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ANTEC
LEYDEN

DECADE

Digital Electrochemical Amperometric Detector

user manual



Edition 9, 2007 120.0010

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CE

DECLARATION OF CONFORMITY

We Antec Leyden B.V., Zoeterwoude, The Netherlands, declare that the product

Electrochemical Detector DECADE (p.n. 120.0035)

to which this declaration relates, is in conformity with the following directives:

Safety (73/23/EEC)

Safety requirements for laboratory equipment (Class I, Installation cat. II, Pollution degree 2)	IEC 1010-1

Immunity (89/336/EEC)

Electromagnetic immunity	IEC 801-2/3/4 & ENV 50140
Radio frequency current injection	ENV 50141 & IEC 1000-4-6
Voltage dips and interruptions	IEC 1000-4-11

Emissions (89/336/EEC)

Electromagnetic radiation	EN 55022, Class B (CISPR 22)

Attention

Use shielded cable(s) to connect all I/O's with other devices. Thoroughly connect the shielding to common. Antec Leyden will not accept any liability for damage, direct or indirect, caused by connecting this instrument to devices which do not meet relevant safety standards.

February 21, 2007

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Intended use

For research purposes only. While clinical applications may be shown, this instrument is not tested by the manufacturer to comply with the In Vitro Diagnostics Directive.

WEEE directive



All equipment of Antec Leyden which are subjected to the WEEE directive shipped after August 13, 2005 are compliant with the WEEE marking requirements. Such products are labelled with the “crossed out wheelie”, depicted on the left site.

The symbol on the product indicates that the product must not be disposed as unsorted municipality waste.

Collection & recycling information

Please ship the instrument back to the manufacturer (Antec Leyden, the Netherlands) at the end-of-life time of the product. The manufacturer will take care of the proper disposal and recycling of the instrument at its facilities.

Shipping address for the end-of-life products:

Antec Leyden
Industrieweg 12
2382NV Zoeterwoude
The Netherlands

In case of questions, or if further information is required about the collection & recycling procedure, please contact your local distributor.

ROHS directive

Our instruments are currently exempt from the RoHS directive because they fall under WEEE Annex IA categories 8 and 9, which includes medical devices and monitoring and control instruments. Nevertheless, we have taken steps to eliminate all restricted substances from our products.

Antec Leyden is an ISO 9001:2000 certified company.

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Symbols

The following symbol are used on the rear panel and oven compartment of the DECADE:



Consult the manual for further safety instructions



Frame or chassis ground terminal

The following pictograms are used in the DECADE II manual:



Caution



Caution, risk of electric shock or other electrical hazard (high voltage)

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Safety practices

The following safety practices are intended to insure safe operation of the equipment.

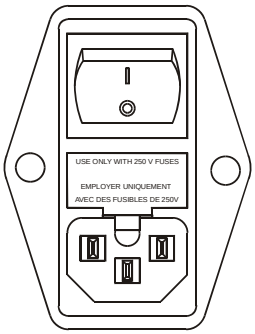
Electrical hazards



The removal of protective panels on the instrument can result in exposure to potentially dangerous voltages. Therefore, disconnect the instrument from all power sources before disassembly. Untrained personnel should not open the instrument.



Replace blown fuses with fuses of proper type and rating as stipulated on the rear panel and specified in the installation section of this manual. The fuse holder is integrated in the mains connector. Ensure that the instrument is never put in operation with fuses of a different type. This could cause fire.





Connect the detector to a grounded AC power source, line voltage 100 – 240 VAC. The instrument should be connected to a protective earth via a ground

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socket. The power source should exhibit minimal power transients and fluctuations. Replace faulty or frayed power cords.
Place the detector on a flat and smooth surface. Do not block the fan located at the bottom of the detector. Blocking the fan will impair the cooling capability of the power supply.

General precautions



Perform periodic leak checks on LC tubing and connections.
Do not close or block the drain.
Do not allow flammable and/or toxic solvents to accumulate. Follow a regulated, approved waste disposal program. Never dispose of such products through the municipal sewage system.
This instrument has a lithium battery inside. Replacement of the battery should be performed by qualified service personnel. Dispose the battery according to chemical waste only.

Spare parts and service availability

Manufacturer provides operational spare parts of the instrument and current accessories for a period of five years after shipment of the final production run of the instrument. Spare parts will be available after this five years period on an ‘as available’ basis.
Manufacturer provides a variety of services to support her customers after warranty expiration. Repair service can be provided on a time and material basis. Contact your local supplier for servicing. Technical support and training can be provided by qualified chemists on both contractual or as-needed basis.

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C H A P T E R 1

DECADE electrochemical detector

Congratulations on your purchase of the DECADE. This detector enables you to perform all applications using electrochemical detection. The DECADE includes a highly stable Faraday-shielded oven compartment accommodating column and flow cell. This flow cell has surprised researchers for its unsurpassed S/N ratio and therefore you now possess the best possible combination for extremely sensitive EC analyses. To further improve the stability of the DECADE an (electrically actuated, option) injector and a high efficiency pulse damper can be incorporated in the oven compartment.

The DECADE covers the DC, pulse and scan mode. Important parameters in the DC and pulse mode can be changed on a time base by user-defined commands, which enables maximum control to fully automate the detection. In addition, crucial settings (start, stop, hold, auto zero, cell on/off) can be controlled by either relays or TTL (open collector type).

The DECADE can be controlled by a computer via the RS232C interface connector (option). Supporting software ‘DECADE Dialogue’ can be obtained. In this way maximum flexibility is warranted.

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C H A P T E R 2

Installation guide

Unpacking

Inspect the *transport box* for possible damage as it arrives. Immediately inform the transport company in case of damage, otherwise she may not accept any responsibility. Keep the transport box as it is designed for optimum protection during transport and it may be needed again. Carefully unpack the system and inspect it for completeness and for possible damage. Contact your supplier in case of damage or if not all marked items on the checklist are included.
Prior to shipment, your detector has been inspected and tested to ensure the best possible performance. The results of the electronic tests are included in the shipkit.

Installation

Please follow the next steps for a successful installation and start-up.

1. To unpack the DECADE, lift it from its transport box by both hands as indicated in Fig. 1A. In any other situation the DECADE should be lifted by both hands under the unit as indicated in Fig. 1B.

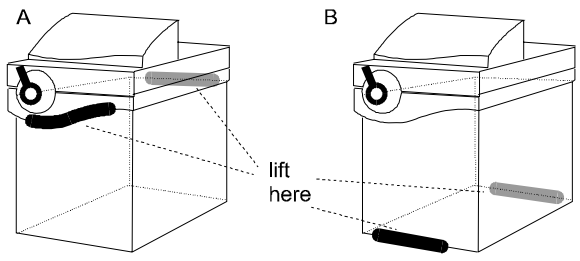


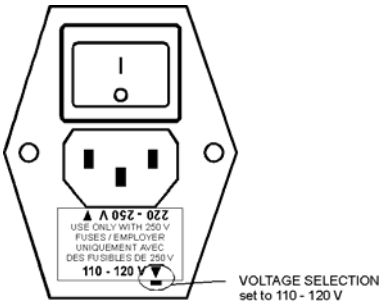
Fig. 1. Lift instructions DECADE.

2. Inspect the system for possible damage and make sure that all marked items on the checklist are included.
3. Check whether the voltage selector is in the correct position i.e. identical with the voltage of your local power supply. If the triangle with the voltage range is pointing towards the small white block, the system is set to that

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line voltage. If not correct, this insert has to be reversed. Use only a supply appliance with protective grounding. The fuses are included in the line connector.

WARNING - RISK OF FIRE REPLACE FUSE AS MARKED		
	FUSE RATING	
INPUT VOLTS	UL / CSA	IEC 127
100-120 V 200-240 V	3.2A 250V TL 1.6A 250V TL	T 3.2A 250V T 1.6A 250V



The correct values are given on the rear panel for the different line sources.
For 110 V (AC) ± 10%, use two 3.2 AT fuses (slow, ¼" x 1¼ ", UL/CSA).
For 220 V (AC) ± 10%, use two 1.6 AT-fuses (slow, 5 x 20 mm, IEC127).

4. Switch 'on' the DECADE by the mains switch on the rear panel.

HPLC connections

Use proper eye and skin protection when working with solvents.
The installation of the flow cell, column and the injection valve (option) and pulse damper (option) is schematically shown in Fig. 2.

5. If ordered, install the pulse damper. Connect the mounting plate with the four bolts supplied to the pulse damper and mount the pulse damper with four bolts. For detailed instructions on the pulse damper see page 75.
6. If ordered, the Antec supplied injection valve is equipped with a Vespel rotor as a standard. For use of strongly alkaline solutions (pH > 10), this should be replaced by a Tefzel rotor. Consult your supplier for details.
7. For installation of a manual injector remove the handle assembly and place the body in the DECADE using the 2 factory-supplied mounting screws. Re-assemble the handle assembly using the 2 set screws.

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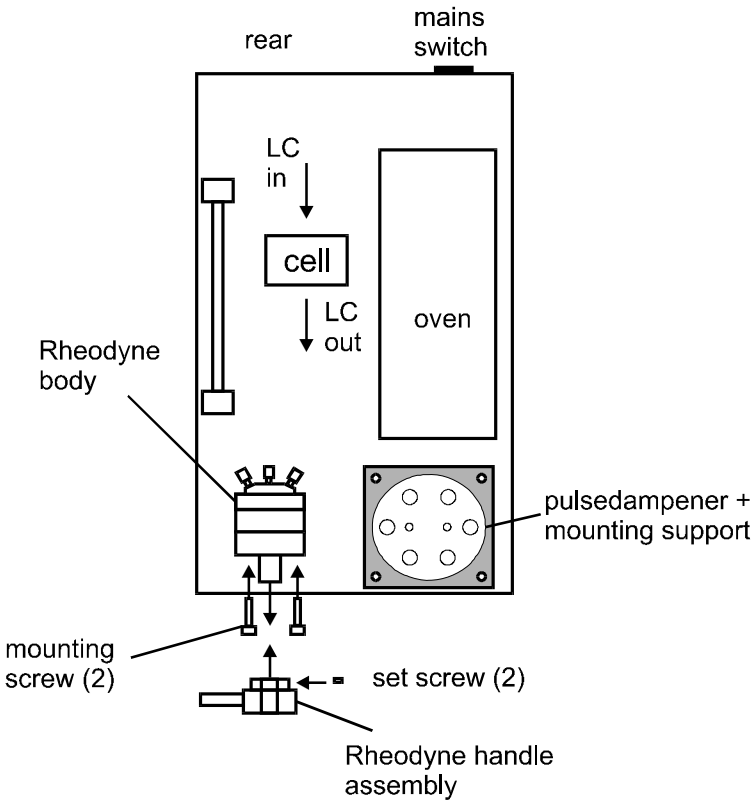


Fig. 2. Installation of the DECADE.

8. If a manual injector is applied, it is only part of the Faraday shield if the yellow wire from the cell cable is clamped on a metal part of the injector. The other end of the yellow cable is connected to 'SHIELD' on the connection plate for the flow cell cable. The sensor cable must be connected to the phone jack (P1) to make the LOAD/INJECT output on the rear panel functional. If no injector is mounted a plug is installed. Use of this plug does not affect the Faraday function.
9. In case of leakage the drain ensures that the oven compartment is not flooded. For proper function of the drain the detector must be placed level.
10. Prior to connection of the HPLC system to the detector all metal parts should preferably be passivated with 15% nitric acid during 20 min. **Make sure that all parts that are not acid-resistant such as: nylon inlet filters, column and flow cell are *not* connected during this step.** The acid is flushed through the pump, the pump tubing, the damper, the injector (in load and inject position) and to waste.
11. After flushing with nitric acid, the system must be thoroughly flushed with demi water. Make sure that no traces of nitric acid are left in the tubing or pulse damper (check with pH paper). Flush the system with HPLC buffer.

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If the ISAAC reference electrode is used, add 2 mmole/l chloride ions (e.g. KCl or NaCL) to the mobile phase. Equilibrate HPLC and continue installation.

12. Before connecting a new column read the manufacturer's instructions. Pre-conditioning of the column may be necessary. A pre-conditioned column is electrochemically clean. If not, the background current may be unacceptably high. For *reversed phase* columns flushing with methanol for 3 days at a low flow rate is recommended.
13. Passage or entrapment of air bubbles in the flow cell will lead to unacceptable noise levels. Therefore, the use of an in-line degasser in the LC system is recommended. In our experience, a one-time degassing step of the HPLC buffer usually is not sufficient.
14. If the detector is used for reductive ECD (at a negative working potential) additional steps should be taken to remove oxygen from the mobile phase. These include degassing with Helium and the use of stainless steel tubing (impermeable for oxygen).
15. Install the flow cell as described in the flow cell manual.

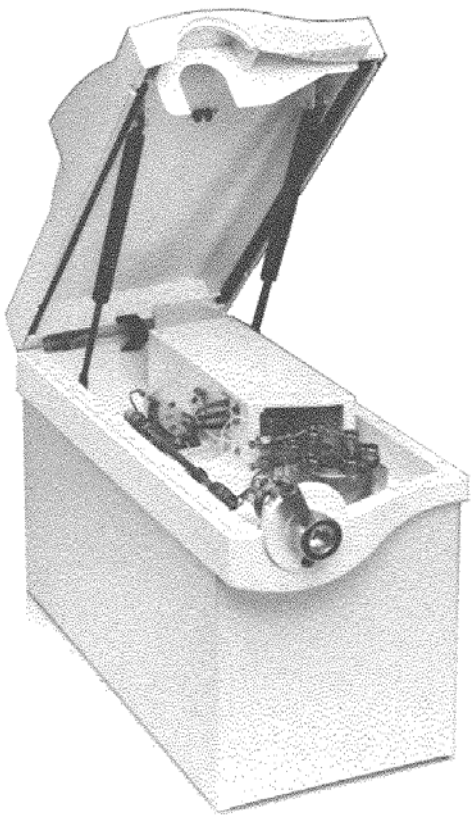
Never switch ON the flow cell when:
- the cell cable is not correctly connected
- the cell is only partly (or not at all) filled with buffer
- the cell is wet outside, particularly the part between the auxiliary and working electrode connection
because substantial damage to the working electrode or electronics may occur.

16. Before switching ON the flow cell, make sure that the buffer is containing electrolyte (buffer ions). If the cell is switched ON with only water or methanol in the mobile phase, a stable baseline will not be obtained. Also make sure that no air bubbles are trapped in the flow cell.
17. The outlet tubing from the flow cell should lead to a reservoir that is at a higher level than the flow cell. This ensures a small back pressure which prevents air-bubble entrapment. The outlet tubing should be *under* the liquid level, to avoid noise by dripping.
18. Set the cell potential, switch ON the flow cell (see page 19) and allow the system to stabilise for approximately 30 min.
19. Connect the data system to the integrator or recorder output (see page 29).

Your system is now ready for use.

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The DECADE has been developed for continuous operation. For maximum stability it is advised to leave the system ON continuously. If preferred, the flow cell may be switched OFF at night.



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C H A P T E R 3

The DECADE controller

Introduction

The DECADE has been designed for maximum functionality and ease of use. The control of ECD parameters is such that without reading this chapter, it should be possible to operate the detector. This chapter is intended as a reference guide in case questions arise during operation.
The information shown in the numerous screens is presented in alphabetical order. For each item an explanation is given, together with the item's nature and the screen(s) of appearance. The nature of an item can be:

- Control: parameters with a cursor box ('☐') can be attained via cursor buttons and changed by the '+' and '-' button.
- Status: without a cursor box a parameter reflects the current status.
- Functions: parameters in CAPITALS are commands accessible via function buttons.

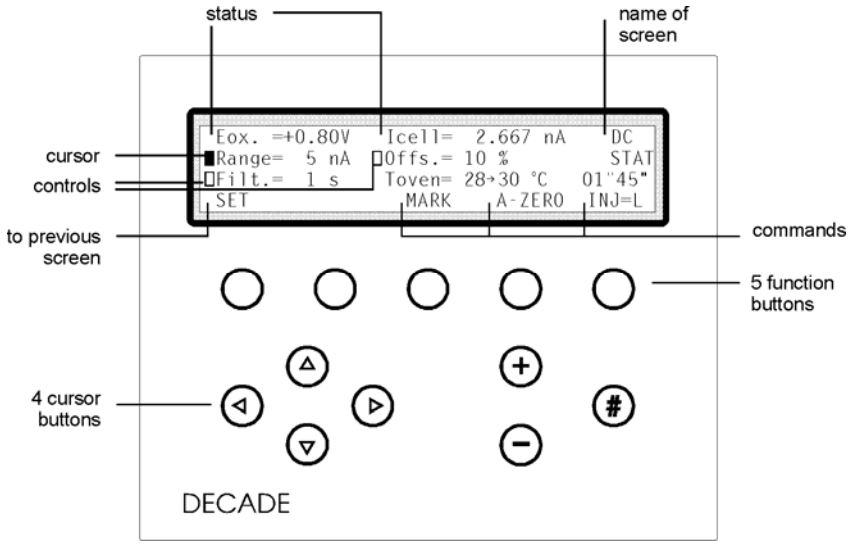
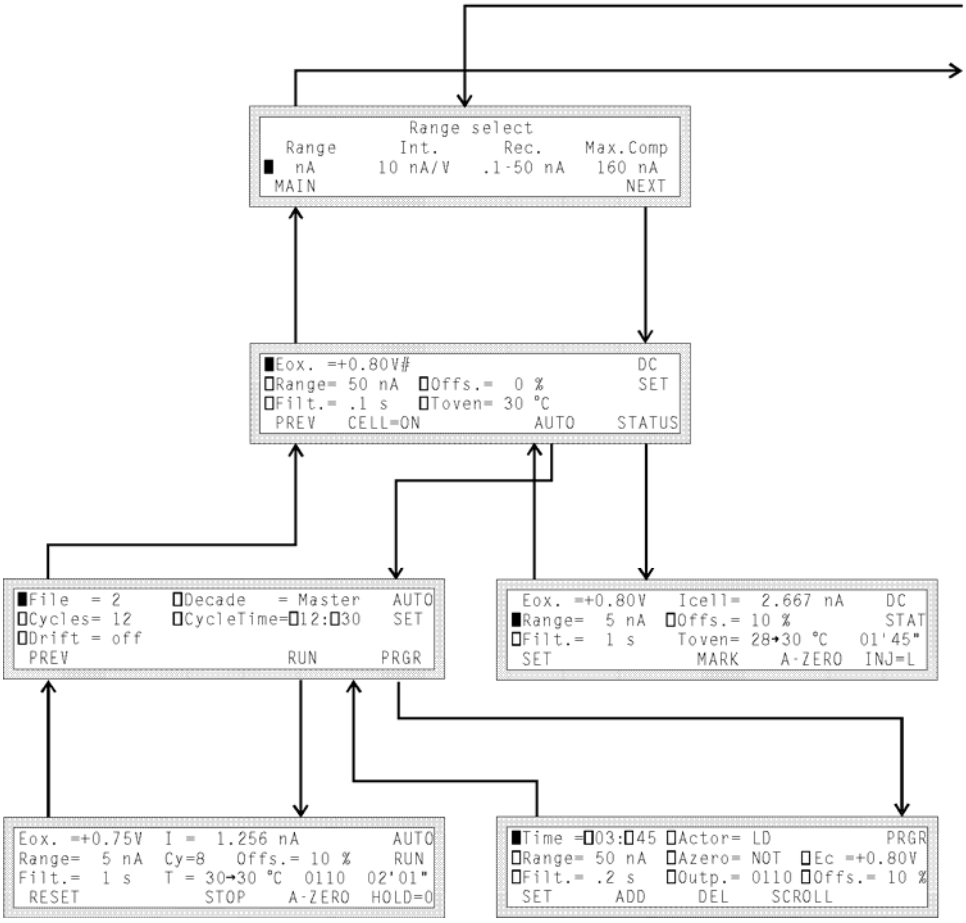


Fig. 3. DECADE keyboard. The cursor is on 'Range' which allows changes using the '-' and '+' button.

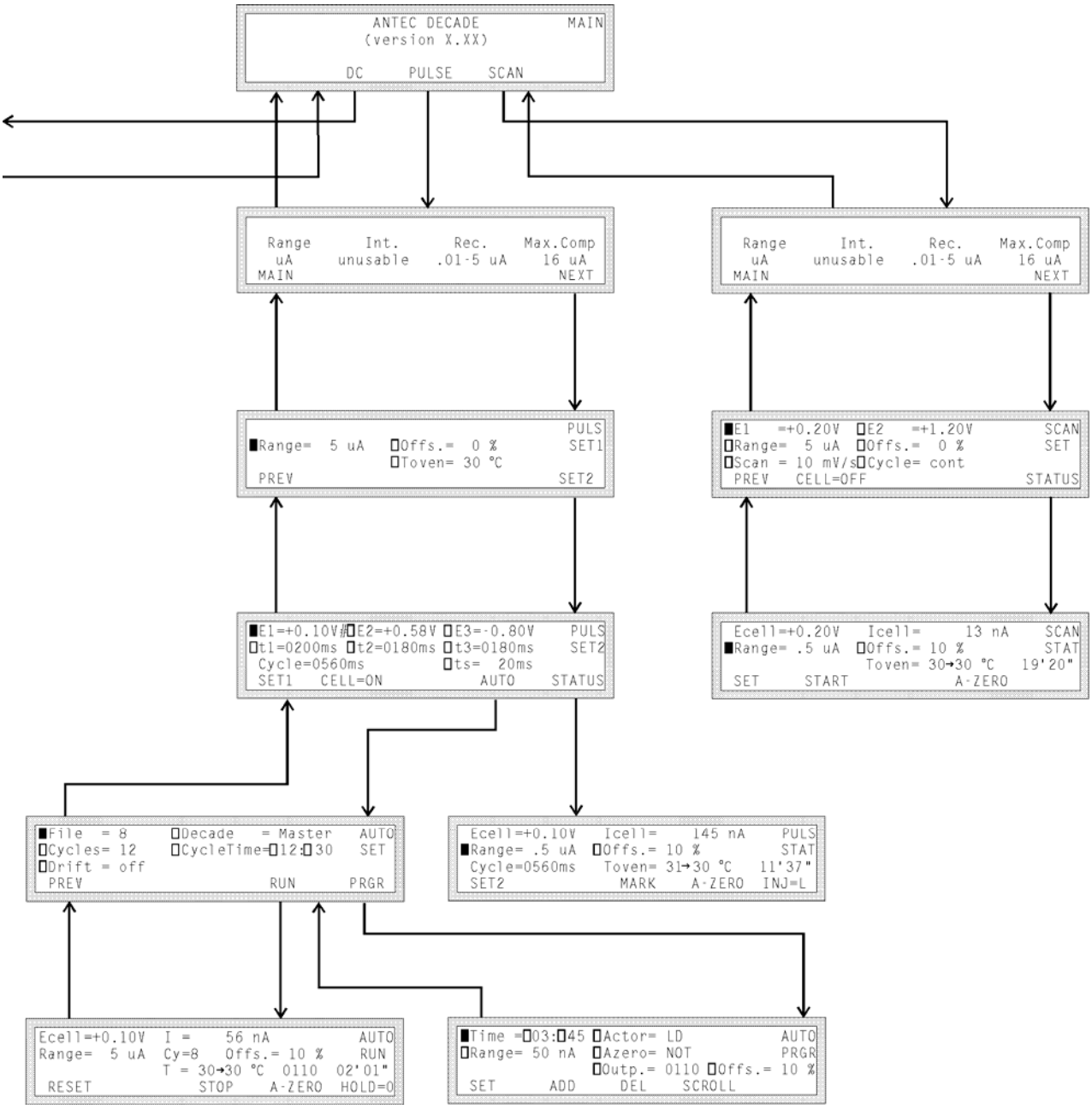
The ENTER button ('#') is only used to accept changes in cell potential. In the top right corner of each screen the name of the present screen is displayed. If available, the most left function button displays a previous screen, and the most right one the next screen.

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Overview of all DECADE screens



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Parameters

Actor

(AUTO) PRGR	control

Controls the electrically actuated injector, during execution of a time file. Forces this valve to load (‘LD’) or inject (‘INJ’) (see page 37).

ADD

(AUTO) PRGR	function

Adds the current data line to the time file. Confirmation is asked for if an existing time is overwritten. As time 00’ 00” always exists, changing this time results in an overwrite warning (see page 37).

AUTO

DC SET, PULS SET2	function

Enters the auto mode (‘AUTO SET’ screen) for editing and running a time file.

A-ZERO

DC STAT, AUTO RUN, PULS STAT, SCAN STAT	function

Sets the recorder and integrator output voltage to 0 V, or to the offset voltage (see page 29).

Azero

(AUTO) PRGR	control

Controls the auto zero, which can be programmed in a time file (see page 37).

CELL=ON/OFF

DC SET, PULS SET2, SCAN SET	function

Toggles between cell ‘ON’ and ‘OFF’. If the cell is switched ON in the pulse mode only E1 is applied, the pulsation starts when PULS STAT screen is entered (see page 51). In the DC or scan mode, Eox./Ered. or Ecell is applied. Software version 3.00 and higher, pulse mode: pulsation occurs as long as the cell is on, irrespective which screen is selected.

Cy

AUTO RUN	status

Displays the cycle counter. In the master mode, if a time file has to be executed more than once (‘Cycles’>1), this is the number of times a time file is started (see page 37).

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Cycle

PULS SET2, PULS STAT	status

Displays the total duration of one pulse (t1 + t2 + t3). As from each cycle only one data point is sent to the recorder output, this duration determines the frequency of the recorder output (see page 51).

Cycle

SCAN SET	control

Controls the nature of the cycle: half, full and continuous. ‘Half’ means that the cell potential runs from E1 to E2 and stops at E2. ‘Full’ means that the cell potential runs from E1 to E2, and back to E1, and then stops. ‘Cont’ means that the cell potential runs from E1 to E2 and back to E1 continuously (see page 59).

Cycles

AUTO SET	control (master)

Controls the number of times a time file has to be repeated. If the DECADE is master this number can be 1 - 99 or continuous. If the DECADE is slave the number of cycles is 1 (see page 37).

CycleTime

AUTO SET	control

Controls the duration of a time file (max. 99’ 59”). When this time is reached the execution of the time file stops. If programmed, the next run is started (see page 37).

Decade

AUTO SET	control

Controls the status of the system, toggles between ‘Master’ and ‘Slave’. If ‘Master’ other parts of the HPLC system can be controlled by the DECADE (see page 37).

DEL

(AUTO) PRGR	function

Deletes the current data line from the time file. Confirmation is asked for. Time 00’ 00” can not be deleted (see page 37).

Drift

AUTO SET	control

Controls the driftmonitor in the auto mode, which intermits the execution of a

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time file when the baseline is drifting. The available drift monitor settings depend on the range selected at time 00:00 in the time file (see page 37). Can be set between 0.1 pA/min and 10 nA/min.

E1, E2, E3

PULS SET2	control

Controls the cell potential settings of the pulse. A change in E1 has to be confirmed with the '#'-button (see page 51).

Ec

(AUTO) PRGR (DC only)	control

Controls the cell potential in a time file (see page 37).

Ecell

PULS STAT, AUTO RUN (Pulse only), SCAN STAT	status

Displays the cell potential during 't1' in the pulse mode (see page 51). Displays the actual cell potential in the scan mode (see page 59).

Eox. or Ered.

DC SET	control

Controls the oxidative or reductive cell potential. Can only be set or changed after confirmation with the '#' button. Passing the 0.00 V value automatically changes the readout from 'ox' to 'red' and in reverse.

Eox. or Ered.

DC STAT, AUTO RUN (DC only)	status

Displays the oxidative or reductive cell potential.

File

AUTO SET	control

Controls the number of the time file to be edited or activated. In the DC mode file numbers 1 - 5 are available, in the pulse mode file numbers 6 - 9 can be selected. The time files remain stored in RAM, also after switching off the DECADE (see page 37).

Filt.

DC SET, DC STAT, (AUTO) PRGR (DC ONLY)	control

Controls the rise time filter settings for the recorder output, which are: 0.1, 0.2, 0.5, 1, 2 or 5 seconds (see page 29).

HOLD=0/1

AUTO RUN, SCAN STAT	function

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Interrupts the execution of a time file or scan. Toggles between 1 and 0. Pressing the hold button again continues the time file or scan were it was stopped (see page 37).

Icell

DC STAT, PULS STAT, SCAN STAT	status

Displays the true, non-compensated cell current, i.e. unaffected by zero or offset. The cell current is one of the most important parameters in ECD.

INJ=I/L

DC STAT, PULS STAT	function/status

Displays or switches the position of the injection valve, toggles between inject (I) and load (L). If a manual injector with position sensor is applied, it echoes the position of the injector. If an electrically actuated injector is used (optional) it is possible to switch the injector with this function button.

MAIN

RANGE screen	function

Returns to the 'MAIN' screen.

MARK

DC STAT, PULS STAT	function

Triggers a marker signal on the recorder output.

NEXT

RANGE screen	function

Enters the next (xx SET) screen

Offs.

DC SET, DC STAT, (AUTO) PRGR, PULS SET1, PULS STAT, SCAN SET, SCAN STAT	control

Controls the percentage offset, can be set between -50 and 50%. The offset % on *both* outputs relates to the recorder range setting (see page 29).

Offs.

AUTO RUN	status

Displays the percentage offset during execution of a time file.

Outp.

(AUTO) PRGR	control

Controls the four output functions in the auto mode. The notation of the output

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'0000' corresponds to the four output controls at the rear panel of the controller (from left to right: relay 2, relay 1, aux 2, aux 1). The position indicated on rear panel refers to the '0000' setting (see page 37).

PREV

DC SET, AUTO SET, PULS SET1, SCAN SET	function

Returns to previous screen.

PRGR

AUTO SET	function

Enters the (AUTO) PRGR screen

Range

DC SET, DC STAT, (AUTO) PRGR, PULS SET1, PULS STAT, SCAN SET, SCAN STAT	control

Controls the recorder range setting, varying from 10 pA to 5 µA full scale, divided in 1, 2 and 5 steps. In the DC mode, selectable recorder ranges depend on the pre-selection of the integration range in the 'Range select' screen. In the pulse and scan mode only the µA range can be used (see page 29).

RESET

AUTO RUN	function

Aborts the time file and returns to the 'AUTO SET' screen. The cycle counter ('Cy') is reset to 1 (see page 37).
Software version 3.00 and higher: the outputs Aux 1 and 2, and Relays 1 and 2 are deactivated (status: 0000).

RUN

AUTO SET	function

Starts the execution of a time file (master/slave). If the DECADE is slave, the system waits for the 'START' input trigger to start the next run (see page 37).
Software 3.00 and higher: In the slave mode the RUN command initialises the AUTO RUN screen, the system waits for the 'START' input trigger to start a time file.

Scan

SCAN SET	control

Controls the scan speed, can be set from 1 - 50 mV/s in 1, 2, 5 steps (see page 59).

SCROLL

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(AUTO) PRGR	function

Scrolls through a time file (see page 37).

SET

DC STAT, AUTO RUN, PULS STAT, SCAN STAT)	function

Returns to the previous (xx SET) screen.

SET1, SET2

PULS SET2, PULS STAT	function

Returns to PULSE SET screen 1 or 2

START

AUTO RUN, SCAN STAT	function

In the DC and pulse mode (master if cycles >1): toggles between STOP and START to control the execution of a time file.
In the scan mode START starts a scan (see page 59).

STATUS

DC SET, PULS SET2, SCAN SET	function

Enters the next (xx STAT) screen.

STOP

AUTO RUN, SCAN STAT	function

In the scan mode, STOP aborts the scan and resets the cell potential to E1.
In the DC and pulse mode (master, cycles >1): toggles between STOP and START to control the execution of a time file. Pressing ‘STOP’ aborts this run, cycle counter (Cy) is not reset. By pressing the same button (‘START’) again, the next cycle is started (Cy = Cy +1) (see page 37).
Software version 3.00 and higher: STOP also deactivates the outputs Aux 1 and 2, and Relays 1 and 2 (status: 0000). This toggle is also active in the slave mode.

t1, t2

PULS SET2	control

Controls the duration of a corresponding step in the pulse mode. The time can be set between 100 and 2000 ms in 10 ms increments (see page 51).

t3

PULS SET2	control

Controls the duration of a corresponding step in the pulse mode. The time can be set between 0 (=off) and 2000 ms in 10 ms increments (see page 51).

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Time

(AUTO) PRGR	control

Controls the time to execute a data line in a time file, can be set with one second resolution. Maximum time is 999 min and 59 s. The time to stop the execution of a time file must be programmed by the CycleTime in the AUTO SET screen (see page 37).

Toven

DC STAT, PULS STAT	status

Displays the actual (left value) and the pre-set oven temperature (right value, set in 'xxSET').

Toven

DC SET, PULS SET1	control

Controls the temperature of the oven. Range: off, 15 – 60^{o}C, selectable in 1^{o}C steps. The oven is stable from 5 ^{o}C above ambient.

ts

PULS SET2	control

Controls the duration of the sampling time in the pulse mode. The time can be set between 20 and 100 ms in 20 ms increments (see page 51).

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C H A P T E R 4

Data acquisition

Introduction

One of the characteristics of electrochemical detection is its tremendous dynamic range. In amperometric detection peak heights may vary from micro-amperes down to the pico-ampere range. The DECADE covers such a wide range from 5 µA down to 10 pA full scale, without being limited by electronic noise.
The DECADE is equipped with two output connections for data acquisition, the recorder ('REC') and the integrator output ('INT'). The *integrator* output has been designed to supply a non-manipulated, analog signal from the I/E converter which is as close as practically possible to the working electrode (WE). The *recorder* signal is manipulated by the CPU of the DECADE. The details on data acquisition in the various ranges will be discussed for both output channels.

Internal organisation

At the working electrode (WE) in the electrochemical flow cell the electron transfer takes place due to an oxidation or reduction reaction. The resulting electrical current is amplified by the current-potential (I/E) converter (Fig. 4).

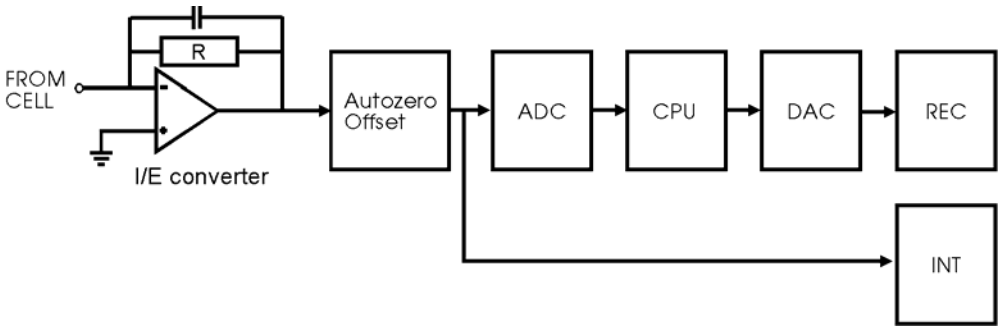


Fig. 4. DECADE signal processing from electrochemical flow cell to REC and INT output. R is a selectable resistor of 100, 10 or 0.1 MOhm corresponding to the pA, nA and µA range respectively.

In the I/E converter a range of 10, 100 or 10000 nA full scale (FS) can be selected, which corresponds to the so-called pA, nA and the µA range,

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respectively. These are the three DECADE integrator ranges that can be set in the 'Range select' screen.

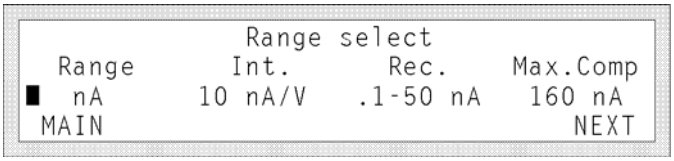


Fig. 5. The DECADE 'Range select' screen. The 10 nA/V corresponds to 100 nA full scale on the integrator output (=10V).

The integrator range selection is the first step in the signal pathway (Fig. 4). It affects both the integrator and the recorder output and has several important consequences for data acquisition (Table I).

Table I. Parameters affected by the integrator range setting.

parameter	output	comment
signal output	INT/REC	gain increases with more sensitive range
available REC ranges	REC	see Table IV
max. compensation	REC/INT	decreases with more sensitive range
I-cell display	screen	resolution increases with more sensitive range

The next step is the auto zero and offset compensation. Then the signal is further manipulated for the recorder output or sent to the integrator output without manipulation.

Integrator output

The integrator output has been designed to supply a clean, purely analog signal from the I/E converter. Except for the auto zero and offset compensation, no further manipulation of the signal occurs. If required, manipulation of a chromatogram (i.e. noise filtering) can be done by integration software. Thus a clean chromatogram will always be available for re-integration.

Table II. Integrator range and maximum zero compensation.

range	current, full scale		max. zero comp.		max. current	
µA	10	µA	16	µA	26	µA
nA	100	nA	160	nA	260	nA
pA	10	nA	16	nA	26	nA

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When data are obtained from the integrator output, it is obvious that the pA range allows the highest sensitivity. Each range has a different maximum zero compensation (Table II). For example, in the nA range a current of 100 nA full scale can be managed. Together with a zero compensation of 160 nA, the maximum current that can be handled is 260 nA.
Due to the nature of data generation the integrator output is unusable in the pulse and scan mode.

Recorder output

Several steps occur before sending the signal to the recorder output. After analog-to-digital conversion (ADC), a number of recorder range settings can be selected in the central processing unit (CPU). This selection occurs in the 'DC SET' or 'DC STAT' screen.

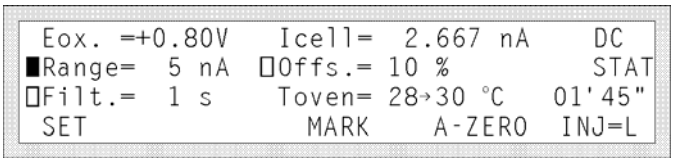


Fig. 6. Selection of the recorder output range in the 'DC SET' or 'DC STAT' screen.

After digital to analog conversion (DAC) the signal is sent to the REC output. The recorder range selection has several consequences for the data acquisition (Table III).

Table III. Parameters affected by the recorder range setting.

parameter	output	comment
signal output	REC	gain increases with more sensitive range
offset	REC/INT	see Table V
marker	REC	10% of full scale REC output

In the DC mode the signal can be smoothened by a rise time filter. In addition, more complex signal manipulation, needed for pulse and scan is possible. Although the name of this output suggests otherwise, it is often used in connection with an integrator.
The recorder output ranges between +1 and -1 V with 12 bits resolution, which means that the output resolution is 0.5 mV (2 V/2^{12}). The best way to exploit this output resolution is to set the range as sensitive as possible.

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There is much overlap in the recorder range settings offering flexibility as to maximum zero compensation (Table IV). For example, if a chromatogram is acquired at 10 nA, the nA or µA range can be selected (Table IV). With a high background current the µA is chosen (max. 16 µA compensation), at a low background the nA range is preferred (max. 160 nA compensation).
The resolution of the zero compensation is 16 bits per selected integrator range. At a high maximum compensation, the compensation circuit uses larger steps to reach a 0 V output, hence the resolution of the zero compensation decreases. Therefore, a compromise is made between maximum zero compensation and resolution. To maintain a high auto zero resolution with accurate zero settings, the maximum compensation is decreased with the integrator range.

Table IV. Recorder ranges and maximum zero compensation.

Range			
pA	nA	µA	
10			
20			
50			
100	0.1		
200	0.2		
500	0.5		range
1000	1.0		overlap
2000	2.0		
5000	5.0		
	10.0	0.01	
	20.0	0.02	
	50.0	0.05	
		0.10	
		0.20	
		0.50	
		1.00	
		2.00	
		5.00	

maximum zero compensation (nA)		
16	160	16000

In certain cases, when a small peak is ‘blown up’ with integration software, a typical stepwise (0.5 mV = 1 bit) peak profile is seen (Fig. 7). In that case the recorder output resolution is not sufficient, and the detector should be set at a more sensitive recorder range.

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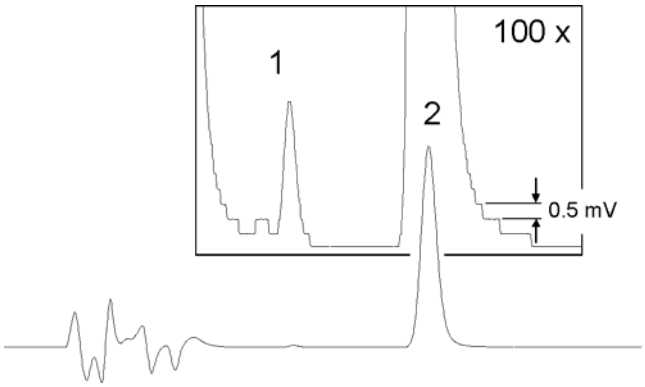


Fig. 7. A 'stepwise' pattern after magnification of a chromatogram.

This phenomenon will not occur at the *integrator* output because this output is purely analog and therefore, in principle, with infinite resolution.

Integrator vs. recorder output

In the pulse and the scan mode, only the recorder output is suitable for data acquisition. In the DC mode both outputs can be used, in that case a choice has to be made.
A specific advantage of the integrator output is the large dynamic range and infinite resolution. It is an analog output which means that the resolution is only limited by the integrator that is used. In most integrators this is approximately 1 µV. The 12 bits recorder output has a maximum output resolution of 500 µV.
Often, the *recorder* output is chosen for data acquisition thus offering the possibility of smoothening by means of rise time filters (Fig. 8). The advantage of having a clean signal from the *integrator* output is not always recognised, or the possibility for smoothening data is not implemented in the integration software.

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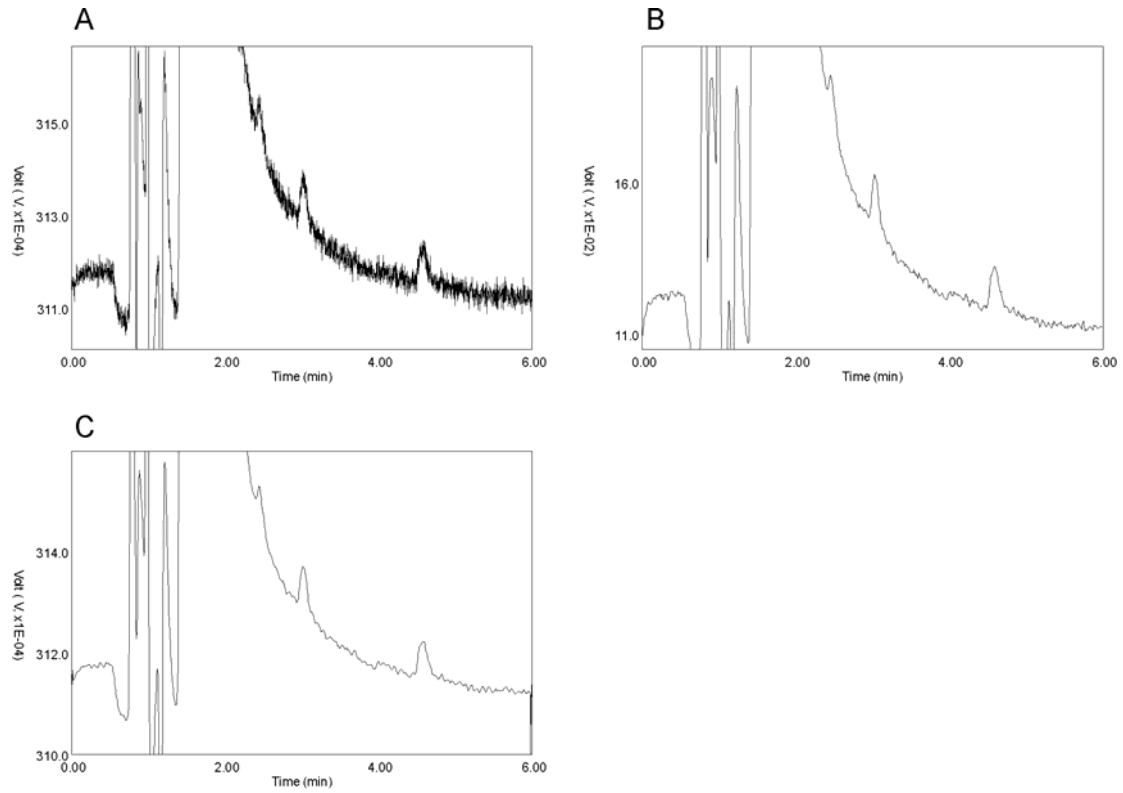


Fig. 8. The clean signal from the integrator output (A) is smoothened by integrator software using a running average filtering (C). This results in a similar chromatogram as obtained from the recorder output using a rise time filter of 1 s (B).

Offset

A maximum offset of +50% and - 50% in 10% steps can be achieved, active on both the integrator and the recorder output. On the recorder output the offset is given as the percentage of the recorder range setting. For example, a 20% offset at 5.0 nA full scale setting will give a 1.0 nA offset. This is a 200 mV offset when the maximum recorder output is 1.0 Volt.
For the integrator output the situation is more complicated because the offset percentage relates to the recorder range setting. The integrator offset (in mV) is given in Table V for a 10 V integrator output.

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Table V. Effect of recorder range on the offset of the 10 V integrator output.

Range			Offset				
pA	nA	µA	10%	20%	30%	40%	50%
10	0.1	0.01	1	2	3	4	5
20	0.2	0.02	2	4	6	8	10
50	0.5	0.05	5	10	15	20	25
100	1.0	0.10	10	20	30	40	50
200	2.0	0.20	20	40	60	80	100
500	5.0	0.50	50	100	150	200	250
1000	10.0	1.00	100	200	300	400	500
2000	20.0	2.00	200	400	600	800	1000
5000	50.0	5.00	500	1000	1500	2000	2500
1	10	1000	Integrator output (nA/V)				

Although this may seem a complex way of compensating the background current, in practise it gives the best possible flexibility and optimum resolution of the 16 bits compensation in each operating range. By simply changing the percentage offset or the recorder range, almost any offset compensation can be set between 1 and 2500 mV on the integrator output.

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C H A P T E R 5

AUTO mode and time files

Introduction

The AUTO mode of the DECADE enables a time-based, automated and full parametric control of electrochemical detection (ECD). This is particularly useful when during a run or between runs settings have to be changed such as the sensitivity, auto zero or control of external equipment (i.e. trigger to start integration software etc.). A Time file contains a series of data lines in which the settings of the DECADE can be changed with 1 second time resolution. A time file is executed only in the AUTO mode.

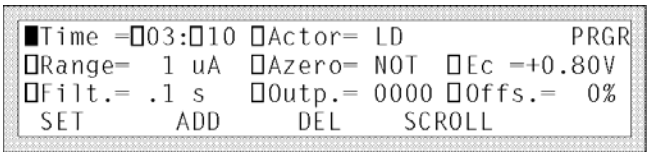


Fig. 9. Programming a time file using the '(AUTO) PRGR' screen.

The file is made using the '(AUTO) PRGR' screen on the DECADE (Fig. 9) or, when the DECADE is equipped with the RS232 option, by using the time file editor in 'DECADE Dialogue for Windows'. Programmable parameters comprise cell potential, range, auto zero, offset, rise time, electrically actuated injector (if present) and the DECADE output contacts to control the status of external equipment.

Range programming

In certain analyses large differences in analyte concentration (and peak height) occur. If the analyte with the highest concentration is on scale, another analyte may be recorded at a low output resolution. When the small peak is magnified with integration software a typical stepwise peak profile is seen (Fig. 7). In such a case a chromatogram can be obtained using a time file to switch the sensitivity of the controller to another range during the run (Fig. 10). In Table VI an example is given of a time file for sensitivity switching between 2 peaks. In this example the system is equipped with an electric valve, which means that programming the switching of the valve is possible (Fig. 9, 'Actor'). At time 00:00 the valve is switched to 'inject', the trigger to start the integrator is connected to the 'INJECT MARKER'. At time 00:10 the valve is

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switched back to ‘load’ to enable continuous refilling of the injection loop. At time 1:26 the sensitivity is increased by a factor of 100 from 50 nA/V to 0.5 nA/V, together with an auto zero command. After passage of the small peak, the range is switched back to 50 nA/V. At t=3:05 the end of the chromatographic run is programmed in the ‘AUTO SET’ screen, using the ‘CycleTime’ parameter.
If the *integrator* range is switched between µA, nA or pA, simultaneously with an auto zero command this may result in an inappropriate baseline setting. Setting the range first is recommended in such case.

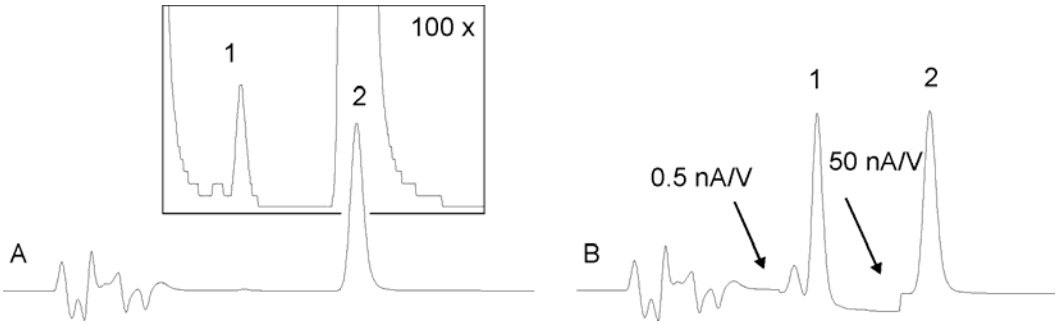


Fig. 10. Example of range programming to maintain the recorder resolution. In chromatogram (A) a range setting of 50 nA/V is used, in chromatogram (B) the output range is automatically switched during the run resulting in a considerable improvement of the output resolution of peak 1.

Table VI. time file used for output resolution programming.

time	int. range	rec. range	rise time	valve	auto zero	offset	output	E cell
00:00	nA	50 nA	1 s	inject	set	00%	0000	0.80 V
00:10	nA	50 nA	1 s	load	not	00%	0000	0.80 V
01:26	nA	0.5 nA	1 s	load	set	00%	0000	0.80 V
01:55	nA	50 nA	1 s	load	set	00%	0000	0.80 V
03:05	Cycle Time (end of run)							

Drift monitor

The AUTO mode of the DECADE is equipped with a drift monitor, which puts the detector on ‘hold’ when the baseline is drifting. The drift monitor is only active at the beginning of a time file, both in the master and slave mode. After starting a time file the baseline is monitored during one minute and the ‘wait..’ message is displayed. When the baseline is not within the pre-set limit, the

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drift monitor remains active. When the drifting baseline is within the pre-set limit the drift monitor is deactivated, and the run continues.
The drift monitor is useful when, for example, after each run a cleaning pulse is programmed to reduce fouling of the working electrode. A cleaning pulse consists of e.g. a 10 seconds potential step at -1V.

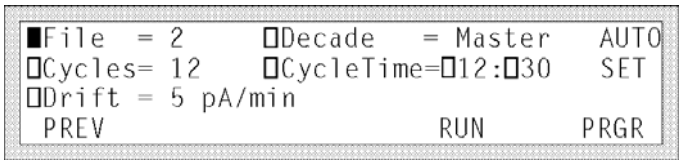


Fig. 11. Programming the drift monitor in the 'AUTO SET' screen.

After this cleaning pulse it takes some time to get a stable baseline again. The drift monitor can be used to ensure a user-definable stable baseline before the start of the next run.
However, the duration of each run will always be at least one minute longer. In this minute the drift in the baseline is monitored.

Step by step example (DECADE = Master)

In this step-by-step guide the example from Table VI will be programmed. In this example the system consists of an HPLC system, a DECADE with an electric valve, an integrator, and an on-line microdialysis set-up.
The DECADE is *master* which means that the DECADE starts a run, and controls the number of automated runs.

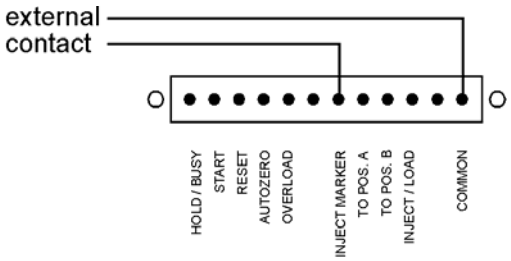


Fig. 12. External contact to start the integrator by switching the electric valve.

Hardware connections:

1. Connect the hardware trigger of the integrator to the 'Inject marker' on the rear panel of the DECADE as indicated in (Fig. 12).

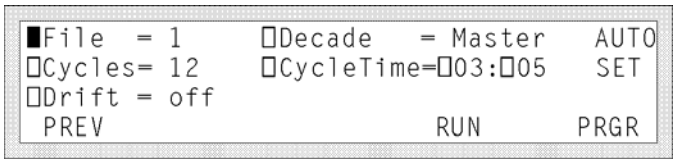
2. Connect the dialysis tubing to the automated injection valve.

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3. In this example the integrator is connected to the REC output at the rear panel of the DECADE.
4. Prepare the LC-EC system for analysis.

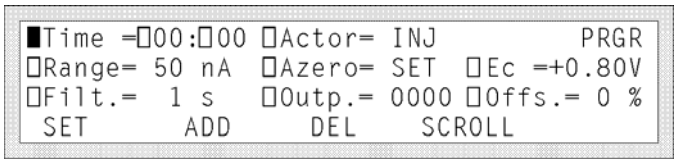
Programming the AUTO mode:

5. From the DECADE 'Main' screen, choose DC, and in the 'Range select' choose NEXT. In the 'DC SET' screen, set the temperature at the desired value (or choose 'off') and choose AUTO. You are now in the 'AUTO SET' screen in the AUTO mode.
6. In the 'AUTO SET' screen select the time file that you want to edit with 'File'. When it is your first file, select nr. 1. There are 5 time files available in the DC mode (and 4 in the Pulse mode). The number of times you want to repeat this time file is set with 'Cycles'. Because the DECADE will give the integrator and switching valve the starting signals, it is set at 'Master'. The duration of one run is set with 'CycleTime'. A step programmed at a time similar to or larger than the cycle time (i.e. t ≥ 3:05), will not be executed!



Before the drift monitor can be set (if required), the first line in the time file has to be programmed. The drift monitor is linked to the range setting of the first line in the time file (at t = 0:00).

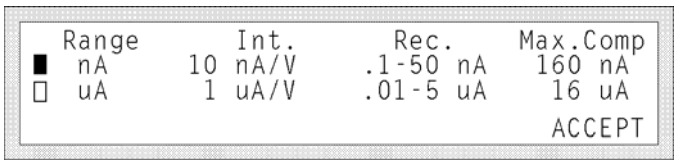
7. Press 'PRGR' to go into the edit mode of the time file. The 'PRGR' screen appears:



When all settings are correct, this line in the time file can be saved by choosing 'ADD'. When the time already exists, the question 'Do you want to overwrite time?' appears. As each new time file contains a t = 0:00, this question will always appear after editing this line.
In our example, after editing t=0:00 an additional screen will appear, asking you in which range you want to operate at the 50 nA/V setting. You may choose between the nA and the µA range. See 'Chpt. CHAPTER 4

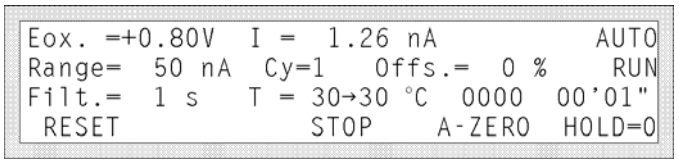
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Data acquisition', page 29, for specific details on differences between both modes.
In our example the nA range is chosen, and confirmed with 'ACCEPT'. The message 'New time is saved' is displayed.

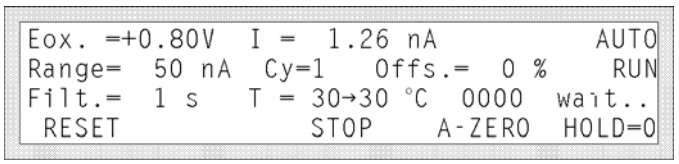


Choosing 'SCROLL' allows you to scroll through your time file. With 'DEL' an existing line in your time file can be deleted (after confirmation).

8. Step 7 is repeated for each line in the time file. When a line is edited and saved, without changing the time, the original line is overwritten (after confirmation). When the time of an existing line is changed and saved, it is saved as a new line without overwriting the original line. Each time file can contain a maximum of 20 data lines.
9. The last line *in the time file* is at t = 1:55. By choosing 'SET' you may return to the 'AUTO SET' screen.
10. In the 'AUTO SET' screen 'CycleTime' is set at 3:05. If required, the drift monitor can be programmed. In the nA range a choice can be made between 'off', 1 pA/min - 0.1 nA/min in 1, 2, 5 steps.
11. Your system is now ready for automated operation. A time file is started by choosing 'RUN' in the 'AUTO SET' screen. The 'AUTO RUN' screen will appear.



This is the status screen of the AUTO mode. Current settings are displayed, including the actual cycle number ('Cy') that is executed.
The auto zero command ('A-ZERO') is always accessible during operation in the AUTO mode.
When the drift monitor is programmed and the drift is beyond the pre-set value, the 'wait...' message is displayed in stead of the time.



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Important note when using the drift monitor:

If an injection or an external event is programmed at t = 0:00, these events are executed immediately while the drift monitor is putting the system on hold. This can be prevented by programming these events at t = 0:01.
Furthermore, the duration of each run will always be at least one minute longer. In this minute the drift in the baseline is monitored.

Interrupting a time file:

12. When 'HOLD' is chosen, the timer is stopped, the message 'HOLD=1' appears in the corner of the 'AUTO RUN' screen. After pressing 'HOLD' again, the timer continues ('HOLD=0').
13. When 'STOP' is chosen, the execution of the time file is interrupted. Starting the next run at t = 0:00 is possible by choosing 'START' (if cycles >1). The cycle counter ('Cy') is increased.
    Software version 3.00 and higher: STOP also deactivates the outputs Aux 1 and 2, and Relays 1 and 2 (status: 0000).
14. When 'RESET' is chosen, the execution of the time file is interrupted and the 'AUTO SET' screen appears. The cycle counter is reset to 0 ('Cy = 0').
    Software version 3.00 and higher: RESET also deactivates the outputs Aux 1 and 2, and Relays 1 and 2 (status: 0000).

Note: In the *master* mode the HOLD, STOP, START and RESET functions are accessible only from the keyboard. In the *slave* mode these inputs are accessible via the rear panel of the DECADE. Accessible keyboard functions in the *slave* mode are: RUN, STOP, RESET and A-ZERO.

Step by step example (DECADE = Slave)

For the same example as given above, a time file will be programmed. The system consists of an HPLC system with autosampler, a DECADE and an integrator.
The DECADE is *slave* which means that a run is started by an external contact (i.e. from autosampler). Also the number of automated runs is controlled externally.

Hardware connections:

1. Connect a hardware trigger of the autosampler to 'START' on the rear panel of the DECADE as indicated in Fig. 13. A contact closure is

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required between ‘COMMON’ and ‘START’ to start a time file. Consult your autosampler manual for details on connecting the external contact to a relay.

2. Connect relay 1 to ‘RESET’ and common as shown in Fig. 13A. From DECADE software version 3.00 and higher: a RESET is not required between runs, this input has been inactivated (Fig. 13B).
3. Connect your integrator to the REC output at the rear panel of the DECADE.

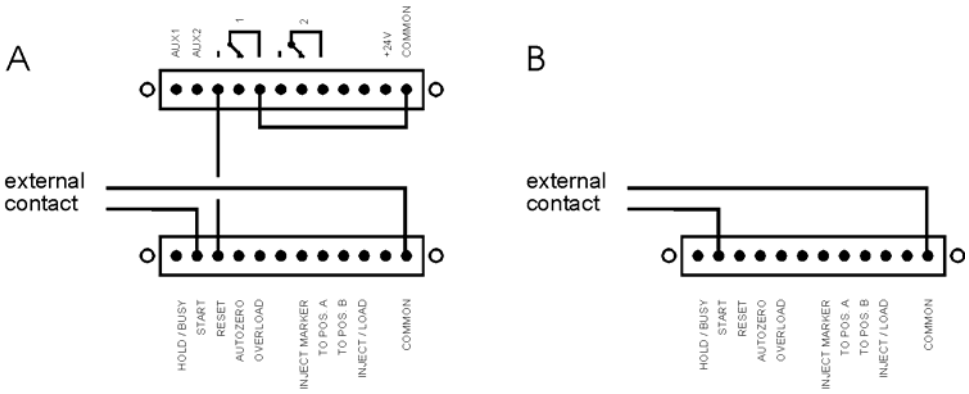


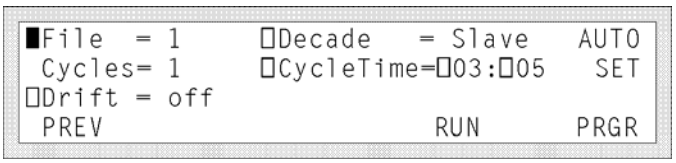
Fig. 13. Input contacts needed for external control of the DECADE (slave mode) A: until DECADE software version 3.00 and B: from version 3.00 and higher .

4. Prepare the LC-EC system for analysis.

Programming the AUTO mode:

The programming of the time file is done in the same way as described for the master mode. In the following steps the differences with the master mode are given.

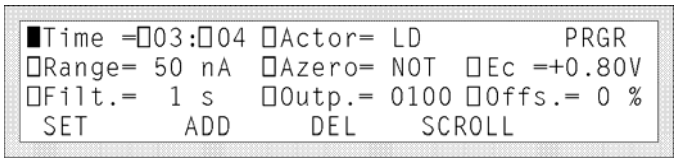
5. In the ‘AUTO SET’ screen choose ‘Decade = Slave’. The number of cycles is controlled by the autosampler, in the DECADE ‘Cy’ is automatically set at 1 and can not be changed.



6. Choose ‘PRGR’ to go in the edit mode of the time file and continue programming the time file as described above. **For DECADE software version 3.00 and higher a RESET command is no longer required: continue with the next step.**
   Up to software 3.00: for continuous operation in the AUTO mode a

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'RESET' of the DECADE is required. This is necessary to be ready for the next run. In our example the following line has to be programmed:



This activates the 'relay1' output ('0100') for 1 second, just before ending the time file. This relay has been connected to the 'RESET' input (Fig. 13A). Note that the 'RESET' function overrules 'CycleTime'. Immediately after this function, the execution of the time file is interrupted, whether the cycle time is met or not. It is therefore recommended to program the 'RESET' 1 second before the cycle time (never at a time ≥ 'CycleTime').

7. By pressing RUN the system is ready for automated operation. The time file is started by an external contact closure from the autosampler (Fig. 13). The duration of this contact closure must be at least 100 ms. Each time a run is started the 'AUTO RUN' screen appears. After the 'RESET' command (via relay1), the 'AUTO SET' screen is displayed.

The auto zero command ('A-ZERO') is accessible during operation in the AUTO mode as long as 'I-Cell' is displayed.
Accessible keyboard commands in the *slave* mode are: RUN, STOP, RESET and A-ZERO. This means that you can also start (and stop) the time file from the keyboard.

Interrupting a time file:

8. In the slave mode the DECADE does not respond to a 'HOLD' command from the keyboard. You can stop the timer by making an external contact closure between 'HOLD' and 'COMMON'. As soon as the contact closure is released, the time file continues.

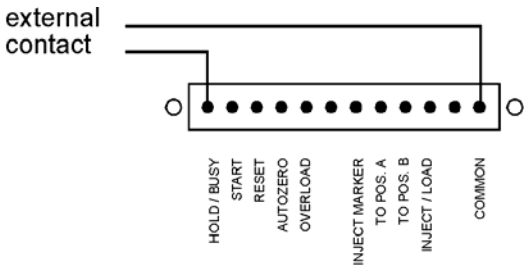


Fig. 14. External contact to give a 'HOLD' command during execution of a time file in the slave mode.

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9. If ‘STOP’ is chosen from the keyboard, the execution of the time file is interrupted. To start again, an external ‘RESET’ and ‘START’ (or ‘RUN’ from keyboard) command is required.
   Software version 3.00 and higher: the STOP command toggles between STOP and START to control the execution of a time file. STOP also deactivates the outputs Aux 1 and 2, and Relays 1 and 2 (status: 0000).
10. When ‘RESET’ is chosen from the keyboard, the execution of the time file is interrupted and the ‘AUTO SET’ screen appears.
    Software version 3.00 and higher: RESET also deactivates the outputs Aux 1 and 2, and Relays 1 and 2 (status: 0000).

Note: In the *master* mode the HOLD, STOP, START and RESET commands are accessible only from the keyboard. In the *slave* mode these inputs are accessible via the rear panel of the DECADE. Accessible keyboard commands in the *slave* mode are: RUN, STOP, RESET and A-ZERO.

Other events

Inject/load and inject marker

A frequently used function is the inject/load (or inject marker) as a trigger for starting the integration software. This trigger is always accessible, not only in the AUTO mode.

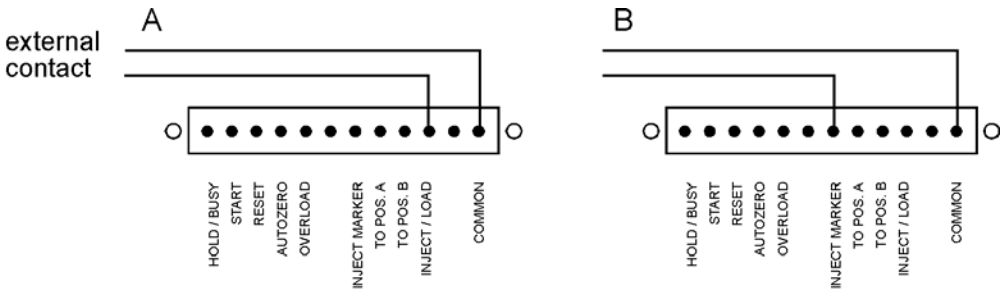


Fig. 15. Output contact needed to start the integrator by switching the manual (A) or an automated electric valve (B).

A manual injector with position sensor has an internal relay which is connected by a cable connection in the oven cabinet of the DECADE to the inject/load of the rear panel. The relay is open when the valve is in ‘load’ position, the relay closes when the valve is switched to ‘inject’ and opens again when the valve is switched back to ‘load’.
The ‘INJECT MARKER’ is only active when an electrically actuated injector is present. This output is high when the injector is in ‘load’ position and low in the ‘inject’ position.

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Hold/busy

The hold/busy is a double function.
Input: when a time file is executed in the *slave mode*, the timer can be stopped externally by connecting 'HOLD' and 'COMMON' as described above (Fig. 14). The timer continues after disconnection.
Output: the 'BUSY' output is active (low) when during operation in the *master* or *slave mode* the DECADE is put on 'hold' by the drift monitor. The 'HOLD' command from the keyboard does not affect the status of the 'BUSY' output!

Overload

Activated when a recorder overload occurs.

Auto zero

Enables external activation of the auto zero command. This function is active only when the 'I-Cell' is displayed.

To pos A, B

Forces the electrically actuated injector to position A (load) or B (inject).

Cell on (off)

Switches on (off) the flow cell. This input command can be used for example to switch on and stabilise the flow cell early in the morning by means of a timer.

Programming output functions

Four output functions can be programmed at each time. The notation of the output '0000' corresponds to the four output controls at the back panel of the controller. These are from left to right: relay 2, relay 1, AUX2, AUX1 (Fig. 16). For example, if AUX1 has to be activated, the output is set to '0001'. If a contact closure has to be made using relay 1, the output is set to '0100'. The contact is made between pin 3 and 5 at the 12 pins connector of the upper I/O connector. At the same time the contact between 4 and 5 is interrupted. The relay position indicated on the rear panel refers to the '0' setting (see Fig. 16). In
Table VII the output commands and the corresponding external contacts are given. Combinations of commands enable control of multiple external

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contacts at the same time. For example, the command ‘0101’ activates AUX1 and relay 1 at the same time.

Table VII. Outputs and commands, combinations are possible.

output	command
AUX1	0001
AUX2	0010
relay 1	0100
relay 2	1000

TTL contacts

The DECADE uses TTL input contacts for START, RESET, AUTO ZERO, TO POS. A and TO POS. B. These contacts require a minimum TTL-low pulse duration of 100 ms to be activated. If multiple activations are required the next pulse must be given after 100 ms TTL-high. If the input is kept low, only one activation will occur.

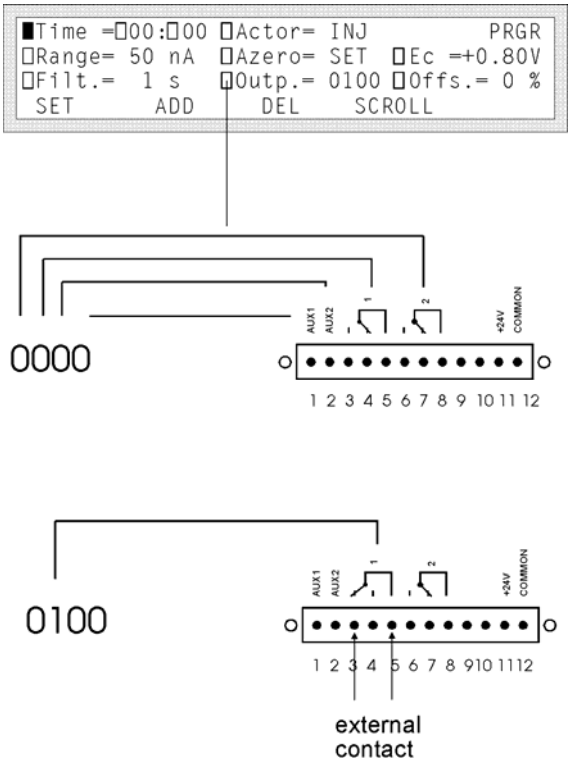


Fig. 16. Programming an external contact closure using the ‘Outp.’ command in a time file.

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There are at least two ways to activate a contact by TTL-low. This can be done by making a contact closure of the input with common (see Fig. 13, 'START' command) or by using an external TTL contact which is made low (see Fig. 13, 'RESET' command). In the latter case it is important that the status of the external contact is known, and that the apparatus is connected to the same ground (by the mains power supply) as the DECADE.

Table VIII. I/O contacts, upper 12 pins connector. Default status of output connections is low (0 V). The connections 1-8 are only accessible in the AUTO mode (master and slave mode).

No.	Name	Function
1	AUX1	open collector output, I max. 250 mA, U max. 28 V
2	AUX2	open collector output, I max. 250 mA, U max. 28 V
3, 4, 5	relay 1	contact between 5 (common) and 4 (default) or 3, I max. 500 mA, U max. 28 V
6, 7, 8	relay 2	contact between 8 (common) and 7 (default) or 6, I max. 500 mA, U max. 28 V
9	Cell off	software 3.00 and higher: trigger to switch off the cell (level triggered)
10	Cell on	software 3.00 and higher: trigger to switch on the cell (level triggered)
11	+24 V	+24 V output, I max. 500 mA
12	common	ground

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Table IX. I/O contacts, lower 12 pins connector. Default status is high (5 V).

No.	Name	Access	Activ(at)e	Function
1	Hold/Busy	slave, master	status: low	Output: active if drift monitor 'holds' the run (master + slave). Input: active as 'HOLD' command (slave mode).
2	Start	slave	level triggered	Starts a time file
3	Reset	slave	level triggered	Resets the AUTO mode
4	Auto zero	always	level triggered	Auto zero command, always accessible when 'I-Cell' is in DECADE display
5	Overload	always	status: low	Active when recorder overload occurs ('REC OVLD')
6	not conn.			
7	Inject marker	always	status: low	In combination with electric valve, high: 'load', low: 'inject'.
8	to pos. A	always	level triggered	In combination with electric valve, forces injector to 'load'
9	to pos. B	always	level triggered	In combination with electric valve, forces injector to 'inject'
10	inject/load	always	status: low	In combination with manual injector with position sensor, high: 'load', low: 'inject'.
11	not conn.			
12	common	always		Ground

Some contacts are *level triggered*, they are activated by making an external contact closure for at least 100 ms with common (= low). Releasing the external contact does not affect the I/O contact function. Other contacts are *status sensitive*. They are active only when the status is low, releasing the external contact closure deactivates (status = high).
Lower contact 1 is only accessible in the AUTO mode (master and slave).
Lower contact 2 and 3 are only accessible in the slave mode (AUTO mode).
Lower contact 4 is always accessible when 'I-Cell' is displayed. Other lower contacts are always accessible.

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C H A P T E R 6

Pulsed amperometric detection

Introduction

Several advanced features are implemented in the DECADE. One of these features is the so-called pulse mode. In pulsed amperometric detection (PAD) the working electrode (WE) is regenerated at a frequency of 0.5 - 3 Hz by the application of a series of potential changes. This is particularly useful for certain applications where the working electrode is rapidly fouled due to adsorption of insoluble reaction products. A well-known application area of PAD is the analysis of carbohydrates (Fig. 17) [1].

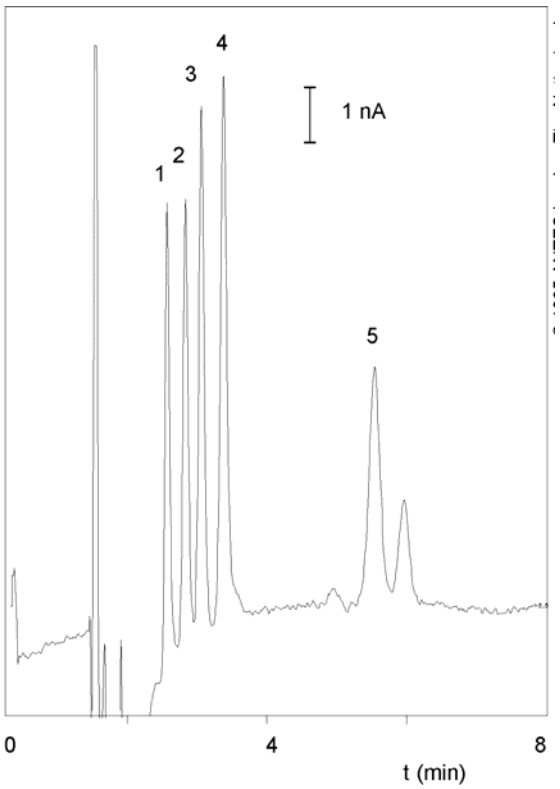


Fig. 17. Pulsed amperometric detection of 100 nmol/l (2 pmol) carbohydrates. Peaks are: sucrose (1), galactose (2), glucose (3), a-lactose (4) and maltose (5).

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The pulse mode is quite different from the DC mode:

- The output signal is sampled during a fraction of the total pulse cycle. This requires electronic manipulation of the signal. Therefore, only the recorder output should be used for detection.
- During the sampling time (ts) the signal generated at the WE is collected and this value is sent to the detector output. Further smoothening of the signal by means of rise time filters is not possible.
- When the frequency of the data acquisition system (integrator) is higher than the pulse frequency a typical stepwise pattern may appear in the chromatogram. This is normal and only visible after considerable magnification of the chromatogram.
- The parameters of the pulse mode are set in the 'PULS SET' screen of the DECADE. The potential sequence starts when the 'PULS STAT' screen is selected. In all other screens in the pulse mode, the E1 potential is applied.
  From DECADE software version 3.00 and higher: the potential sequence is *always* applied if the cell is on.
- The background or cell current is usually considerably higher (100 - 1000 nA) than the maximum compensation in the nA range (160 nA). Therefore, only the µA range is available in the pulse mode. If the RS232 option is installed, the pA and nA range can be used via the 'DECADE Dialogue' software.
- The yellow crocodile clamp from the cell cable is connected to the injection valve to ensure proper grounding of the LC system. However, when an external injection valve is used (auto injector) in combination with a PEEK column (CarboPac) and with PEEK tubing, a grounding problem may arise. In that case a metal low dead volume connector should be placed near the flow cell which is connected to the crocodile clamp. However, it is *not* advisable to use metal tubing as inlet tubing for the flow cell!
- After prolonged use of the flow cell with a gold working electrode (WE) in the pulse mode, the gold oxide which is generated at the WE, precipitates on the auxiliary electrode (AUX). This gold oxide coating may electrically isolate the AUX and result in an increase of the noise. Simply polishing the working electrode on a regular basis (e.g. every month) prevents this.
- If a salt bridge Ag/AgCl REF is used, the pH in the salt bridge will increase. Eventually the colour of the (white) cotton wool frit turns brown. Maintenance of the REF on a regular basis (e.g. every month) ensures a good performance.
- If a mobile phase is used with a high pH (pH>10, carbohydrate analysis), the standard Vespel rotors from the injection valve should be replaced by Tefzel rotors which are pH resistant.
- For carbohydrate analysis, only CO_2-free sodium hydroxide should be used since carbonate anions may disturb the ion exchange

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chromatography. The CO_2-free sodium hydroxide is available from several suppliers as a 50% solution (19.2 mol/l). NaOH pellets are not recommended because of their high CO_2 content.

- The accuracy of certain pH-electrodes is poor at high pH. For applications at high pH it is sometimes better to *calculate* the pH from the OH^- concentration.
- Organic modifiers (acetonitrile) strongly attenuate the signal of most carbohydrates in PAD.

Some of these aspects will be discussed in detail.

Pulse settings

In PAD of carbohydrates the working potential is applied as a series of 3 potentials. During time interval t1 the detection potential is applied. The data collection occurs within t1, during time interval ts (sampling time). The time difference t1 - ts is the stabilisation time.

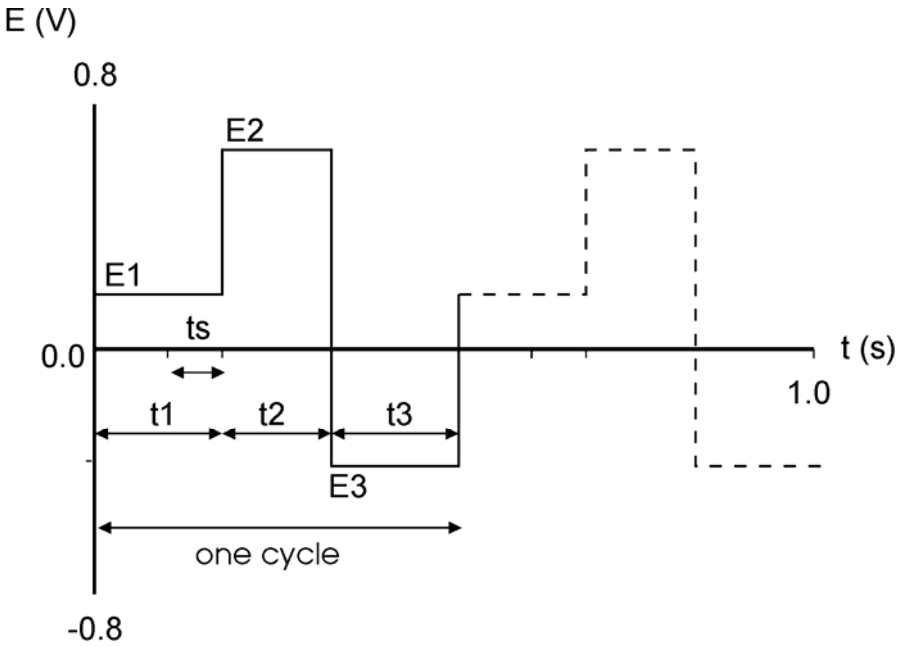


Fig. 18. Potential steps in pulsed amperometric detection. A part of t1 is used for detection (ts). The metal oxide layer that is formed during t2, is removed during t3, resulting in a renewal of the electrode surface.

During the next time interval (t2) a monolayer of metal oxide is formed at the working electrode due to the high positive potential. This monolayer is electrochemically removed from the electrode surface during time interval t3, by applying a negative potential.

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Optimisation of wave forms

LaCourse and Johnson [2-4] have published several papers on optimisation of wave forms in PAD. Several considerations are important for the choice of the pulse duration. Optimisation is depending on the working electrode material, the sample constituents and the required detection frequency. The impression may arise that the number of variables, 3 potential steps and 4 time settings, may lead to a time-consuming optimisation procedure. In practice, the pulse mode is more straightforward.
The potential for the cleaning steps, E2 and E3, are determined by the WE material. At alkaline pH gold oxide is already formed at E2 > +200 mV (*vs.* Ag/AgCl). At a higher potential the formation of a metal oxide layer is accelerated and a shorter time setting may be chosen. In practise an E2 value of +750 mV during 200 ms (t2) gives good results.
The choice of t3 is depending on the potential E3 and the t2 and E2 setting. It is essential that the duration of t3 and the magnitude of E3 is such that a complete removal of the metal oxide is achieved. Reductive dissolution already occurs at E3 < 0 mV, but a more negative voltage speeds up this process. An E3 value of -800 mV during 200 ms (Table X), or -300 mV during 360 ms [4] can be used.
The measuring potential is compound dependent, usually literature data can be used as a starting point for further optimisation. A sampling time ts can be chosen between 20 and 100 ms in 20 ms steps. These are multiples of the 50 Hz, to prevent noise due to oscillations of the AC power supply. Until a certain limit, increasing ts will result in an increase of signal. A limiting factor is the accumulation of adsorbed species at the working electrode that attenuate the signal. Another consideration, not only for ts but for all time settings, is that increasing the time will decrease the detection frequency.
Before sampling a stabilisation time is applied, set by the duration of t1. In practice the stabilisation time determines the level of the background current. When, for example, t1 = 100 ms and ts = 100 ms, there is no stabilisation of the current before sampling (t1 - ts = 0 ms). Depending on the potential setting of E2 and E3, a large positive or negative background current (micro amperes) may be detected which is seriously limiting the detection. In practice, often a 100 - 400 ms stabilisation time is used.

Recorder output frequency

An important difference between the DC and the pulse mode is the frequency of the output signal on the recorder output. In the DC mode the signal has a 9 Hz frequency, in the pulse mode the frequency is determined by the duration

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of the pulse. Once every cycle, the ts signal is sent to the output. This can be visualised by magnification of a peak in the chromatogram (Fig. 19).

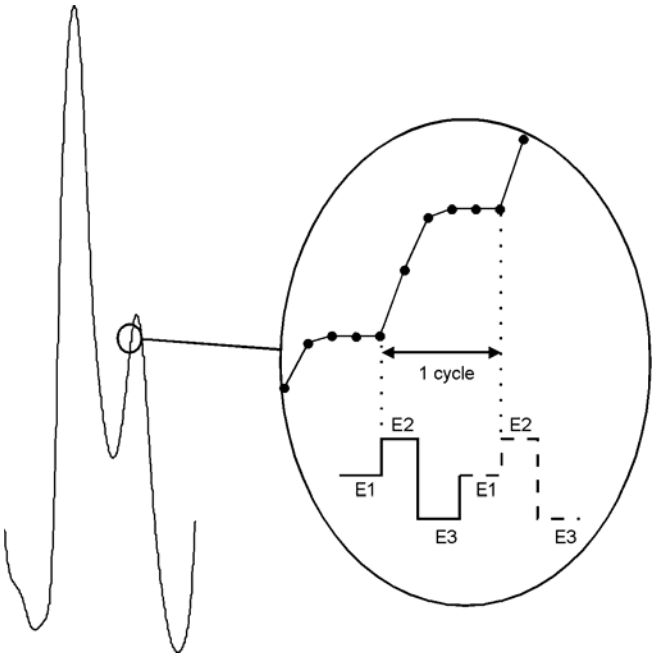


Fig. 19. A magnified view of a chromatogram obtained with PAD. The integrator frequency is 5 times higher than the detector output frequency resulting in a typical stepwise signal.

A stepwise pattern in the chromatogram is only seen on an (analog) chart recorder, or on an integrator that has a higher sampling frequency than the output frequency of the detector. In fact, when this pattern is seen this means that the integrator has an unnecessarily high sampling frequency. This leads to large data files, but certainly not to a better chromatogram.

Peak width and integrator frequency

There are two important considerations with respect to integrator frequencies applied in HPLC. If the frequency is too low, data will be lost and artefacts may be introduced. If the frequency is too high, large data files are generated which take up an unnecessary large amount of disk space. As a rule of thumb, the sampling frequency of the integrator is set such that a chromatographic peak is build up of at least 10 data points. For a peak width of 10s this means that a sampling frequency of 1 Hz should be sufficient.

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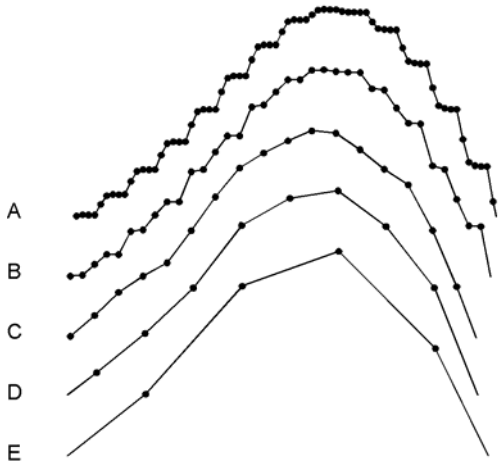


Fig. 20. A detailed part of a chromatogram acquired at different integrator frequencies. The integrator frequency is (A) 5x, (B) 2.5x, (C) 1.2x, (D) 0.6x and (E) 0.3x the frequency of the pulse.

In case of PAD the duration of the pulse should also be taken in account. When the frequency of the pulse is 2 Hz, it makes no sense to acquire data on an integrator with a significantly higher frequency. This would result in acquisition of multiple data points containing the same output value (Fig. 20A and B). Matching the frequencies keeps the peak shape unchanged (Fig. 20C). Decreasing the integrator frequency to less than half the pulse frequency, changes the peak shape (Fig. 20E).
When the peak width is too small there are two options: either less data points are collected for such a peak, or the pulse and integrator frequency are both increased. In the latter case the pulse duration is decreased which will change other detection parameters as well. In practise, the pulse frequency almost never interferes with the HPLC analysis.

Working electrode material

Gold and platinum are used as working electrodes for PAD. Glassy carbon appears to be unsuitable due to the high electric capacitance of this material. Furthermore, resurfacing of the noble metal working electrode is based upon formation and removal of a (metal-) oxide layer. This is impossible with glassy carbon.
The change in cell current during the pulse mode is illustrated in Fig. 21. When the potential is changed, a large charging current is detected (Fig. 21, peak 1, 3 and 5), followed by a stabilisation of the current (Fig. 21, part 2, 4 and 6). The output signal is sampled during a fraction of part 2, depending on the pulse settings. The response of the glassy carbon material is considerably

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different from the noble metals. The capacitance of the electrode material is very high, such that the charging current is not stabilised before start of the next potential step. This pattern makes detection impossible.

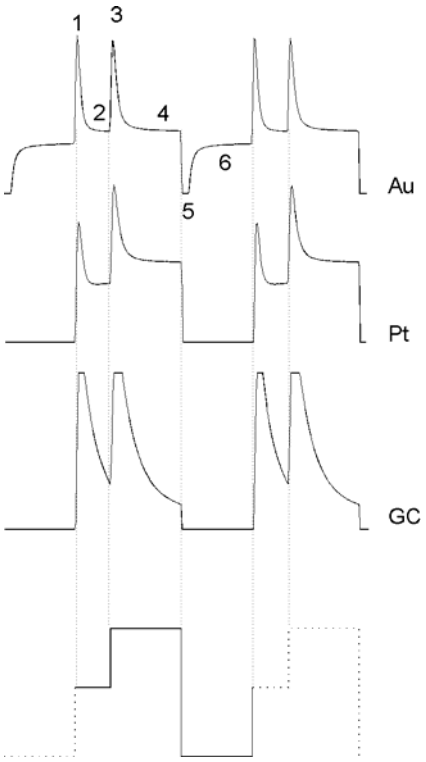


Fig. 21. Change in cell current during PAD. The cell current of the noble metals gold (Au) and platinum (Pt) is stabilised faster than the cell current of glassy carbon (GC), due to a much lower capacitance of the noble metals. For Pt and GC the negative peaks run far off-scale, however the profile is similar to the mirror image of the positive peaks.

Examples of carbohydrate analyses are given in Fig. 17. Typical PAD pulse settings are given in Table X and
Table XI, these settings may be used as starting point for further optimisation. Carbohydrates are oxidised at a pH of 12 or higher, which puts specific demands on the HPLC system used (see above).

Table X. Potential settings for PAD of carbohydrates at a gold working electrode.

	s	1	2	3
t (ms)	100	400	200	200
E (mV)		+150	+750	-800

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Table XI. Potential settings for PAD of glycols, alcohols, aldehydes at a platinum working electrode.

	s	1	2	3
t (ms)	20	300	100	100
E (mV)		+200	+1300	-100

Table XII. LC-EC conditions for PAD of carbohydrates.

detector	DECADE, Antec Leyden
column	CarboPac PA1, 4x250mm
flow rate	1.0 ml/min
mobile phase	200 mM NaOH
sample	disaccharides 100 nmol/l, 20 µl injection
temperature	30 ^{o}C
flow cell	VT-03 flow cell with 3.0 mm gold working electrode mounted with 50 µm spacer
REF	Ag/AgCl, filled with saturated KCl/AgCl
I-cell	ca. 435 nA

References

1. D.C. Johnson, D. Dobberpuhl, R. Roberts and P. Vandeberg, *Review. Pulsed amperometric detection of carbohydrates, amines and sulphur species in ion chromatography - the current state of research*, J. Chromatogr. 640 (1993) 79-96
2. D.C. Johnson en W.R. LaCourse, *LC with pulsed ECD at gold and platinum electrodes*, Anal. Chem., 62 (1990) 589A-597A
3. W.R. LaCourse en D.C. Johnson, *Optimization of waveforms for pulsed amperometric detection of carbohydrates following separation by LC*, Carbohydrate Research, 215 (1991) 159-178
4. W.R. LaCourse en D.C. Johnson, *Optimization of waveforms for pulsed amperometric detection of carbohydrates based on pulsed voltammetry*, Anal. Chem. 65 (1993) 50-55

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C H A P T E R 7

Optimisation of working potential

Introduction

A current - voltage (I/E) relationship, or voltammogram, characterises an analyte. It gives information on the optimum working potential, which can be used to improve detection sensitivity and selectivity.
There are several ways to obtain a voltammogram. A *hydrodynamic* voltammogram is obtained in the DC mode by running several chromatograms at different working potentials. Both peak height and background current are plotted against the working potential. A *scanning* voltammogram is obtained in the so-called scan mode of the DECADE: the voltage runs between two pre-set values and the current is measured. Optimisation of the working potential and the construction of a voltammogram is described.

Electrochemical reactions

In electrochemical detection (ECD) a reaction of the analyte at an electrode surface is monitored. This distinguishes ECD from most other detection techniques where detection is based on the physical properties of an analyte (i.e. mass spectrometry: molecular mass, absorbance detection: molar absorptivity). For electrochemically active compounds, the potential between reference electrode (REF) and working electrode (WE) determines the reactivity of the analyte at the WE. The potential difference supplies the energy level needed to initiate or enhance the electrochemical reaction. Different analytes may have different oxidation or reduction potentials, which determines the selectivity of ECD.

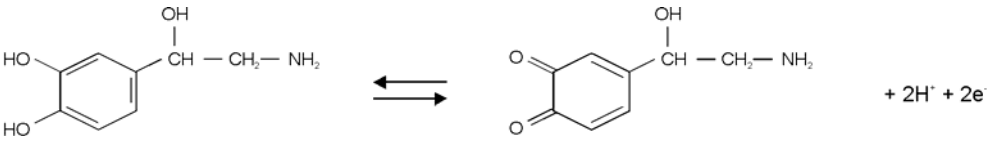


Fig. 22. Oxidation/reduction reaction of nor epinephrine.

An example of an electrochemical reaction is shown in Fig. 22, nor epinephrine is converted into a quinone by oxidation at the WE. Two

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electrons are transferred at the WE resulting in an electrical current that is amplified by the controller.

Hydrodynamic and scanning voltammogram

A *hydrodynamic* voltammogram is constructed when the pure analyte is not available and separation over an analytical column is required. Furthermore, under real chromatographic conditions reliable information about the S/N ratio is obtained

In case of metal working electrodes it is also advisable to use a *hydrodynamic* voltammogram. On the metal working electrode an oxide layer is formed which affects the electrochemical reaction and makes the interpretation of a scanning voltammogram difficult.

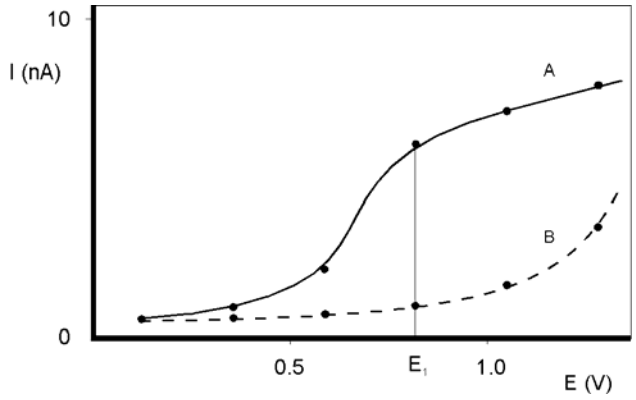


Fig. 23. Hydrodynamic voltammogram of nor epinephrine (A) at a glassy carbon working electrode, and the current of the baseline (B). At E_1 the electrochemical signal becomes diffusion limited.

An alternative for the chromatographic construction of an I/E relationship is the application of scanning voltammetry. The working potential runs between two pre-set values and the current is measured while the analyte is continuously flushed through the flow cell.

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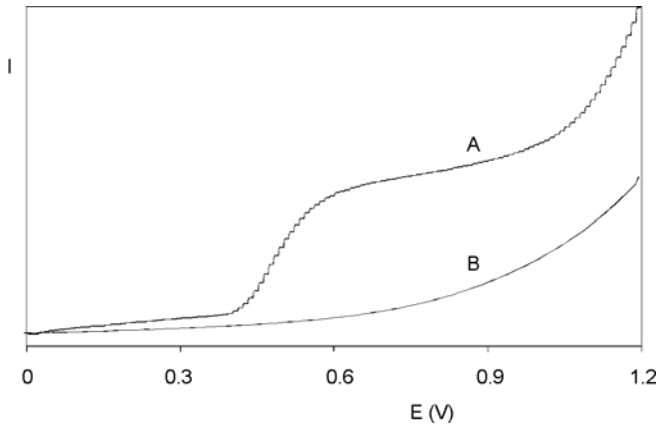


Fig. 24. Scanning voltammetry of 1.0 µmol/l nor epinephrine (A) at a glassy carbon working electrode, at a scan speed of 10 mV/s. Scan (B) is the blank solvent.

As peak heights are used, the signal in Fig. 23, line A is only due to the analyte. The signal in Fig. 24, line A is the sum of the analyte signal and the background signal. Subtracting both lines in Fig. 24 results in a similar I/E relationship as in Fig. 23, line A. It takes only a few minutes to construct a *scanning* voltammogram. This is an advantage, especially when a number of analytes have to be characterised. However, as the scan is obtained in flow injection analysis (FIA, without analytical column), it is a prerequisite to have the *pure* analyte dissolved in buffer. **Any contamination may lead to artefacts**. A blank scan of the buffer should be used to distinguish between solvent peaks and analyte peaks.
As can be seen in both Fig. 23 and Fig. 24, when the working potential is increased the electrochemical reaction is enhanced hence the signal increases. At a certain potential the I/E curve flattens. All analyte molecules that reach the working electrode are converted at such a high rate that the analyte supply becomes the limiting factor. At the working electrode surface a stagnant double layer exists, where molecular transport takes place by diffusion only. Therefore, the current at (and beyond) this potential is called the *diffusion limited current*.
With respect to *sensitivity*, a high working potential is important. However, at higher working potentials, more analytes are detectable. So, as to *selectivity*, a low working potential will be favourable.
Working at a potential on the slope of the I/E curve will result in less reproducibility. Not only a small fluctuation in the applied potential, but any change in the system may result in a large difference in current.
In practice the choice of the working potential is a compromise between sensitivity, selectivity and reproducibility. In the example of Fig. 23 a working potential (E_1) of 0.8 V is chosen.

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Optimisation using a voltammogram

Sometimes, when interfering peaks appear in the chromatogram, it is possible to optimise the method with regard to selectivity. If the interfering compound has a higher oxidation potential, a working potential is chosen that gives the best selectivity, i.e. the largest difference in peak height. In the example of Fig. 25 the selectivity for compound X is improved considerably by decreasing the potential to E_2 or E_1. Obviously, if compound Y is the compound of interest, optimisation of selectivity in this way is not possible and the chromatography has to be optimised.
Electrochemical detection differs from most other LC detection methods in that a reaction takes place in the detection cell. Due to reaction kinetics an increased temperature speeds up the oxidation/reduction reaction. However, this not only holds for the analyte but also for the background current and possible interferences. An elevated temperature will therefore not automatically lead to a better detection. A *constant* temperature is of paramount importance for a stable baseline and reproducible detection conditions.

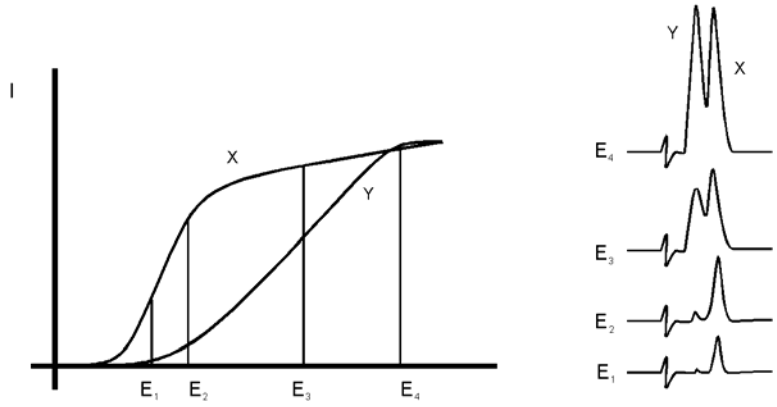


Fig. 25. Selectivity in LC-EC of compound X and Y is optimised by choosing the working potential with the largest difference in peak height.

Electrochemical reactions are pH sensitive (Fig. 26). For nor epinephrine the I/E curve is shifted to a lower potential at higher pH. When the working potential is high (E_2), and the signal is diffusion limited, an increase in pH will result only in a small increase of the peak height. When the working potential is lower (E_1), and the signal is not diffusion limited, the signal will strongly increase at higher pH. In both cases the background current increases at a higher pH.

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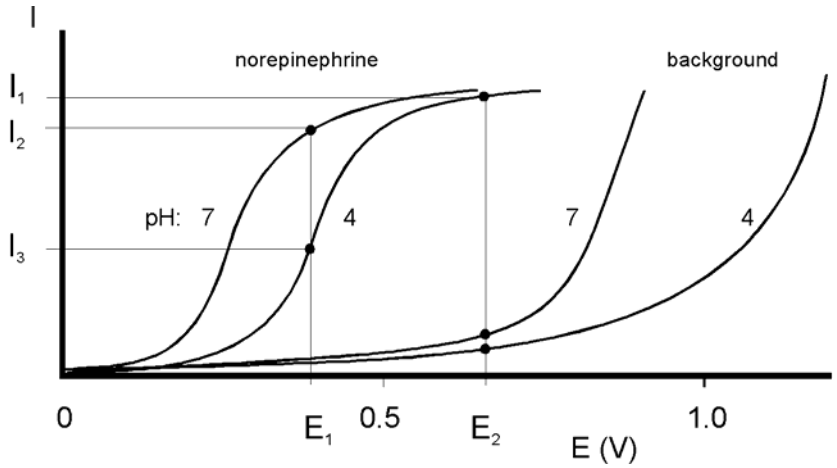


Fig. 26. At a higher pH the I/E curve of nor epinephrine is shifted to the left.

Reaction kinetics predict that electrochemical detection is mass flow dependent. When the LC flow is stopped in LC-EC, the analyte will be oxidised completely and the signal decreases rapidly. This means that the flow rate not only affects temporal peak width and analysis time but also peak height. Also the background signal is sensitive towards fluctuations in the flow rate. Therefore, it is important to use a pulse-free solvent delivery system.

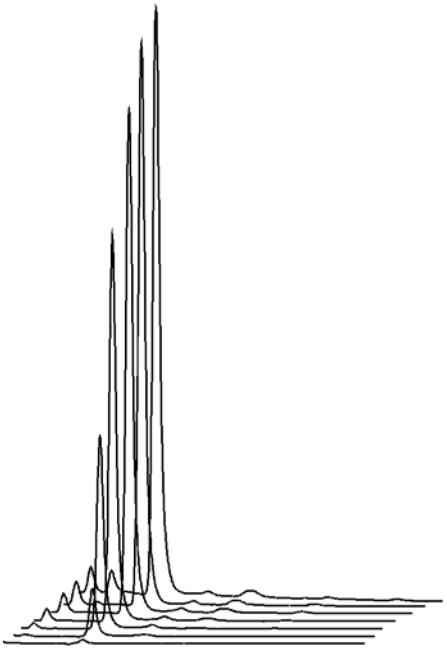


Fig. 27. Construction of a hydrodynamic voltammogram for nor epinephrine. Chromatograms are obtained at cell potentials ranging from 1.0 V (back) to 0.4 V (front), with 100 mV steps.

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Construction of a hydrodynamic voltammogram

Before a hydrodynamic voltammogram can be obtained, the chromatographic conditions should be optimised. Then the following steps are taken:

1. A solution of the analyte at a concentration between 1 - 100 µmol/l, is prepared in mobile phase.
2. The electrochemical detector is stabilised in the DC mode at a high potential. After stabilisation the background current is read from the display of the detector (I-cell) and the noise is measured.
3. The run is started by injecting the compound. When at the high working potential no signal is obtained, it may be concluded that the compound is not electrochemically active. In such a case derivatisation of the compound may be an option.
4. If a peak is measured, the working potential is decreased by 50 or 100 mV and step 2 to 4 is repeated until the lowest potential setting (Fig. 27).
5. The peak heights and the background currents are plotted against the working potential (Fig. 23).
6. The working potential which gives the best sensitivity is obtained by plotting the signal-to-noise ratio against the working potential.

Construction of a scanning voltammogram

The scan mode is programmed in the ‘SCAN SET’ screen of the DECADE. Depending on the data acquisition software that is used and the experimental set-up, a full, half or continuous scan cycle can be chosen.

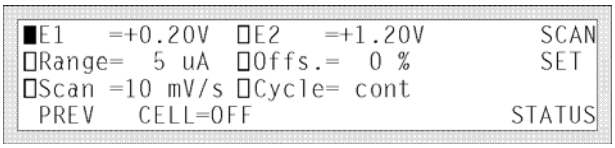


Fig. 28. Programming the scan mode in the 'SCAN SET' screen.

In the example of Fig. 24 and Fig. 29 a ‘half’ scan is used, sweeping the potential from 0.2 V to 1.2 V. A full scan would include the reverse scan, i.e. from 0.2 V to 1.2 V and back to 0.2 V. In the continuous mode the voltage is swept up and down between both potentials.

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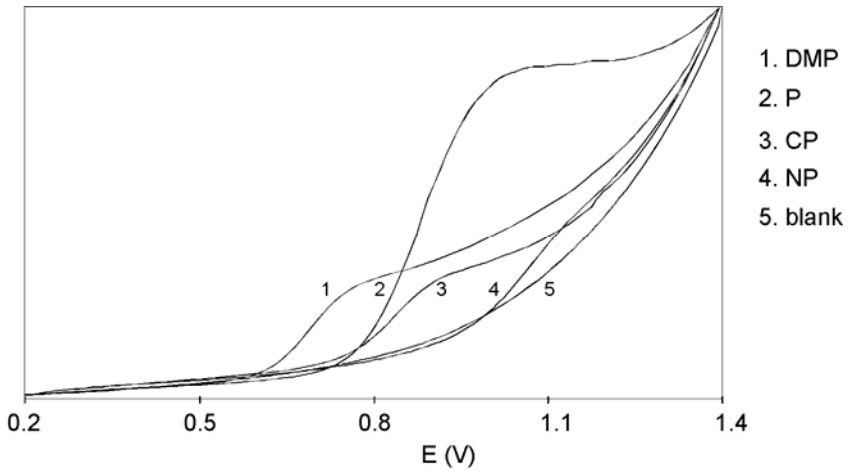


Fig. 29. The scanning voltammograms of 2,4-dimethylphenol (DMP), phenol (P), 2-chlorophenol (2-CP) and 4-nitrophenol (NP).

The following procedure is used to obtain the voltammograms in Fig. 24 and Fig. 29:

1. The column is removed from the LC system. The voltammogram is recorded in the flow injection analysis (FIA) mode.
2. The pure compound is dissolved in (preferably) the HPLC buffer at a concentration of ca. 10-100 µmol/l. When the analyte is already in solution, it should be diluted in HPLC buffer until the desired concentration.
3. An injection loop of 100 µl is installed and the LC flow rate is set at 40 µl/min. The analyte plug will than be detected during approximately 2.5 minutes. The flow rate is lowered if more scanning time is needed.
4. An initial run is started in the *DC mode* at a high potential to estimate the required start and stop time of the scan after sample injection (Fig. 30). In the scan mode, the scan is obtained at the flat top of an analyte plug. **The analyte delivery should be constant. Fluctuations result in unreliable results.**

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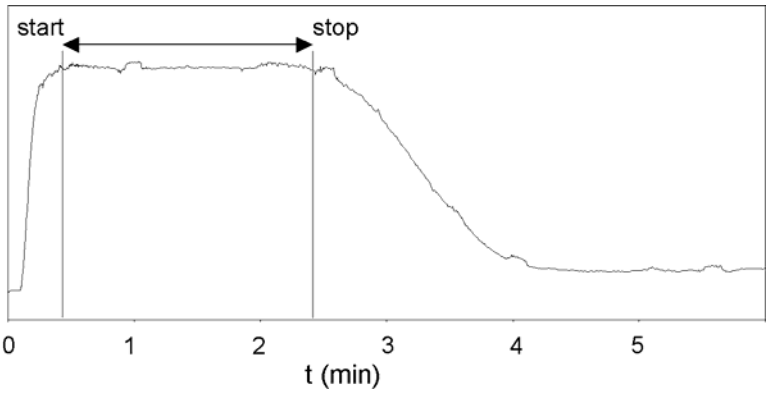


Fig. 30. Chromatogram of the analyte plug obtained in the DC mode. Scanning takes place on top of the broad peak between 0.5 and 2.5 min after injection in FIA mode.

5. The sampling frequency of the integrator is set at 1 Hz. This is the same frequency as the voltage steps during the scan. If a higher sampling frequency is chosen a typical stepwise pattern may appear.
6. In the 'SCAN SET' screen an upper and a lower potential is chosen. The cycle is set at half. The range is set at 5 µA. A scan speed of 10 mV/s is selected. The integrator (or recorder) must be connected to the REC output of the DECADE.
7. The analyte is injected and the scan is started by pressing the 'START' in the 'SCAN STAT' screen of the DECADE at the time the analyte plug enters the flow cell (see 4).
8. A background scan is obtained by scanning the HPLC buffer.
9. For reliable results it is recommended to repeat each scan three times.

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C H A P T E R 8

Specifications DECADE

General specifications

Power	110-120/220-240 VAC, 50/60 Hz
Operating modes	DC, Pulse and Scan
Potential range	between +2.00 and - 2.00 V in 10 mV increments
Recorder output	between +0.1 and - 0.1 or between +1.0 and -1.0 V
Current ranges integrator	1 nA, 10 nA and 1 µA/V
Integrator output	between +10.0 and -10.0 V
Offset	between +50% and - 50% of recorder output, 10% steps
Drift monitor	0.1 - 10 nA/min (Pulse), 0.1 pA/min - 10 nA/min (DC)
Event marker	10% of recorder output
Auto zero	range determined by integrator setting, in µA range: 16 µA, in nA range: 160 nA, in pA range: 16 nA; triggered by keyboard, rear panel contact closure, or RS232C control
RS232C	full parametric instrument control (option)
Injector sensor	starts system clock if Load → Inject
Oven	length 40 cm, from 5°C above ambient to 60°C, accuracy 0.5°C, stability 0.1°C; accommodates injector, column, pulse damper and flow cell
Environmental	Humidity: Max. 80% relative humidity, non condensing (5°C - 30°C), linear decreasing to 50% rel. humidity at 40°C

DC mode

Current ranges recorder	10 pA - 5 µA in 1, 2, 5 steps
Filter (time constants)	0.1 - 5 s in 1, 2, 5 steps
Noise	< 2 pA with a dummy cell (load of 300 MOhm and 0.5 µF) with 0.1 s filter; with 2 s filter the noise is < 1 pA

PULSE mode

Range	10 nA - 5 µA in 1, 2, 5 steps
Pulse times	t1: 100 - 2000 ms; t2: 100 - 2000 ms; t3: 0 (off) - 2000 ms in 10 ms steps
Sample times	20, 40, 60, 80 and 100 ms

SCAN mode

Range	10 nA - 5 µA in 1, 2, 5 steps
Scan rate	1 - 50 mV/s in 1, 2, 5 steps
Cycle	half, full or continuous
	Start/Stop, Hold and Auto zero, Starting potential (E1), End potential (E2)

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AUTO mode

DC mode (5 files) and pulse mode (4 files), master/slave mode, cycle time, number of cycles, drift monitor
Time-based control of 20 time points as to sensitivity, filter settings, output contacts (2 open collector, 2 relays), auto zero, offset, inject/load position of electrically actuated injector (option) and E-cell (DC only). Switching time electrically actuated injector: 80 ms

Rear panel I/O connections

Mains, Recorder (12 bits) and Integrator (analog), 2 open collector (AUX 1 and 2) I max. 250 mA,U max. 28V and 2 relay outputs I max. 500 mA,U max. 28 V , cell on, cell off, 24 V output I max. 500 mA, Common, Hold/Busy, Start, Auto zero, Overload, Inject marker, Electrically actuated injector control, position of manual injector, RS232C connector (option)

Physical specifications

Dimensions	48 (L) x 22 (W) x 36.5 (H) cm = (18.75” x 8.6” x 14.3”)
Weight	15.5 kg (34.2 lbs) with injector and without pulse damper

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C H A P T E R 9

Error messages

Error	Message
Error 1	Current overload, maximum current + maximum compensation has been exceeded. Advise: use less sensitive range in ‘Range select’ screen.
Error 2	A ROM failure has been detected. Please contact supplier.
Error 3	A RAM failure has been detected. Please contact supplier.
Error 4	The system cannot detect the cell controller board. Please contact supplier.
Error 5	The system cannot detect the I/O board. Please contact supplier.
Error 6	The dipswitches on the I/O board have been wrongly set. Please contact supplier.
Error 7	A critical failure has been detected. False data have been written in RAM. Please contact supplier.
RECOVLD	Recorder output is either above +1.0 V or under -1.0 V. Pressing ‘A-ZERO’ may give an adequate read-out again. If the message ‘ERROR 1’ is displayed, immediately after pressing ‘A-ZERO’, the auto zero function is unable to compensate for the offset and is out of the recorder range. Advise: use less sensitive range in ‘Range select’ screen (see also ‘ Saturation of output’ page 74).
OVLD	In pulse mode: charging current out of range. Pressing ‘A-ZERO’ may give an adequate read-out again. If not, it is advisable to change the pulse settings (larger t1) or to use a less sensitive range.

Dipswitch settings I/O board

switch	comment	on	off
1-1	electrically actuated injector	present	absent
1-2	injecto	present	absent
1-3	not used		
1-4	not used		

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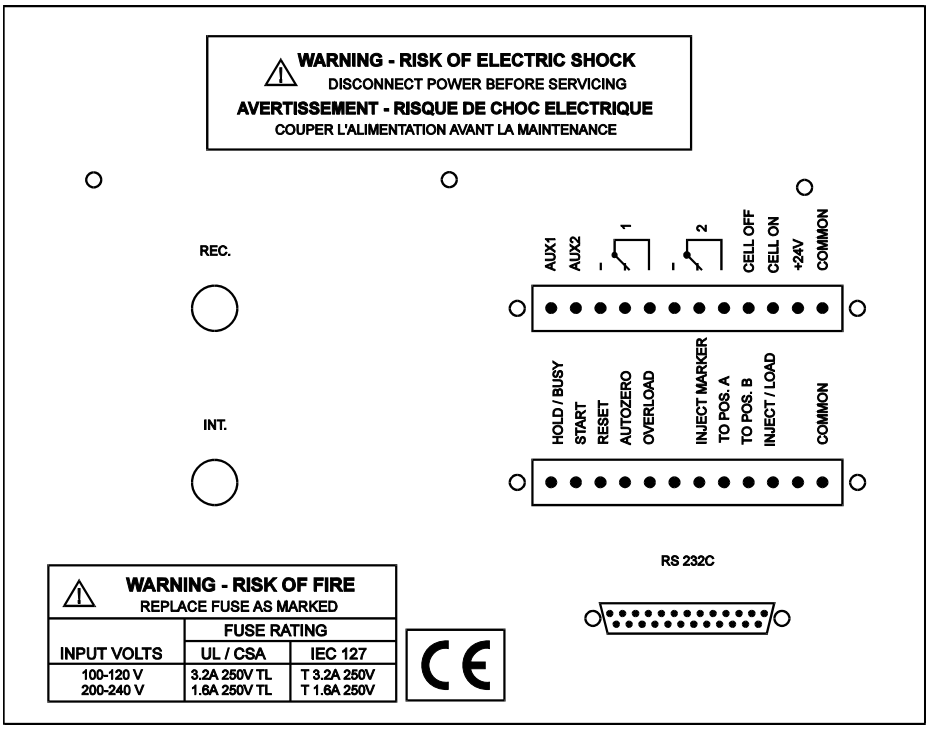
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C H A P T E R 1 0

Rear panel

TTL inputs

The inputs on the lower I/O connector strip, ‘start’, ‘reset’ and ‘auto zero’ require a TTL-low pulse (minimal 100 ms) to be activated. One TTL-low pulse produces one activation, if more activations are required the next pulse must be given after 100 ms TTL-high. If the input is kept low, only one activation will result. See page 48 for detailed information on the I/O contacts.

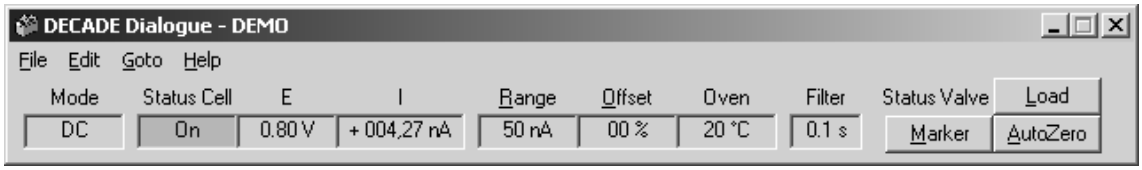


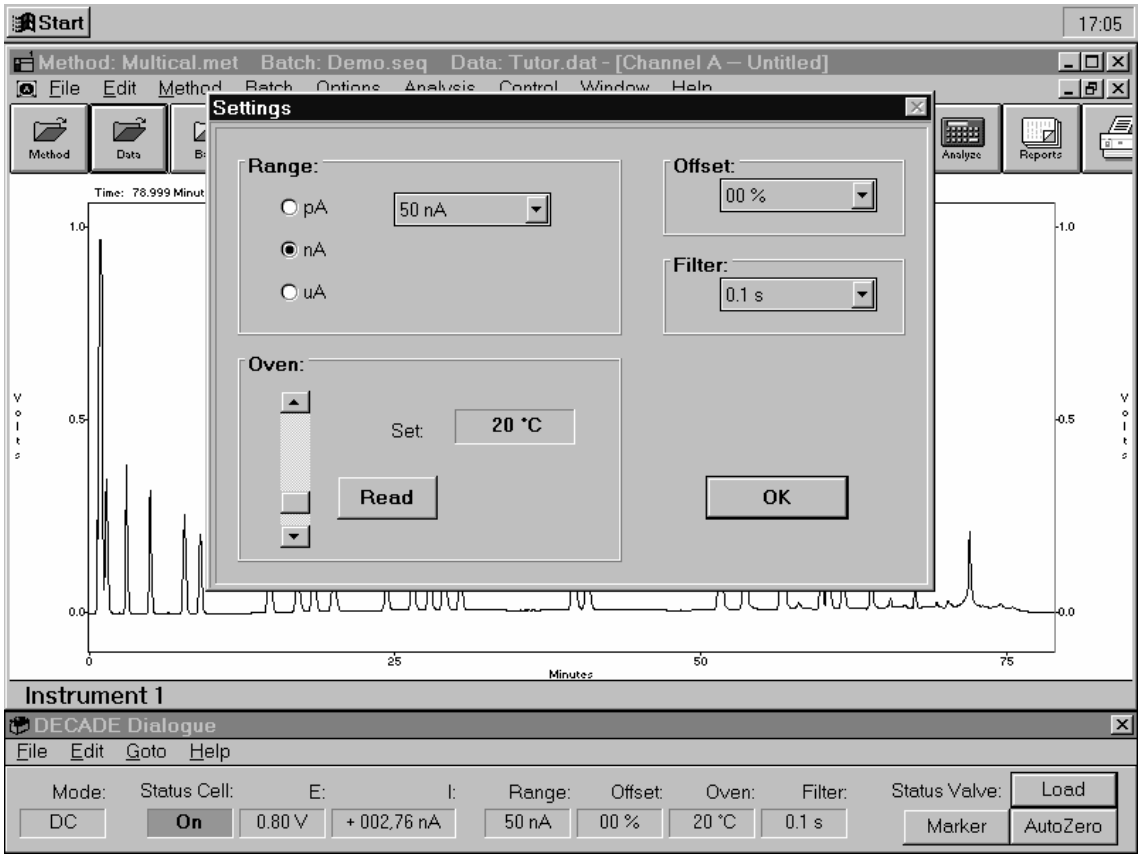
RS232C

The RS232 option consists of a computer program, DECADE Dialogue for Windows, and another DECADE EPROM with R-extension.
DECADE Dialogue for Windows is a multi-functional control bar which handles all important settings of the DECADE via the RS232C port. The program runs simultaneously with your favourite Windows-compatible

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integration software or any other Windows program. The time file editor provides a well-organised spreadsheet for convenient writing of time files. Each time file provides a stepwise, time based, full parametric control with a time resolution of 1 second. Programmable parameters comprise cell potential, range, auto zero, offset, rise time, electrical injector and control of DECADE output contacts for control of external equipment.
For users of integration software running under DOS DECADE Dialogue may still offer an attractive option. A time file can be transmitted from a PC to the DECADE and executed from in the auto mode of the DECADE, independently from the computer. The possibility to construct a time file in a Windows environment is always available.





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C H A P T E R 1 1

Troubleshooting guide

No detector response

Possible cause	Remedy
No power	Check line voltage setting, plug in power cord
Power switch off	Turn this switch 'on' (at the rear panel)
Faulty fuse	Replace fuse
Divergent mains voltage	Check line voltage, see page 13
Cell disconnected, or switched off	Check connection
Recorder/integrator disconnected	Check connection
Fouled WE	Clean WE (see flow cell manual)

High cell current

Possible cause	Remedy
Contaminated buffer	Replace buffer, do not recycle the buffer
High WE potential	Optimise potential, if possible: use smaller WE diameter
Salt bridge in REF not saturated	Refill with wetted KCl crystals
Retained peaks from previous runs	Wait for elution of these (very) broad peaks
Column is 'bleeding'	Replace column
High amount of Fe^{++} in buffer	Add EDTA to buffer, rinse metal parts with 15% HNO_3

Noisy baseline

Possible cause	Remedy
Salt bridge in REF not saturated	Refill with saturated KCl, add wetted KCl crystals
Air bubble in REF or in cell	Remove air bubble, continuously degas the mobile phase
Slow temperature fluctuations	Isolate detector cell, set oven temperature
Fouled WE	Clean WE (see flow cell manual)
Leaking REF or cell	Tighten connections with care

Decreased sensitivity (low S/N ratio)

Possible cause	Remedy
Fouled WE by dirty samples	Clean WE (see flow cell manual), if possible: dilute samples

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Possible cause	Remedy
Cell potential too low	Optimise potential
Contaminated buffer (high I_{cell})	Replace buffer, do not recycle the buffer

Baseline oscillations

Possible cause	Remedy
Malfunctioning pump (regular pattern)	Check pump (seals, valves)
Overtightened cell bolts	Adjust cell bolts, check pump pressure
Air bubbles in cell or REF	Maintenance REF (see flow cell manual)
Temperature oscillations	Set oven temperature
Contaminated buffer (high I_{cell})	Replace buffer, do not recycle the buffer
Fouled WE	Clean WE (see flow cell manual)
Fe^{++} in buffer	Add EDTA, passivate metal parts with HNO_3

Saturation of output

Possible cause	Remedy
Damaged REF	Check with spare REF, replace if necessary
Damaged WE	Replace cell block
Cell incorrectly connected	Check connections (REF: black, WE: red, AUX: blue)
Cell potential too high	Optimise cell potential

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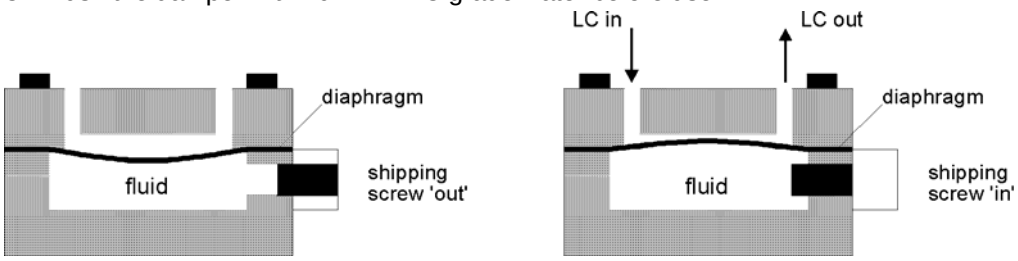
C H A P T E R 1 2

Pulse damper

The current version of the SSI pulse damper is SSI part no. 12-**06**25. This damper is ready for use, as supplied. The older version of the SSI damper (part no. 12-**01**25) is supplied with shipping screw in the full out (counter-clockwise) position to provide additional space for the fluid to expand during the temperature extremes of transit. Failure to tighten the shipping screw before operating can result in the loss of compressible fluid and subsequent damage to the diaphragm.

Installation

1. **SSI 12-<u>01</u>25 damper only**: Turn the shipping screw fully clockwise and tighten to 120 inch-pounds or 'as tight as possible by hand' using the factory supplied 1/4" hex key.
2. The damper should be placed between HPLC pump and injector. Connect the stainless steel pulse damper using the factory supplied standard connection set (ferrules and nuts). The flow geometry through the pulse damper is symmetrical, i.e. each one of the two connections can be used as inlet or outlet.
3. Flush the damper with 20 ml HPLC grade water before use.



The shipping screw on the SSI pulse damper part no. 12-**<u>01</u>**25 must be firmly tightened (turn clockwise) before operating, or damage to the unit will result. The SSI pulse damper part no. 12-**<u>06</u>**25 is ready for use as supplied.

Operation

Operation of the SSI pulse damper is automatic. The pulse damper works best if the pressure is at least 500 psi (3.5 MPa) and preferably 1000 psi (7.0 MPa) or more. In case of low pressure it may be desirable to install a restrictor between damper and injector to the pulse damper outlet to enhance unit performance. Advised operating temperature is between 15 – 35 ^{o}C.

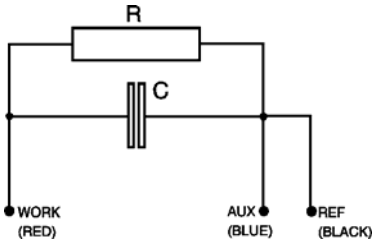
Always release pressure from the system slowly. A rapid pressure release could cause the pulse damper diaphragm to rupture.

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C H A P T E R 1 3

Dummy cell

A successful dummy cell test confirms that the controller, including the cell cable, functions properly. If the result of the noise measurement with the dummy cell is within specs, the controller is excluded in a trouble shooting procedure.



The dummy consists of a resistor (R) of 300 MOhm and a capacitor (C) of 0.47 µF in parallel. The current is measured over the resistor according to Ohm's law (V = I x R), hence with a working potential of 800 mV the current drawn will be about 2.67 nA. Slight differences as to this (ideal) value are due to the tolerance of the resistor (± 1%). The capacitor functions as a 'noise generator' and in fact resembles the capacitance of a well-functioning VT-03 flow cell in an ideal HPLC set-up.
The noise generated via the dummy should be less than 2 pA if the filter of the controller is set to 0.1 second, provided that the dummy is within the fully closed Faraday shield at the same position as the flow cell (see Table XIII for settings). With a 1 second risetime the noise should be better than 1 pA.

Table XIII. Dummy cell test settings.

Parameter	Setting
Cell potential	800 mV
Cell current	2.67 +/- 0.05 nA (read-out)
Oven	30 °C, stable
Risetime filter	0.1 s (or as specified)
Range	nA range, 0.1 nA/V
Output	Recorder, data acquisition at 1 V

The results of the dummy test must be comparable with the test sheet supplied with your controller. If not, please consult your supplier.

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C H A P T E R 1 4

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