of the serial port (important only if you use the AMEL 568).

Additional options:
Amel 568 function generator
    Make sure that this checkbox is marked if you use the AMEL 568.
Microstar simultan board
    Make sure that this checkbox is marked if you use the microstar simultan board.

Number of points/CV to acquire
    You can define the resolution of the CV. Values from 800-1000 data points are recommended for a single CV. For two scans use 1500 points. At very high scan rates the program reduces the number of data points.

DAP Performance [cycles/s*channel]
    This value is determined by the performance and configuration of you DAP board. Use the values indicated in the DAP performance settings (technical reference).

42 Data acquisition (Menu Acquisition)

Shortcut
<F9> or "Data acquisition" button in the button bar .
  "Data acquisition" button

_____

dialog box options

OK
    Starts the acquisition. Previously loaded or acquired CV('s) will be lost.

cancel
    Escapes the acquisition. Previously loaded or acquired CV('s) are not lost.

Note:
CACYVO disables the *Windows* screen saver during data acquisition to prevent information loss. Third party screen savers should be disabled manually.

43 Menu Filters

44 CV-Filters (Menu Filters)

The filters can be used to reduce any high frequency noise (as compared to the CV scan rate). It is recommended to filter your CV
1. if *peak auto detect* is on.
2. before data reduction

Note: In case of overlaid CV's, all CV's will be smoothed!

There are two types of filters available:
1. Golay Sawitzki
  "Golay Sawitzki" filter button

The filtering process is according to the formula:

where
i_n is the current value of the point to be smoothed.

n is the index of the actual smoothed point (only currents are smoothed!)
f is the filter constant you have to enter in the input box.
This filter does not effect peak values severely.

2. Sliding average
  "sliding average" filter button

The filtering process is according to the formula:

µ §

i_n is the current value of the point to be smoothed

n is the index of the actual smoothed point (only currents are smoothed!)
f is the filter constant you have to enter in the input box.
The sliding average filter may reduce peak heights.

Note: In case of a sharp spark use the *spreadsheet* to eliminate the noise manually.

45 Reduce data (Menu Filters)

This option is used to reduce the data points. It is recommended to filter your data before reducing them.
Recommended for copying CV's to clipboard.
Do not evaluate peak data on reduced CV's.

Note: All loaded CV's will be reduced!

46 Spreadsheet (Menu Filters)

The spreadsheet has an own menu with several options:

Quit spreadsheet
　　Quits *spreadsheet* and goes back to the *main menu*

E/i data points
　　All E/i values of the current CV('s) are represented in two rows. You can scroll down the
　　spreadsheet and edit them.

ip, Ep and Q values
　　Evaluated ip, Ep, E° and E½ are represented in the spreadsheet. You can mark the values and
　　copy them to clipboard.

Select all
　　Selects all values in the spreadsheet, a useful option to copy them to clipboard.
　　Shortcut
　　<Ctrl> + <A>

Selected area to Clipboard
　　Copies the selected area of the *spreadsheet* to clipboard.

How to mark an area:
1. Set the mouse cursor to the first cell you want to mark and click
2. scroll to the last cell you want to mark
3. Press the <Shift> key and click on the cell.

How to edit a cell value:
- Double click on the cell to be edited and enter the desired value or
- Click on the cell and enter any number
After editing press Enter to confirm.
CV data points can be edited, evaluated peak heights and integrals can not be edited.

47 Menu Display

48 2-Dim-Settings (Menu Display)

This dialog box allows you to control the 2-dim-display of the CV's.

Shortcut
<Ctrl> + <D> or "2-Dim-Settings" button in the button bar .
  "2-Dim-Settings" button

_____
Dialog Box Options

Line styles / colors

Different line styles
    If the check box is enabled, overlaid CV's are shown in different line style.
Different colors
    If the check box is enabled, overlaid CV's are displayed and printed in different colors.
Symbols only
    If the check box is enabled the CV's will be represented by different symbols without
    connecting lines.
Display peak evaluation
    Only if the checkbox is enabled, evaluated data are displayed.

E- and i-direction
    Gives you complete control over the direction of the current and voltage axes.

Font
    The two options are Arial and Times New Roman (Font size: 10 to 20 points). Further font
    types and sizes can be used after importing the graph into *Corel Draw* or *Word*.

Axes position/height

default settings
    If the option is enabled, the origin of the axes is moved to the left down corner.
E-axis intersects i-axis at [mA]
    You can position the E-axis at any current within the limits indicated in the gray field below.
i-axis intersects E-axis at [V]
    You can position the i-axis at any current within the limits indicated in the gray field below.
Grid
Selecting this field will display a grid, with a frequency determined by the major tick settings.
    Notes: The "**reference i**" check box is not enabled if the "**Grid**" check box is selected!
    The grid is not displayed properly in *Corel Draw*. See also *Copy to clipboard*.
reference i
You can change the origin and length of the reference current by the settings in the corresponding
boxes.

Note: The "**Grid**" check box is not enabled if the "**reference i**" check box is selected!

PREVIEW
A preview of the CV is displayed upon clicking according to your settings.

ticks/line/caption settings
default caption
The default caption of the axis are displayed.
ticks outside
The ticks are displayed outside of the axis if selected, otherwise inside.
E-axis resp. i-axis:
> **caption**
Only available if "default caption" is not selected. Lets you annotate the E and I axes.
> **#maj. ticks**
Selects the number of major ticks and the frequency of the grid.
> **#min. ticks**
Selects the number of ticks between the major ticks.
line thickness
Determines the thickness of the lines of the axis and the CV's. Values between 1 and 4 are accepted.

49 i-normalization (Menu Display)

_____

Dialog Box Options

You can toggle between the following current normalizations:

1 (no normalization with sweep rate)
1/µ §
1/ sweep rate

Dependent of the above normalization you can toggle between current and current density.

Note:
If you evaluate currents the program uses always non-normalized values.

- Charge calculation is only possible if no normalization is selected.
- The program only displays a reference i if no normalization is selected (see *2-Dim-Settings*).

50 Mouse coordinates (Menu Display)

Enables or disables of the mouse coordinates-display.

51 3-Dim Parameters (Menu Display)

CACYVO lets you display overlaid CV's in a perspective 3-Dim fashion. The 3rd dimension is any of the parameters shown below.

_____

Dialog Box Options

3rd Dimension:
> Any of the following parameters can be selected for the 3rd dimension:
> · Number of CV
> · Sweep rate
> · [El.act.sp.]
> · [Electrolyte]
> · [Additive]
> · Temperature
> · Time (acquisition, format: dd.mm.yyyy hh:mm:ss)

z-axes scale:
> linear or logarithmic.

Angle:
> Any value from 0 to 90° is allowed. It may be changed via the text box or via the scroll bar.

Rel. length of z-axis:
> You can change the rel. length from 0% to 100%. For 2 to 5 loaded CV's a value from 20% to 40% is recommended, for 6 to 10 loaded CV's, a value from 40% to 100%.

The above selections show up if *Show 3-D* option is on.

52 Show 3-D (Menu Display)

Displays the CV's in three dimensions according to the settings in the *3-Dim Parameters*. This option is only active if several are overlaid (see *Overlay CV*).

53 Menu Analysis

54 ip, Ep -Evaluation (Menu Analysis)

This option lets you evaluate peak heights and potentials (follow the messages in the information bar at the bottom of the window).

Shortcut
<Ctrl> + <i> or "ip, Ep -Evaluation" button in the button bar .
  "ip, Ep -Evaluation" button

1. set the turning point of the tangent: Move the mouse cursor to the turning point of the wave to be evaluated and click.
2. set the slope of the tangent: Move the mouse until the slope matches and click.
3. position tangent: Move the tangent without changing its slope for a best fit. Click if done.
4. set peak: *Peak Auto detect on*: Move the mouse cursor close to the peak and click (the program will position it at the accurate peak position). *Peak Auto detect off*: Position the mouse cursor exactly onto the peak and click. Position the cursor onto the plateau current in case of a catalytic wave and click.

Note:
Evaluation of peak values is only displayed, if **Display peak evaluation** in the *2-dim-settings* menu is selected!

55 Q-Evaluation (Menu Analysis)

Lets you evaluate the faradayc charge (i.e. the area between the CV-trace and the capacitive contribution). Follow the messages displayed in the information bar at the bottom of the window.

Shortcut
<Ctrl> + <q> or "Q-Evaluation" button in the button bar .
  "Q -Evaluation" button

1. set the turning point of the tangent: Move the mouse cursor to the turning point of the wave to be evaluated and click.
2. set the slope of the tangent: Move the mouse until the slope corresponds and click.
3. position tangent: Move the tangent without changing its slope for a best fit. Click if done.
4. Set left and right limit of integration: Position the cursor at the left integration limit and click. (+) will appear at this position. Now position the cursor at the right integration limit and click. The result of integration is displayed mC.

Note:
Evaluation of charge values is only displayed, if **Display peak evaluation** in the *2-dim-settings* menu is selected!

56 Assign Peaks (Menu Analysis)

An anodic and a cathodic peak can be assigned to each other, if they are evaluated (See *ip, Ep Evaluation*). Certain single CV mechanisms, e.g. E_{rev}-C_{irrev}, can only be evaluated if two peaks have been assigned.

1. Position the mouse cursor next to the cathodic peak to be assigned. Upon recognition, the peak is marked with a red circle. Click the left mouse button to confirm.
2. Position the mouse cursor next to the corresponding anodic peak and click. Upon recognition, the peak is marked with a red circle and the two assigned peaks with the same blue number. Assigned peak are stored as pairs to the file upon saving the CV.

The program assigns the peaks and displays a blue number next to the Ep-value of the peaks. (See important note!) Corresponding peaks have corresponding numbers.
Assigned peaks are also stored to file.

Important note:
Assigned peaks are only marked, if **Display peak evaluation** in the *2-dim-settings* menu is selected.

57 Delete evaluation (Menu Analysis)

Evaluated data (ip, Ep, Q, assigned peaks) of all loaded CV's are deleted.

58 Peak auto detect (Menu Analysis)

If selected, the mouse cursor jumps automatically onto the closest peak upon mouse click during *ip, Ep evaluation*. If disabled, the effective mouse cursor position at the click is read as peak position during *ip, Ep evaluation*.
Note: Use *Peak auto detect* only on reasonably smooth CV's

59 Single CV mechanism (Menu Analysis)

The following mechanistic cases are currently available:
E (rev)   assigned couple only
E (rev2)
E (q-rev)   assigned couple only
E (irrev)
E (rev) - C (irrev)   assigned couple only
E (rev) - C (cat)

E (rev2), E (irrev) and E (rev) - C (cat) are active if at least one wave has been evaluated (see *ip, Ep-Evaluation*).
E(rev), E (q-rev) and E (rev) - C (irrev) are available only if a pair of waves have been evaluated and assigned (see *Assign Peaks*).

Important note: Only one mechanistic case per CV can be stored on disc.

60 E (rev) (Menu Single CV mechanism)

Criteria: peak separation must be 60/n [mV].
Needs an assigned pair. The program calculates n, D or [el.act.sp] according to [1]:

$$\mu \ \S$$ is solved for E°
$\mu \ \S$ is solved for n

$$\mu \ \S$$ is solved for D_O resp. D_R

Note: A warning message will appear, if the program is forced to make a division by zero. In this case check the corresponding fields for their values. If Do or D_R is known, the program can calculate the concentration of the electroact. species (click the selection box).
Calculated values are displayed in red.

61 E (rev2) (Menu Single CV mechanism)

Criteria: peak separation must be 60/n [mV].
The program calculates D and $E_{1/2}$ according to [1]:

$$\mu \ \S$$ solved for $E_{1/2}$

$$\mu \ \S$$ solved for D

Note: A warning message will appear, if the program is forced to make a division by zero. In this case check the corresponding fields for their values.
Calculated values are displayed in red.

62 E (q-rev) (Menu Single CV mechanism)

Criteria: peak separation must be 64 < DEp < 200 [mV].
Needs an assigned pair. The program calculates k^o from the peak separation according to [1]:

$$\mu \ \S \ \ \mu \ \S \text{(Table)}$$ is solved for k

Note: A warning message will appear, if the program is forced to make a division by zero. In this case check the corresponding fields for their values. a influences the calculation only if D_R is not equal D_O.
The value of Y is calculated according Table 6.5.2 (p. 231) in Lit.[1]

IR-compensation is just a reminder for the operator, it does not influence the calculation.
Calculated values are displayed in red.

63 E (irrev) (Menu Single CV mechanism)

Criteria: DEp > 200 [mV].
The program calculates k^o (if E^o is known), a and D according to [1, 2]:

μ $\S$ solved for k°

μ $\S$ solved for D

μ $\S$ solved for a

Note: A warning message will appear, if the program is forced to make a division by zero. In this case check the corresponding fields for their values. If not specified differently, default value ($E°=0$) is used for ko calculations.
Calculated values are displayed in red.

64 E (rev) - C (irrev) (Menu Single CV mechanism)

Criteria: $i_{pc}/i_{pa} < 0.8$ or $i_{pc}/i_{pa} > 1.2$.
1.   Ox + e⁻ « Red
2a   Red ® Red'   (k)
2b.   Red + Additive ® Red' + Additive'   (k_{2nd})
The program calculates k_f or k_{2nd} according to [2]:

μ $\S$ solved for k_f and k_{2nd}

Note: A warning message will appear, if the program is forced to make a division by zero. In this case check the corresponding fields for their values. The program assumes in case of a second order reaction no depletion of Additive in the reaction layer, *i.e.* (Additive) >= 10*(Ox)

The k_{ft}-value is calculated according to Table XI, p. 719 in Lit. [2]

65 E (rev) - C (cat) (Menu Single CV mechanism)

Criteria: $i_{plateau}$ is independent of *v*.
1.   Ox + e⁻ « Red
2.   Red + Additive ® Ox + Additive$_{(oxidized)}$ k_{cat}
The program calculates k_{cat} from [2, 4]:

$$\mu \quad \S \text{solved for } k_{cat}$$

Note: A warning message will appear, if the program is forced to make a division by zero. In this case check the corresponding fields for their values. The calculation assumes that the 'peak current' is measured at the plateau of the steady state current and that (additive) >> (el.act.species). Calculated values are displayed in red.

66 Show kinetic data (Menu Analysis)

Displays a window with the evaluated kinetic data that can be copied to clipboard.
Mark the area to copy, then press <Ctrl> + <Insert>.
You can switch between different evaluated CV's by selecting one in the drop down box.

67 Analyze series of CV (Menu Analysis)

Available only if at least three evaluated CV's are overlaid (see *overlay CV* for more information).

Exit analysis
       Quits *analysis* and leads to *main menu.*

Copy to clipboard
       Copies the graphic or the selected area of the *spreadsheet* to clipboard. The graphic can be copied into any word processor or graphic program.
       The content of the *spreadsheet* can be copied to any word processor.

Print graphic
       Prints the current graphic to the default printer. The graphic is always printed in landscape.

Save to disc
       Saves the graphic (as *Windows* metafile) or the *spreadsheet* (as text file) to disc.

_____
Other dialog box options

Title
       You can annotate the top of the graph.

y-axis settings

    Variable

  Select the peak value for y-variable presentation from the drop down box.

    Cath. or Anod. peak:

  Select the current direction to be correlated.

    Y-axes caption:

  You can annotate the y-axis. Press 'actualize graph' afterwards.

x-axis settings

    Variable

  Select the X-axis variable from the list:

v	scan rate
$(v)^{0.5}$	µ §
[additive]	conc. of additive
[elact. sp.]	conc. of the electroactive species
t (exper.)	acquisition time (continuos scans, format: dd.mm.yyyy hh:mm:ss)
T [K]	temperature

    scale:

  Chose linear or logarithmic (base 10) for the x-values

    x-axis caption:

  You can annotate the x-axis. Press 'actualize graph' afterwards.

actualize graph (command button)

  Actualizes the graph, if the changes do not show up in the graph.

dropdown box

  Lets you toggle between the graph and the worksheet.

calc. + show linear fit

  Calculates the linear fit of the marked x-y data (third row 1=marked, 0=not marked). Edit the third row to define the limits of the linear fit.

68 Menu Help

69 Contents

Loads the main window of the *CACYVO* help file.

70 Search for...

Loads the *CACYVO* help file and shows a window for context search.

71 Info

Shows a window with the copyright notice and the names of the authors, as well as some system information and the registered user's name.

72 Registration...

Displays the registration dialog box (appears as long as the copy is not registered).

73 Technical reference

74 System requirements

The program needs *Windows* 3.1 or 3.11, it does not run under *Windows* 3.0 and *Windows* NT.
The program was tested with a 386DX-25 (4MB RAM), a 486DX-50 and a 486DX/2-66 (both 8MB RAM).
The program approximately needs 2.5MB on your Hard Disc.

75 Serial cable (RS232)

The 25 pin plug connections PC-AMEL 568 are shown below:

µ §

Check if the settings for RS232 communications are the same on AMEL 568 and on the PC. (See also *preferences*).

76 DAP Performance settings

Table of DAP board settings to be used in the *preferences* dialog box. (Menu *Acquisition*):

DAP-Board	A/D-conversion rate [kHz]	w. simultan-b.	w.o. simultan b.
1200/4	156	26300	35000
1200/2/3	50	8429	11218
2400/4	156	26300	35000
2400/5/6	235	39619	52724
800/1	75	12644	16827
800/2/3	105	26000	35100
801/1	60	14857	20057

1200e/4	166	41105	55491
1200e/6	312	77257	104297
2400e/4	166	41105	55491
2400e/5	250	61905	83571
2400e/6	312	77257	104297
3200e/101	312	77257	104297
3200e/102	312	77257	104297
1216e/4	100	24762	33429
2416e/4	100	24762	33429
2416e/6	100	24762	33429

Note:

The values in gray fields are calculated but not checked.

If the CV is not complete, increase the value entered in the "DAP Performance" box. If data acquisition continues after the final potential is reached, decrease the value entered in the "DAP Performance" box.

77 Possible errors

Error: display not actualized
It may happen that the graphic of *CACYVO* is not actualized, e.g. when switching between different *Windows* applications. You can actualize the graph by pressing the "Normal size" button (button bar or Menu Edit).
® press "Normal size" button:

Error: graphic not copied properly
Sometimes the graphic is not copied properly to clipboard. This is an error of "*Graphics Server*" (see also *Copy to clipboard*). You then have to exit *CACYVO* and restart it. If this still doesn't help, you have to exit *Windows* and restart it.
® leave *CACYVO*

Error: tangent or cross not deleted
If you switch to another *Windows* application during evaluation (especially if you draw the tangent), there will be two lines when you switch back to *CACYVO*. The program uses the more recent tangent for calculations. Anyway, it is not recommended to switch between applications during evaluation!
® do not switch between applications during evaluation

Error: Data acquisition not possible
Sometimes, the DAP-A/D board can not be addressed by the computer. In that case you can not acquire data.
We have observed the following problem with the DAP 1200/4:
DapView (DV.EXE) could not be started from the *Windows* environment if *Windows* was loaded by the autoexec.bat file (error message: DAP communication could not be established).
® start DV.EXE form c:\dap before starting *Windows*.

78 Literature

[1] A.J.Bard, L.R.Faulkner, Electrochemical Methods, Wiley & Sons (1980)

[2] R.Nicholson, I.Shain, Anal.chem., **36**, 706, (1964)

[3] H.Matsuda, Y.Ayabe, Z.Elektrochem., **59**, 494 (1955)

[4] J.M.Saveant, E.Vianello, "Advances in Polarography", I.S.Longmuir, ed., Vol I, 367, Pergamon Press, New York 1960

Ordering form
for CACYVO V2.0 (full version)

Name: _____

Address: _____

ZIP Code: _____   City: _____

Country: _____

University or company: _____

Phone: _____   Fax: _____

E-Mail address: _____@_____

Signature: _____

I remit:

                        o 200 US$ for Industrial Customers
                        o 80 US$ for Academics.

to banking account: Schweizerischer Bankverein, SK 90-237.830.0
                        PD Dr. Lorenz Walder
                        Institut für organische Chemie
                        Universität Bern
                        CH-3012 Bern, Switzerland

The registration code (transforming the demo version into a full version) will be mailed upon confirmation of your money transfer.

Please send this form to:
L. Walder/ B. Flueckiger, Freiestrasse 3, University of Berne, CH-3012 Berne, Switzerland
Fax: ++ 41 (0)31 631 44 99

Note: Reports on major bugs or important modifications of CACYVO 2.0
will be honored with a free upgrade.