LABTECH®

Analyzer of the organically bound halogens

LTX Unique

User manual

Brno **April 2018**

Ver. 1.05

Introduction

Chapter 1

Analyzer LTX-Unique is assigned for the determination of halogens bound in organic halogenated compounds. Information serves as a group parameter of anthropogenic contamination of the environment by organohalides. Analyzer enables to determine organohalides adsorbable on activated charcoal (AOX), extractable by organic solvents (EOX) or purgeable from the sample by a stream of oxygen at 45°C or 60 °C (POX). X in the symbols AOX, EOX and POX means halogens: chlorine, bromine and possibly even iodine. Determination of the above parameters can be performed in waters (tap, surface, ground waters and effluents), in aqueous leachates, suspensions or in organic extracts of soils, sediments, and waste materials. Principle of the determination of analytes separated by the above mentioned techniques is combustion of in the flow of oxygen or in the mixture of oxygen and argon and **determination of formed hydrogen halides by argentometry with microcoulometric generation of Ag^+ and with potentiometric detection of equivalence point.** Therefore, determination of fluorocompounds is not possible by the used procedure.
Separation of the organohalides from the analyzed samples is performed under conventional conditions by the procedures described in relevant standards, e.g.:

- **AOX** according ISO 9562, DIN EN 9562, DIN 38 414-S18, ASTM D 4744-89, EPA Method 450.1, EPA Test Method 9020
- **EOX** according NEN 6402, DIN 38409-H8, DIN 38414-S17
- **POX** according DIN 38414-S17, EPA Test Method 9021.
- **TX** according EPA 9076

These procedures and standards are not parts of this user manual.

1.1. Principle of separation and determination of the group parameters .OX

Determination of POX should precede the determination of the determination of other groups of halogenated organic compounds (DIN 38 414-S17). Separation of this group of organohalides is performed by purging with proper oxygen flow introduced into the sample placed in suitable washing bottle kept at prescribed temperature (45 or 60 °C). Vapour of analytes in the oxygen flow are introduced directly into the combustion tube, where corresponding hydrogen halides are formed. It is recommended to remove volatile organohalides if the samples may contain them in significant concentrations before EOX and particularly AOX determination even in cases, when POX determination is not requested to prevent uncertainty of the results obtained by the above techniques (ISO 9562).
Determination of AOX comprises sorption of organohalides from the analyzed aqueous sample on activated charcoal according some of the above mentioned standardized procedures. Concentrate on the charcoal,obtained by batch or column techniques is the introduced semiautomatically on the quartz sampling boat into the combustion region of the tube furnace. Charcoal with preconcentrated

organohalides is combusted at 950 °C in the same way as at POX determination in the oxygen flow. Originated hydrogen halides are then introduced through the water absorber into the electrolyte in the titration cell and determined (with the exception of F^-) by argentomeric microcoulometric titration with potentiometric indication of the equivalence point. Results are expressed as organically bound chlorine. It is possible to determine, alternatively, also organohalides sorbed on sludges, sediments, and possibly on soils or other geological materials after addition of charcoal and removal of soluble inorganic halides (according DIN 38 414-S18).

Determination of EOX is performed after standardized extraction technique of organohalides from the sample being analyzed by the aid of prescribed organic solvent (usually hexane; see above listed standards). Extract is introduced by the aid of precise syringe into the evaporation region of the furnace and thereafter its vapors are swept by argon flow into the combustion region. Vapors of solvent and organohalides are therein combusted in additional oxygen flow at 850 °C. Originated water vapor is absorbed in washing bottle with conc. sulfuric acid, as in previous techniques, and hydrogen halides are introduced into the titration cell and determined again by argentomeric microcoulometry.

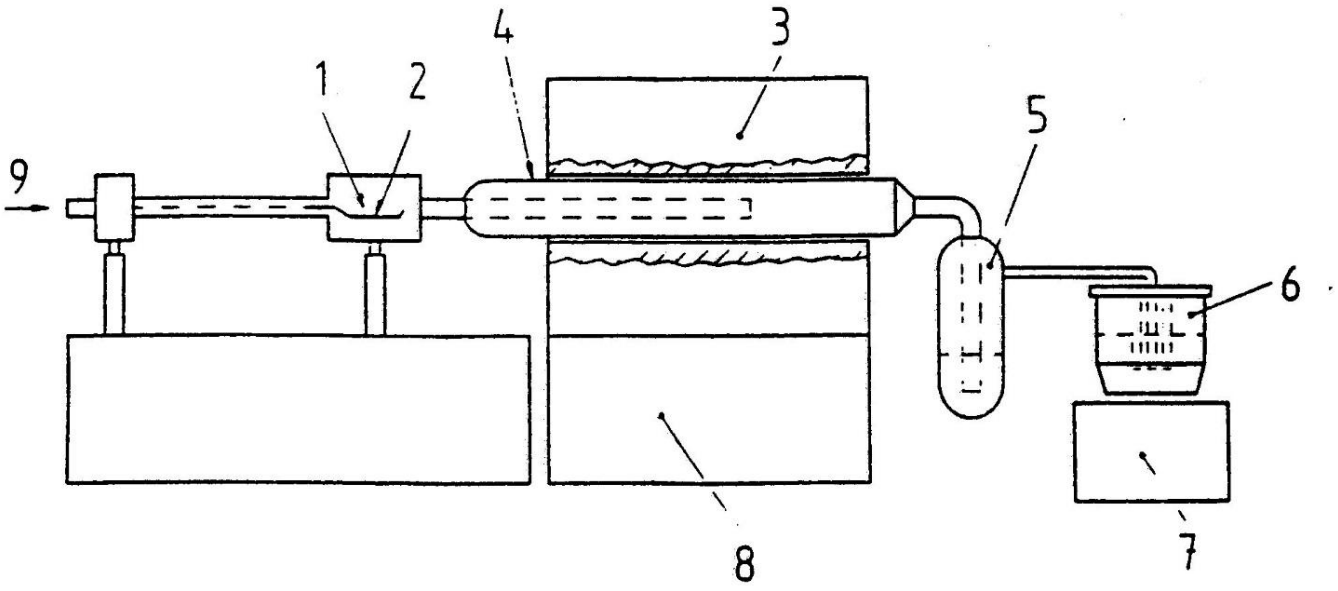
Determination of TX is done from the original sample (without any separation). Sample is introduced either on the boat (in the case of solid sample or non-volatile liquids, e.g. heavy oils or suspensions in such liquids with high flash points) as in the case of AOX determination. Liquid samples without dispersed solid phase can be introduced also into the evaporation region of the furnace by the aid of syringe as in the case of EOX determination.

Description of the analyzer

Chapter 2

Instrument LTX Unique consists of 3 basic structural units:

- Combustion unit: horizontal tube furnace with combustion tubes and temperature controller
- Automatic microcoulometer
- Titration unit: water vapor absorber and titration cell



1. Sample introduction
2. Sampling boat
3. Tube furnace
4. Combustion tube
5. Water vapor absorber
6. Titration cell
7. Magnetic stirrer
8. Main instrument
9. Gas inlet

Fig. 1 Block diagram of the analyzer LTX UNIQUE

2.1. Specification of the instrument

Dimensions of the instrument (L x W x H):	*580 x 360 x 290 mm*
Dimensions of the AOX module (L x W x H):	*392 x 180 x 229 mm*
Dimensions of the EOX module (L x W x H):	*435 x 180 x 229 mm*
Weight:	*25 kg excluding PC*
Supply:	*230 V / 50 Hz*
Power input:	*max. 1100 W*
Horizontal tube furnace:	*Controlled temperature in the center of the furnace Adjustable up to max. 1200 °C,*
Combustion temperature:	
Combustion tubes:	*quartz tubes specified either for AOX or EOX determination*
Water vapor absorber:	*glass washing bottle with conc. H_2SO_4 and with heated introduction capillary*
Coulometer:	*generation currents: 2000, 200, 20 and 2 µA*
Titration cell:	*all glass of special geometry enabling minimizing the influence of the generation current on the indication cell during the titration*
Electrolytes:	*Halogens: 3.5% $NaClO_4$ in 60% CH_3COOH*
Electrode systems:	*generation anode: Ag with defined surface*
Halogens:	*generation cathode: Pt separated by glass frit*
	indication electrode: Ag with defined surface
	reference electrode: $Hg/HgSO_4$
Meter resolution:	*0.01 µg Cl-;*
Detection limit:	*0.03 µg Cl-;*
Measuring range:	*0.1 -200 µg Cl-;*
Reproducibility:	*better than 2% (at 10 µg Cl-)*
Stability of the indication cell:	*better than 0.15 mV/min.*
Time of analysis:	*5 - 10 min*
Gases:	*Oxygen 4N5 (99.995%) or better*
	Argon 4N6 (99,996%) or better (for EOX determination)
AOX module	*Automatically closed sampling chamber, motorized sampling boat drive into/out of the furnace, removable quartz sampling boat*
EOX module	*linear pump drive with constant shift speed, precision and repeatability of the pump 0.5%, gastight sampling syringe V = 250 µl with needle, sampling chamber with silicone septum 1/2" diameter.*
Analyzer control:	*PC, interface USB*

2.2.Front panel

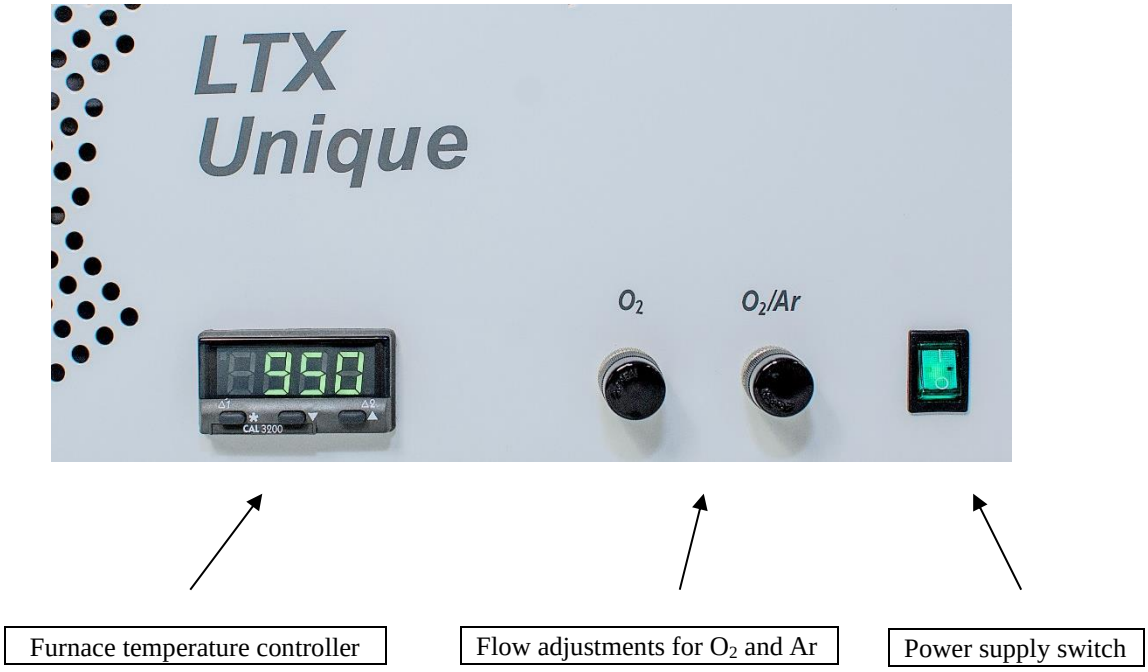
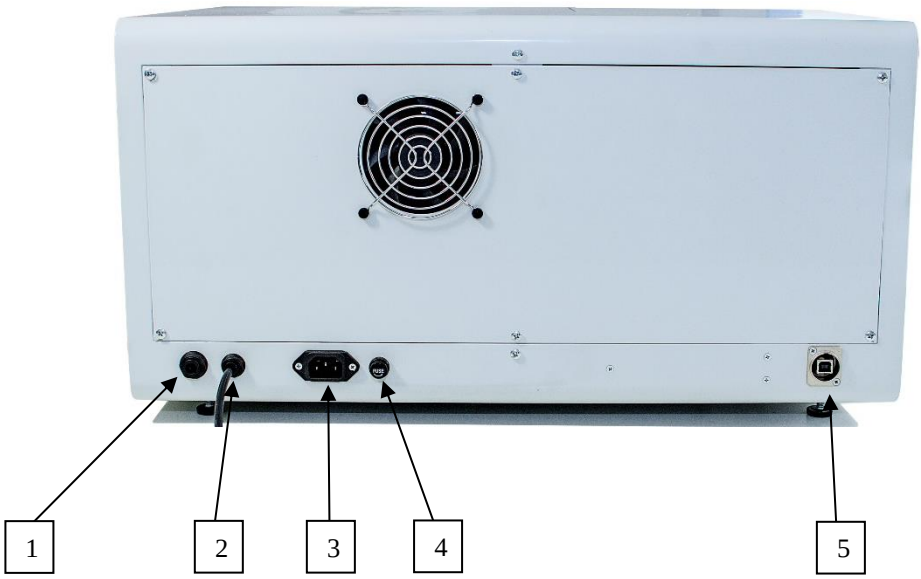


Fig. 2 Front panel of the analyzer

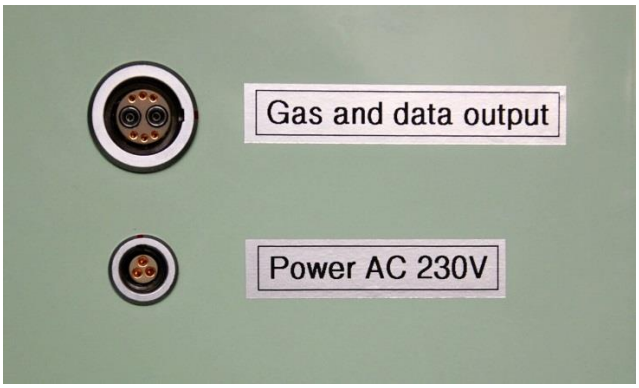
2.3.Rear panel



1. Quick connector for Ar supply
2. Quick connector for O_2 supply
3. Power input plug (230V/50Hz)
4. Fuse 4A
5. Interface USB connection

Fig. 3 Rear panel of the analyzer

2.4.Side panel



1. Connector for gases O_2 and Ar supply and for control signals output for module
2. Power output plug (230V/50Hz) for module

Fig. 4 Side panel of the analyzer

2.5.Modules for sample introduction

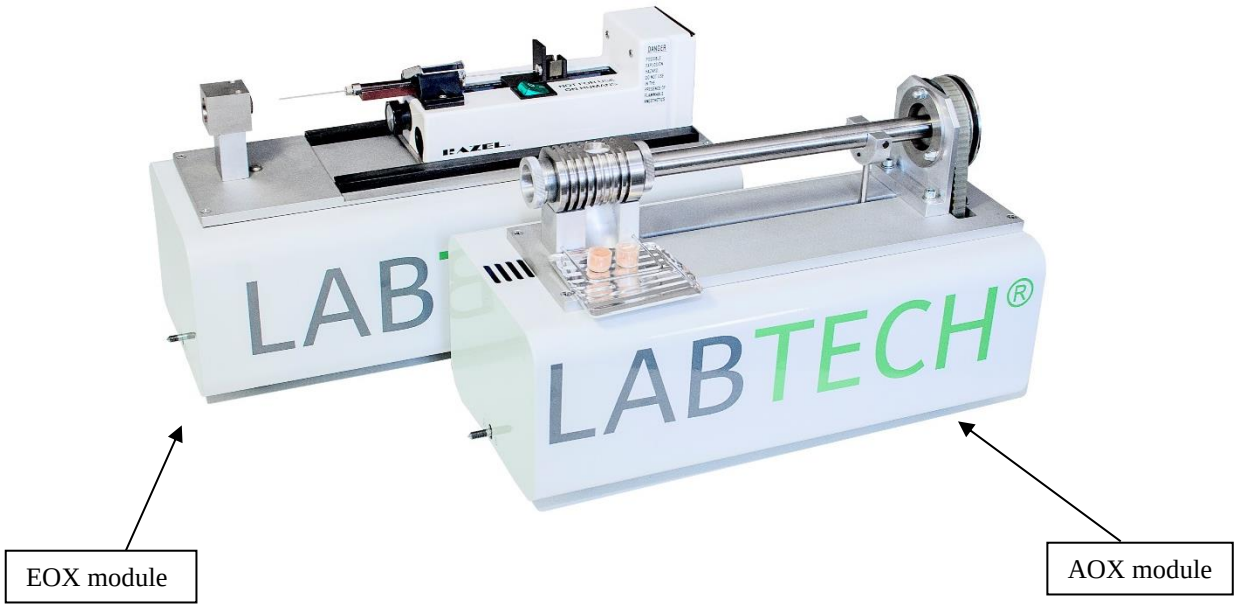


Fig. 5 AOX and EOX modules

Analyzer LTX Unique is delivered with AOX or EOX modules. Sampling modules separate modules with connection to right side of of the main control unit by central screw. The furnace position is adjustable in vertical direction.. The modules are adjustable vertically by the aid of setting screws. Adjustment is accomplished during the installation of the analyzer.

Module AOX (Fig. 5)
consists of combustion quartz tube for AOX and the AOX unit. Inlet of the tube is connected into the sampling chamber trough the O-ring. Stainless steel tube with the quartz rod driver is connected into the sampling chamber from the right side. The sampling chamber is working on the principle of two-way tapered shut-off cock. The adjustment of this cock is done by the right nut of the chamber. The transport of oxygen is connected into the right end of the stainless steel tube. Removable quartz sampling boat is put onto the ring of the rod driver. Movement of the boat from the sampling chamber into the combustion tube is accomplished by sliding of the U-holder of the permanent magnets along the metal tube with driving rod furnished with other permanent magnets. Movement of the U-holder with magnets is done by the motorized screw feed and is controlled by the software.
The boat with sample is inserted into the chamber from the top and at the end of analysis it fall down out of chamber (Fig. 7 EOX module connection
). The boat could be either cylindrical boat with bottom or special AOX cylindrical quartz frit.

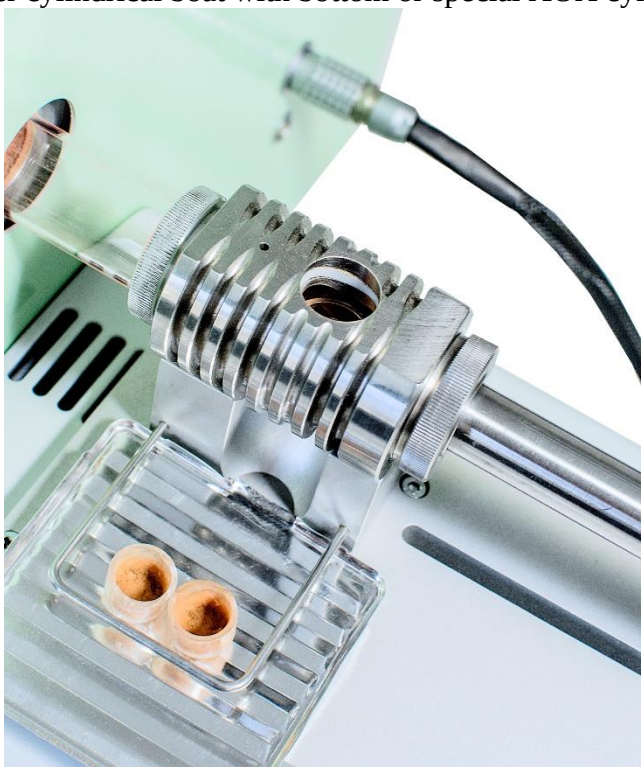


Fig. 6 AOX sampling chambre and AOX module connection

Module EOX (Fig. 7 EOX module connection
7)
consists of the combustion quartz tube for EOX, which is inserted by its entrance into the O-ring on the left side of the sampling chamber. Chamber has on its right side silicone septum for the introduction of the needle of a syringe. Syringe is driven by linear pump controlled by the software. Combustion oxygen is introduced by the side arm directly into the combustion tube, transport gas (Ar) is led by the side connector of the chamber.

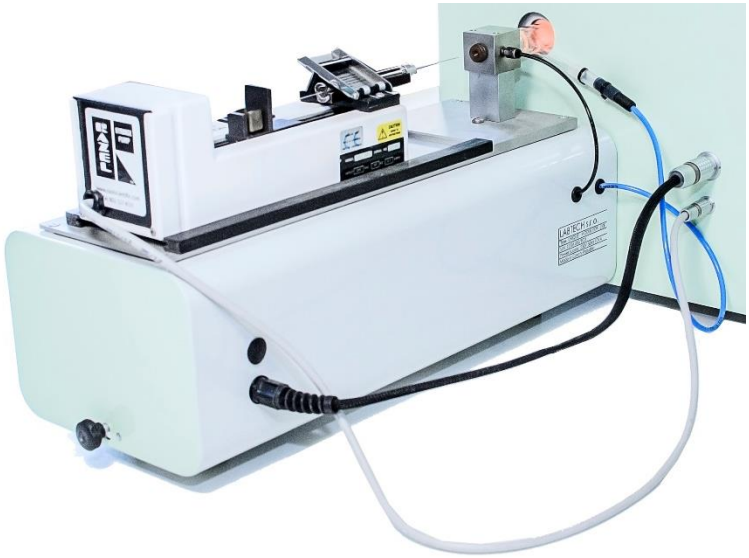


Fig. 7 EOX module connection

2.6. Combustion tubes

Two combustion tubes of quartz glass can be used in the analyzer: one for the determination of AOX, POX and TX (Fig. 6) and the other one for the determination of EOX (Fig.). Both types have on the entrance concentric tube for sample introduction. These introduction tubes differ in both types. Both types are equipped by the side tube for oxygen supply close to the entrance port and by a hemispherical ground joint on the exit to couple the tube with water vapor absorber. Combustion tubes are inserted into the tube furnace from the right side.

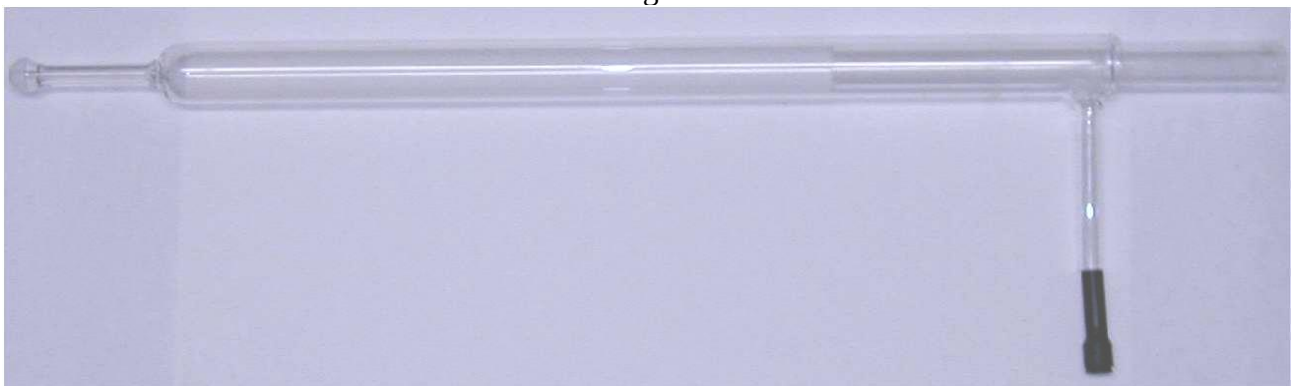


Fig. 6 Combustion tube for AOX

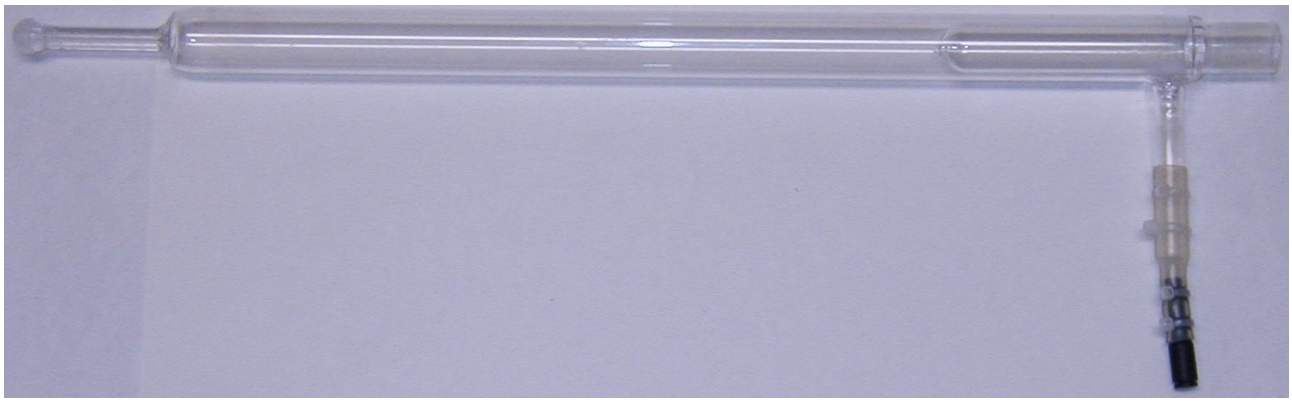


Fig. 7 Combustion tube for EOX

2.7. Combustion furnace and temperature control

Combustion furnace comprises furnace body and the control unit. Furnace body is situated inside the instrument and is protected against touching hot parts. Inner function ceramic tube is 300 mm long with 28 mm inner diameter. Temperature is measured by the K type thermocouple placed in the center of the furnace..
Temperature of the furnace is controlled by the PID controller. The control parameters are set by the producer and it is not recommended to change them. Controller serves to maintain the desired temperature of the furnace (combustion temperature is usually defined in the relevant standard). Setting up the desired temperature is done by pressing and holding the button ✶ till setting in ^{O}C appears and then by the buttons ➘ or ➚ set the proper temperature, then release the button ✶.
Combustion temperature for determination of AOX is usually set on 950 ºC, 850 ºC for EOX and 1000 ºC for TS determinations.

CAUTION!!! Do not cover by anything the ventilation grating on the upper side of the instrument. It may cause the overheating of the instrument.

CAUTION!!! Ceramic tube of the furnace becomes conductive at high temperatures and touching it may lead to the injury by electricity.

2.8. Water vapor absorber

Glass washing bottle of the special design to absorb water vapor from the combustion products with conc. H_2SO_4 is attached on the stand in the titration cell compartment. Its entrance capillary is heated by a heating band to prevent condensation of water vapor and is coupled with the exit capillary of the combustion tube by a hemispherical ground joint. Absorber is closed by a tapered ground joint cover serving both for filling the absorber by conc. sulfuric acid and to draw gases through capillary exit into the titration cell. Stopcock at the bottom serves to discharge used H_2SO_4. Switching the tape heating on/off *(together with electromagnetic stirrer)* is done simultaneously with switching on/off the analyzer.
Attention! Sulfuric acid is strongly corrosive and may cause heavy burns!!! There must be permanently some beaker below the absorber to catch drips or spilled acid!!!

2.9. Titration cell and the electrode systems

Glass titration cell stands on the electromagnetic stirrer in the box protecting it from the influence of the direct light and thus decomposition of AgCl. Special design of the titration cell enables geometric configuration of the electrodes in such a way, that the influence of changeover and the magnitude of the generation currents on the indication cell is suppressed. The proper arrangement of the electrodes in the titration cell is shown in the scheme sticked on the inner side of the hatch of the titration cell compartment. Electrode systems are described in paragraph 2.1.

Fig. 4 Electrode system and the titration cell.

2.9.1. Titration cell

Titration cell is covered with the PTFE cap tightened by a silicon O-ring. There are 4 holes in the cap. Two larger holes determined for generation anode and indication electrode, which are fastened in the cap by silicone rings. First of the remaining 2 holes serves for the introduction of gases from the absorber in such a way to transport bubbles first to the generation anode in the direction of agitation. It conducts by the adapted joint design simultaneously remaining gases out of the titration cell. The second of these openings serves for the dosing of solutions in the case of chlorides determination or during the checking of the correct function of the coulometer.
In the central part of the titration cell is put the magnetic mini stirrer.
Gases escaping from the titration cell contain vapors of acetic acid. It is therefore desirable to assure venting to the fume hood (possibly at least out of the working area) or to lead them into the absorber with diluted solution of NaOH. The level of the solution in the absorber should be maintained only a little bit above the mouth of the introduction capillary to prevent extra increase of pressure in the titration cell and water vapor absorber, which may cause sucking of sulfuric acid into the heated introduction path in the case of some variation in flow rate of combustion gases.
Platinum cathode is placed to one of the side arms of the titration cell, which is separated from the central titration part by a fritted glass. Reference (mercury(I)sulfate) electrode is placed through ground joint in the opposite side arm, separated by capillary from the titration part of the cell. Those two electrodes are used in all methods.

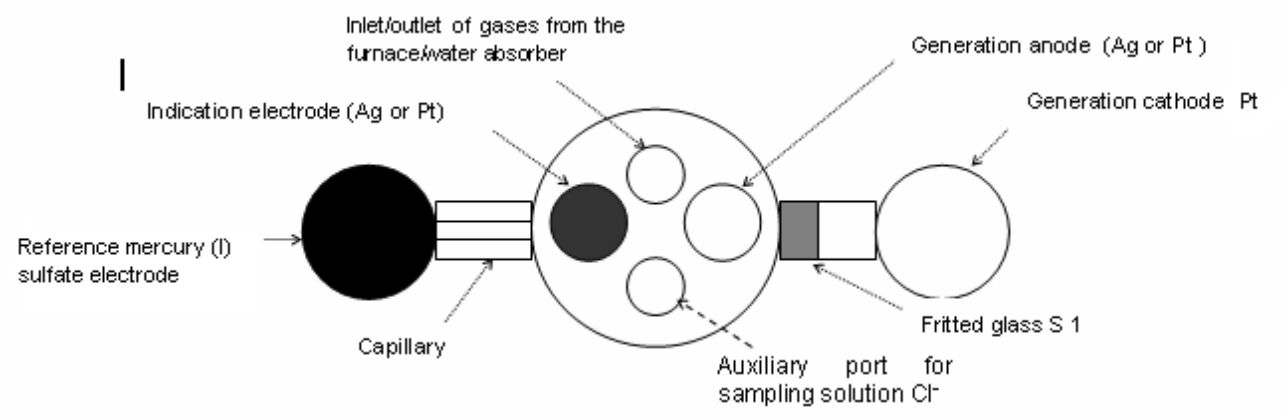


Fig. 5 Arrangement of the electrodes in the titration cell

Titration cell including the side arms should be filled by about 30 - 35 ml of the electrolyte in such a way to ensure the functional surface of the electrodes to be quite immersed. Compositions of the electrolytes and their preparation are described in part 4.2.

2.9.2. Electrode system

Electrode system (Fig. 4) comprises 2 electrode pairs - generation and indication ones which are partially different for the determination of halogens.

Indication electrodes

Halogens

- Generation Ag anode is with exception of the active surface covered with protective PTFE coating. The electrode is pressed in the PTFE plug having silicon O-ring seal.
- Indication electrode is also made of Ag and is of the same construction as the generation one.

Generation electrodes

Generation cathode and reference electrodes are the same for both types of determination.

- Generation cathode is Pt helix fused in the glass tube with ground joint. The cathodic compartment is separated from the central part of the titration cell by a porous glass disk S1.
- Reference electrode is saturated mercury(I)sulfate electrode separated from the titration part of the cell by a glass capillary.

All 4 electrodes are delivered with the connecting cable equipped with the BNC connector. They are to be connected to the sockets in the rear wall of the box of the titration cell and the water vapour absorber. The sockets are labelled to prevent improper connections.

Chapter 3

Description of the software Engine LT

Software Engine LT has been designed especially to control and manage the analyzer LTX UNIQUE and to gather and to process data. It works under the operation system Windows 7.

Access to the software is determined using the system of logging permissions for single persons. According to the access level some operations should be denied for manipulation. Service operations are accessible only for authorized persons (service technicians).

3.1.Start the program

Start of the program is done by **double click on the LTX Unique icon**. After short appearing of the LABTECH logo accessing panel appears (Fig. 10).

Fig. 6 Log in panel

When user name (Login) and password are entered the user logs in by clicking on the LOGIN button. In right down corner is version of the program information and icons allowed

- Window ENGINE LT minimalization

- Return one level back, end of the program

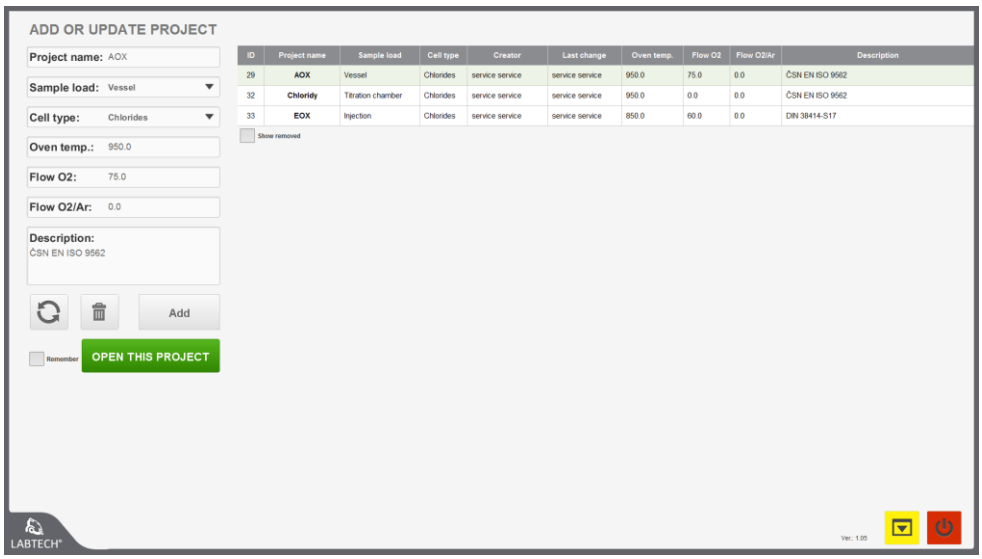
3.2.Project selection

When a user logs on, the **window of the ENGINE LT** appears (Fig. 11) for the project selection. Three basic projects are preset by manufacturer:

- AOX – parameter AOX determination in waste water according to ČSN EN ISO 9562
- Chlorides – chlorides determination in an aqueous sample by dosing directly into the titration vial (coulometer verification) according to ČSN EN ISO 9562
- EOX – parameter EOX determination according to DIN 38414-S17

Project selection is executed by marking and clicking of the left button of the mouse on the project description in the table in upper right part of the window. Selected project is opened with using icon:

Fig. 11 Project ENGINE LT selection window



The projects are linked to the currently used instrument LTX UNIQUE.

There is possible selection of the sample loading into the instrument:

Sample load:

- *Titration chamber* – sample is loaded directly into the titration cell
- *Vessel* – sample is loaded onto the boat of the AOX/TX module
- *Injection* – sample is loaded using the syringe of the EOX module

And selection of used detection system

- *Chlorides* – chlorides (halides) determination by argentometric microcoulometric titration

The other parameters are informative only and are not controlled directly by the software. They are manually set up as described in previous chapter. This is a:

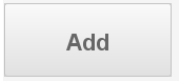
- Oven temp. – temperature of the furnace in °C
- Flow O2 – oxygen flow in a dimensionless unit
- Flow O2/Ar – argon flow in a dimensionless unit

Depending on access permission settings, trained operators can create additional projects, delete or modify existing projects. Icons are used for this purpose:

- Save the modified project

- Deleting an existing project

- Adding new project



3.3. Main menu

After selecting and running the project, the program performs a test of connection of the device to the computer and opens the ENGINE LT main window (Fig. 12).

There is a choice between three bookmarks in this window:

- **Measure** – in this window, the initial value of the potential (E_{BIAS}) is set, the stability of the coulometric detector (drift) is checked, samples are entered for analysis. The gas flow values, the graph of the potential over time and the results of the analyzes already performed are shown here.

- **Results** – access to a complete database of results with the option of filtering by date, projects, used hardware and search by sample name. From this window you can print results, export data in *.xls format, write comments to results, or convert to other values of the blank sample (modify) and make simple statistics and enter the value of the blank experiment on the samples prepared for analysis.

- **Settings** – this window allows to set access rights for each user, parameters of the methods and graphically displays the current status of the instrument, there is also the basic setting of the device that is accessible only to users with service authorization.

3.3.1. Menu measure

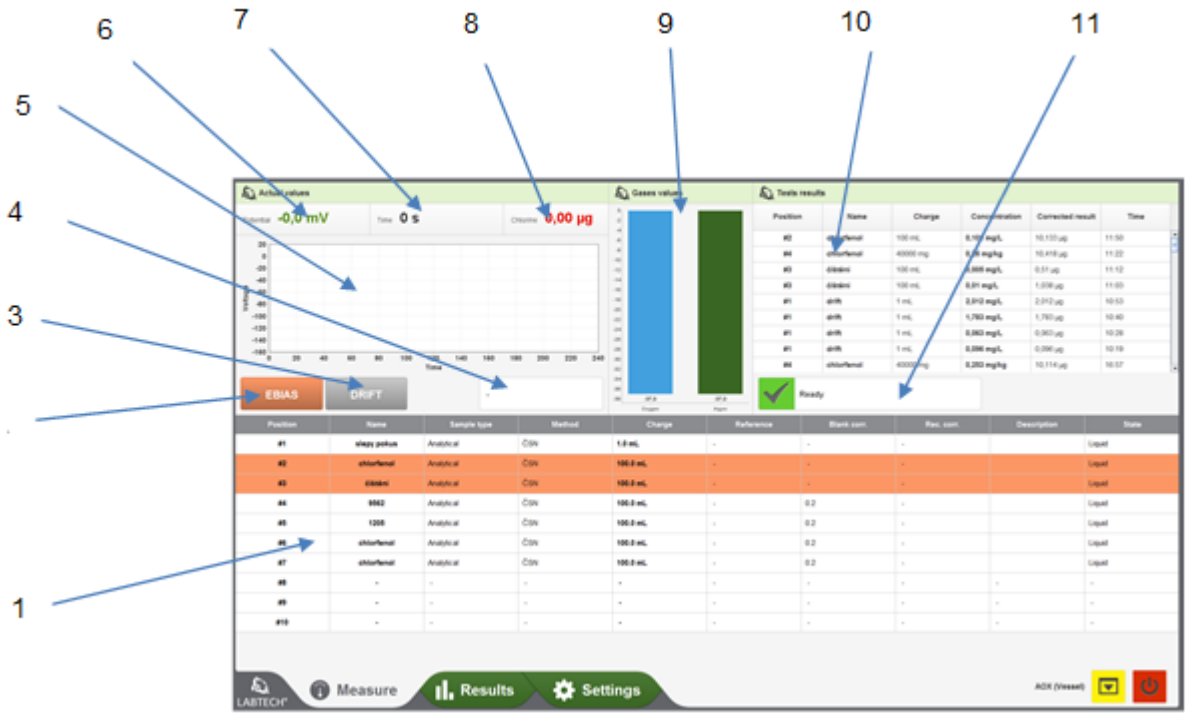
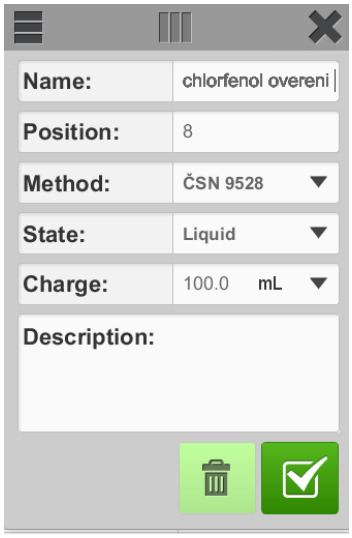


Fig 12 Main window ENGINE LT – bookmark Measure.

1. Table for input of samples for analysis
2. E_{BIAS} -102mV button
3. Button for drift measuring
4. Information window (drift value, starting potential)
5. Potential over time (titration curve)
6. Current potential value
7. Value of the used titration current
8. Absolute value of chlorine content
9. Bar chart of gas flow
10. Results table
11. Status line

3.3.1.1. Input of samples for analysis

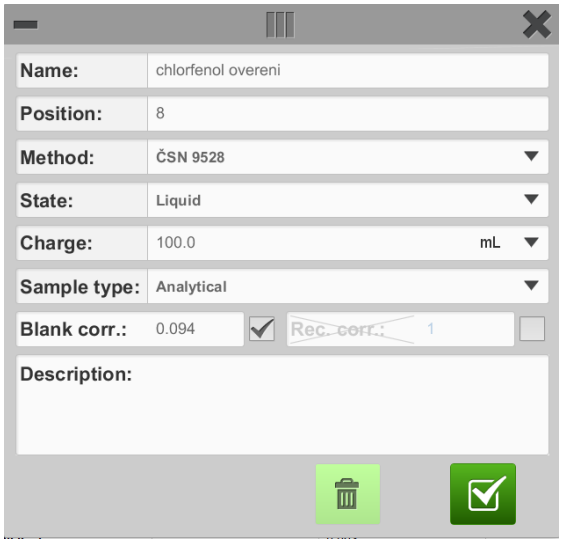
There are 10 positions at the bottom of the ENGINE LT main window to enter the sample. Editing is done by double clicking on the selected position (row) in the table.



- Switch to advanced sample editing, exit
- Sample name
- Position in the table (autosampler)
- Used method
- Sample state (liquid, solid)
- Sample amount for analysis (volume, weight)
- Sample description

Fig. 13 *Sample input – abbreviated*

By clicking on the icon in the top left corner of the window, you can go to the advanced sample entry, where type of sample and blank experiment and yield correction are entered.



- Type of sample (analytic, blank, yield)
- Blank correction, recovery (yield) correction

Fig 14. Sample input AOX – advanced

Fig. 15 Sample input EOX – advanced

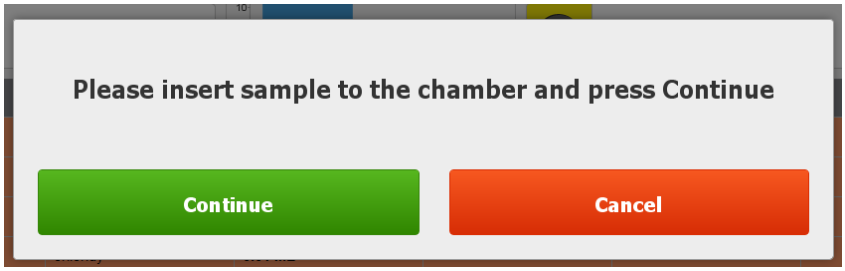
3.3.1.2. Setting of the E_{BIAS} value and drift control

The default value of the potential (-102mV) is set by clicking the E_{BIAS} button. The whole process takes place automatically. Read the actual value of the potential, according to the difference from the desired value, the instrument will select the corresponding current and titrate to -102mV and will automatically terminate this operation.

When the titration is complete, the stability of the detector is checked by pressing the DRIFT button. In the upper left window, the graph of the potential over time is displayed graphically, and after 120 seconds the value of the potential drift in mV/minute will appear in the information window. To terminate this operation click the STOP button in the status bar.

3.3.1.3. Selection and start of the analysis

Left mouse button marks the sample we want to analyze. A sample label appears in the status bar. Left click the start icon to start the analysis. The loading chamber opens and pull rod moves to the position where the boat can be inserted.



After the boot is loaded, the analysis starts with the Continue button, the next analysis is automatically controlled by the software.

3.3.2. Menu Results

All data on projects, methods, samples and results are automatically stored in the database. To view them, use the Results tab in the main ENGINE LT window.

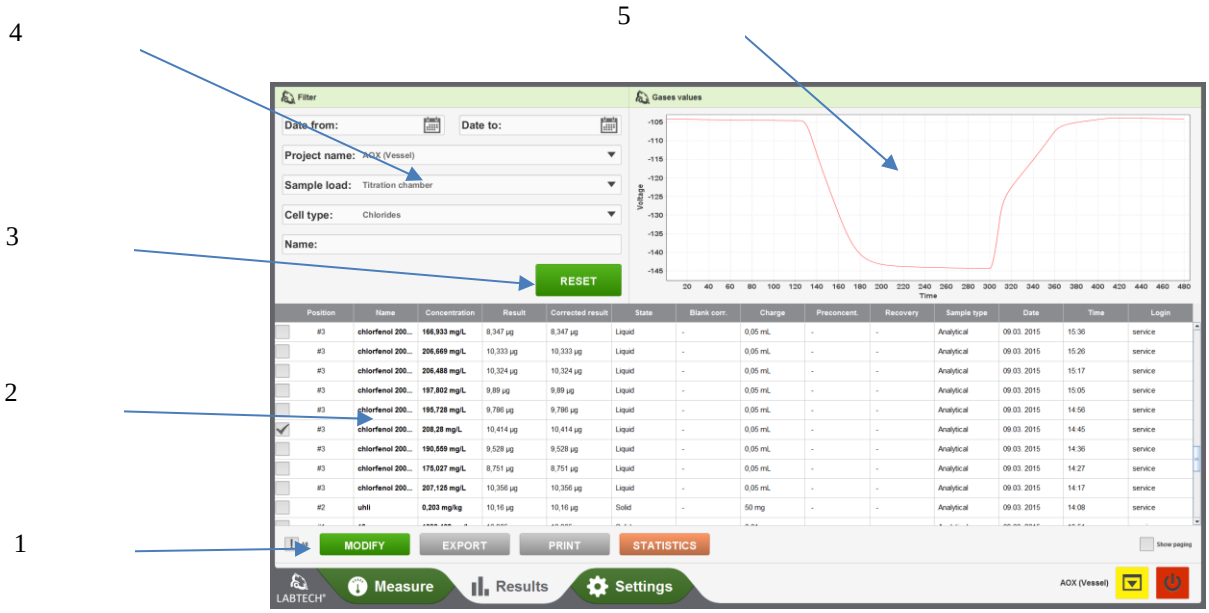


Fig 16 Main window ENGINE LT – bookmark Results

1. Buttons for manipulation with selected results
2. Table of analytical results
3. Reset – cancel the selected filter
4. Set the filter in the database by date of analysis, project name, sampling method, type of used cell and sample name
5. Graphical display of the analysis of the selected sample

3.3.2.1. Modify, export, statistics and results printing

Before using these option, it is necessary to mark the rows (samples) in the results table with which the respective operation will be performed. To do this, use the check mark in the first column of the table. Press the corresponding button to selected the results.

- MODIFY – insert a note on the selected sample or calculate the concentration to a different blank value
- EXPORT – export to a user-selected directory in .xls format
- PRINT – print selected results
- STATISTICS – to enter a blank trial correction into the table in the window MEASURE, it is necessary to select at least one BLANK result

3.3.2.2. Editing display data

ENGINE LT allows you to edit the data that is displayed and printed. Right click on the first of the results table (description of the columns). The option is displayed:

- Change columns
- Return to the original columns (Default columns)

When Change columns is selected, a menu of parameter options is displayed, from which you can select the desired option.

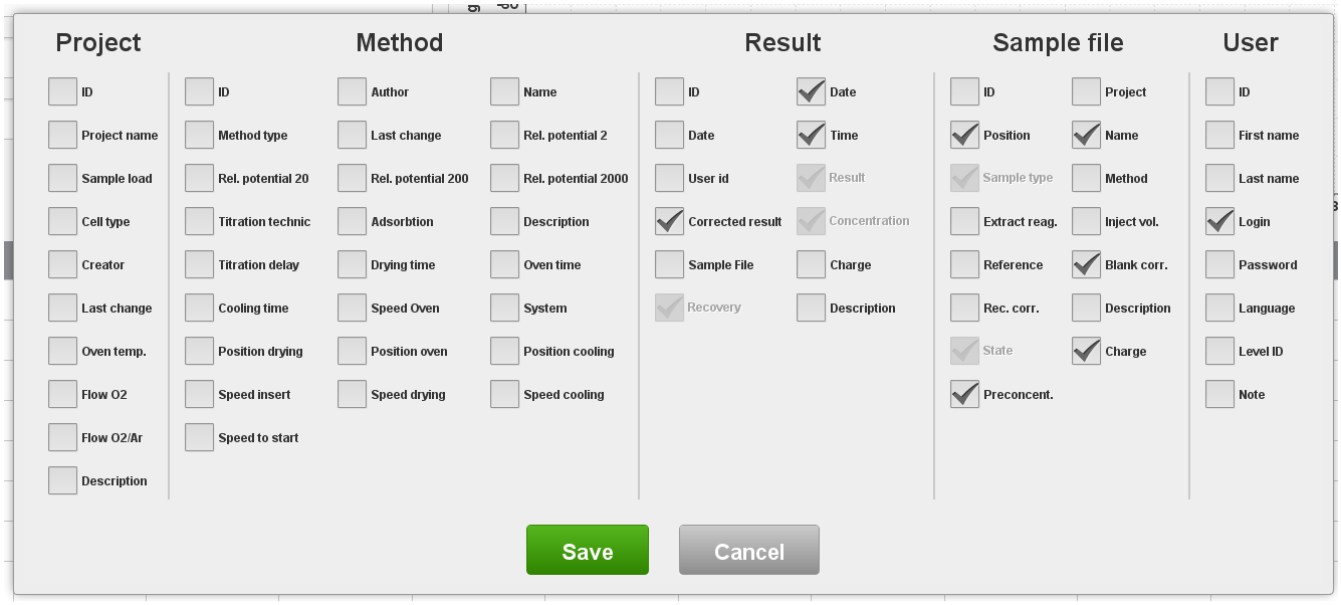


Fig. 17 Selection window for displayed parameters

3.3.3. Menu Settings

In the bookmark settings, the choice from the menu on the left side of the screen is possible:

- Device - diagnostics
- Method
- Database
- Service – displayed only for Service users

3.3.3.1. Diagnostics – graphical display

This window displays the current status of the device graphically. Colors show individual parts and their current status. Green – ready for analysis, orange – in use and red – out of standard specifications. The “vessel out” and “vessel in” buttons are used when changing the rod.

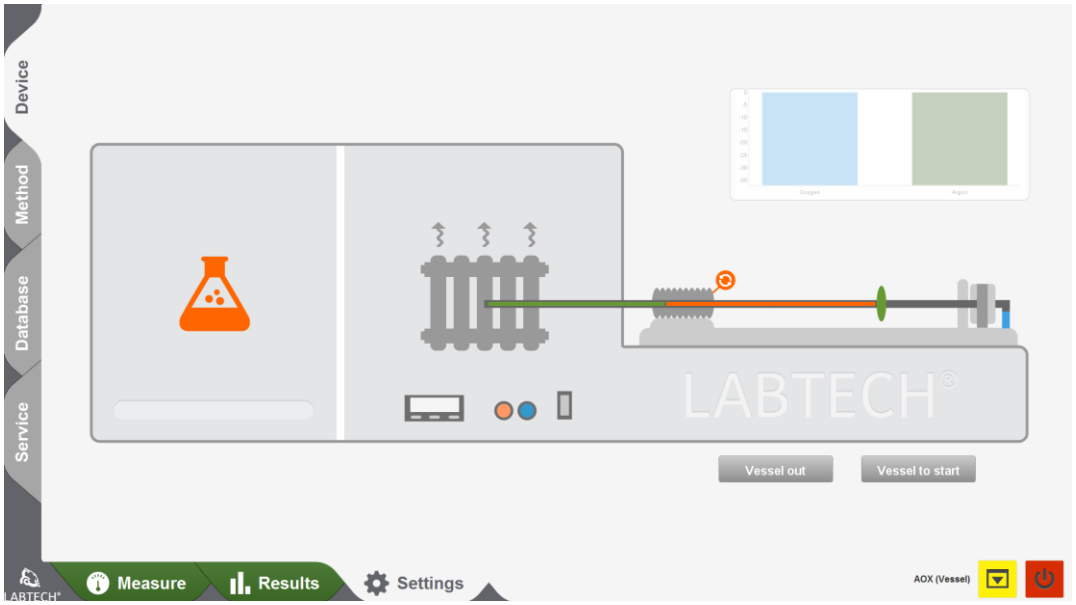


Fig. 18 Main window ENGINE LT – bookmark Settings – Device

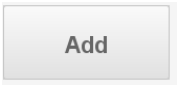
3.3.3.2. Menu Edit Method

This option displays all programmed methods for the currently opened project. At the factory preset methods are included standard set of the methods. Depending on access permission settings, the trained user can create additional methods, delete or modify existing methods. To do this use the icons:

- Save modified method

- Delete existing method

- Add new method



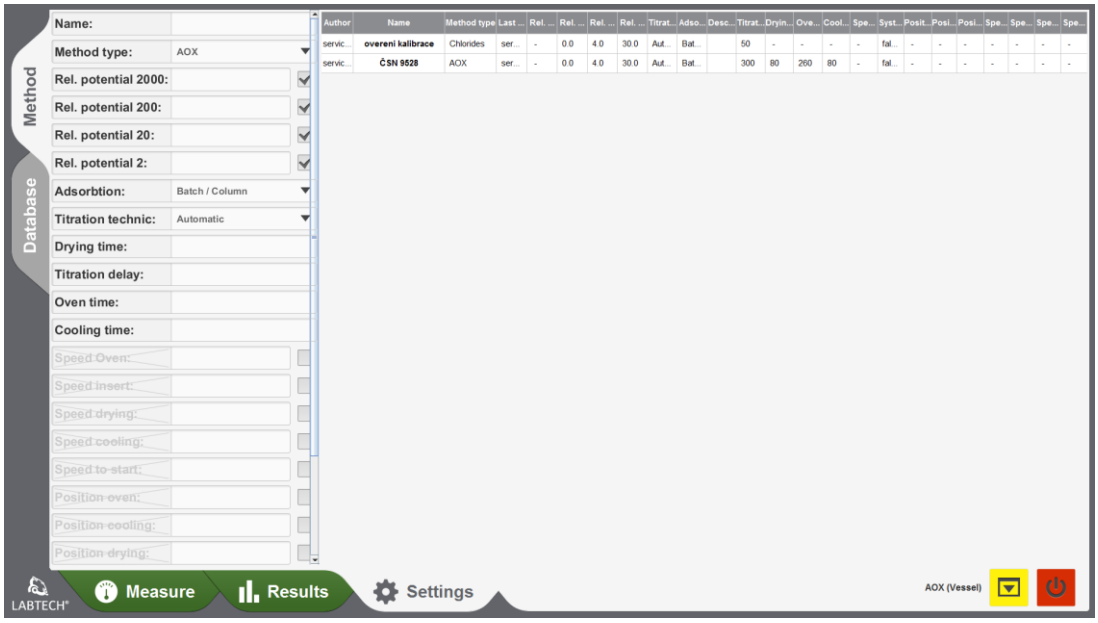


Fig. 19 Main window ENGINE LT – bookmark Settings – Method

3.3.3.3. Database editing of users

ENGINE LT allows you to set up three levels of access rights:
Administrator – can set access rights to other users, edit projects, methods and sample files
Method administrator – can edit methods and sample files
Laboratory technician – can edit sample files

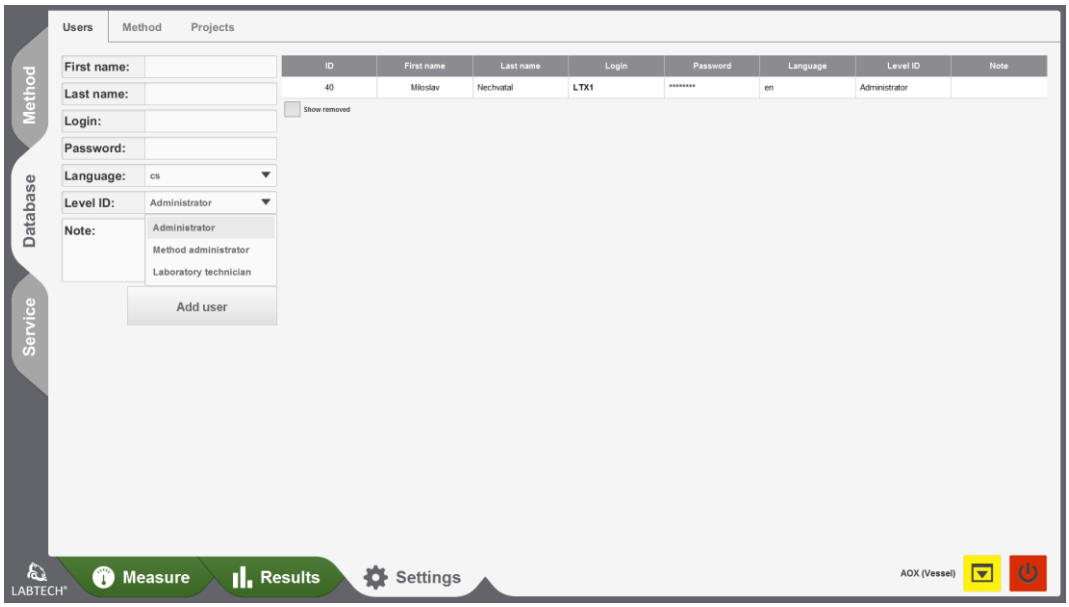


Fig. 20 Main window ENGINE LT – bookmark Setting – Database

3.4. End of program

Termination of ENGINE LT is done by clicking on the icon  , the software goes into the project selection window and by repeatedly clicking the left mouse button on the same icon, the program terminates.

Principle of the operation.

Chapter 4

4.1.Principle of the determination

Analyzer LTX Unique was designed with respect to the existing, especially standard procedures of the determination of organic halogenated compounds in waters, waste and their leachates, sludges, sediments, soils and heavy oils.

During combustion at defined temperature in oxygen are halogens bound to organic molecules converted to corresponding hydrogen halides.

Combustion products contain besides hydrogen halides and sulfur dioxide, as the object of the final determination, also CO_2, water and other compounds as the products from the combusted matrix:

Sample/matrix	Combustion products 850 - 1000^{O}C
X, C, H, N, P + O_2	**HX > X_2** CO_2 H_2O NO > NO_2 P_2O_5,

Where X represents Cl, Br and eventually I.

Determination of adsorbable and adsorbed organic halogenated compounds (AOX) is performed by combustion of activated charcoal (AC) serving as sorbent for sorption of the above mentioned compounds from waters, leachates and extracts from acidified water sample *or determination of these compounds adsorbed on the matrix of the sample. Inorganic halides, which should not be included in the result of determination, are eluted from the sorbent by a solution of $NaNO_3$ or KNO_3.*
In the case of the determination of organohalides adsorbed on soil, rock and similar matrices activated charcoal is added to the sample suspended in water. AC is used to catch the analytes during washing out of inorganic halides by solution of $NaNO_3$ or KNO_3.

Determination of volatile, organohalides (POX, VOX), represents the compounds capable to be stripped by a oxygen flow at a defined temperature (usually 40 or 60 °C) from the solution or suspension of the sample being analyzed. Water vapor and vapor of other volatile, often organic compound, are a matrix in this case.

Determination of extractable organohalides (EOX) represents a group of halogenated organic compounds with lower polarity able to be extracted from aqueous media with organic solvents with low solubility/polarity in water and containing not a traces of halogens. It is possible to use, in the case of extraction from a solid phase, even solvents with higher polarity and so expand the range to the more polar compounds. Therefore, it is necessary to state always, together with the results, also

the solvent used for extraction if it is not strictly stipulated by the used standard. Matrix is represented in this case by vapor of the used solvent and its combustion products (usually only CO_2 and H_2O) and transport of the sample from the evaporation into the combustion region of the furnace is influenced by volatility of the used solvent.

Determination of total halogens (TX) represents concentration of both organic and most of inorganic halides. Matrix in represented by the matrix of the analyzed sample and its combustion products often of complex composition.

In the case of determination of halogens the combustion products pass the heated path preventing condensation of water vapor and then absorber with conc. sulfuric acid to absorb water before entering the titration cell with the electrolyte (see 4.2). The cell is equipped with the generation electrode pair Ag/Pt and the indication pair $Ag//Hg/Hg_2SO_4$.

Determination of halides (Cl^-, Br^- and possibly I^-) absorbed in the electrolyte in the titration cell is carried out after combustion by microcoulometric precipitation titration according to:

$$Ag^+ + X^- \rightarrow \downarrow AgCl \qquad (1)$$

where concentration /activity of Ag^+ or Cl^- is determined by the solubility product:

$K_{S,a} = a_{Ag+} * a_{Cl-}$ (1a), depending on the reaction medium.

$K_{S,a}$ is estimated to be in the used medium in the order 10^{-14} and so concentration of $Ag^+ \approx 10^{-7}$ mol/l in the equivalence point.

Ag^+ is produced by the anodic oxidation of the silver anode by the stepwise decreased current i_t (2000 → 200 → 20 μA)>

$$Ag \rightarrow Ag^+ + e^- \qquad (1b)$$

when on the cathode, separated by a fritted glass disc, takes place reduction at the same time:

$$2H^+ + 2e^- \rightarrow \uparrow H_2.$$

Generation current is successively decreased according the preprogrammed manner as the titration proceeds and the voltage of the indication cell increases (see **Chyba! Nenalezen zdroj odkazů.**., REF _Ref151479572 \h * MERGEFORMAT **Chyba! Nenalezen zdroj odkazů.** and **Chyba! Nenalezen zdroj odkazů.**, **Chyba! Nenalezen zdroj odkazů.**):

$$\Delta E = E_i - E_r, \text{ where}$$

E_r is the potential of the reference and E_i the potential of the indication electrode dependent on the concentration/activity of Ag^+:

$$E_i = E_0 + RT/F \ln a_{Ag}$$

Reduction of the generation currents and so the rate of Ag^+ generation is controlled in such a way to ensure termination of the titration as accurately as possible in the equivalence point or better in the preselected (initial) voltage of the indication cell Ebias = -102,0 mV close to the equivalence point corresponding to only small excess of Ag^+.

Amount of Ag^+ generated by the coulometer is proportional to the charge Q passed the generation cell in coulombs (C):

$$M = A.Q \qquad (2)$$

where

A is the electrochemical equivalent $A = a/nF$ (2b)

with n number of exchanged electrons (in the case of reaction (1b) n = 1),

a is atomic mass and

F - Faraday charge (F = 96484 C).

The charge passing through the electrolyte in coulombs (C) at the variable current i_t (A) in the time interval 0 - t (s) is then:

$$Q = \int_0^t i_t \, . \, dt \qquad (3)$$

where

$\int_0^t$ is the integral value of the current (A) in the time interval 0 - t. As the molar concentration of Ag^+ is equivalent to the molar concentration of Cl^-, then 1 Faraday charge corresponds also according (1 and 1b) to 1 gramequivalent of Cl^- = 35,46 g.

Microcoulometry determines low concentrations of Cl^- to express the concentration of AOX, POX or EOX and often even TX. Therefore, the more convenient dimension of the charge is mC, and 1 mC corresponds to 0,0104 μeq, it is 1,1218 μg Ag^+ or 0,3675 μg Cl^-.

Amount of the determined halogens, expressed as chlorine, is calculated according the above relation and then 20μA.s ≈ 0.0073μg Cl^- supposing oxidation of the generation Ag anode to be quantitative (according 1a) and if there is no loss of Ag^+ by sorption on the precipitated AgCl and no decomposition of the precipitate. Under these conditions is the differentiability of the measuring device 0,01 μg Cl^- and the detection limit 0,03 μg Cl^-.

Composition of the electrolyte: 3.5% $NaClO_4$ in 60% acetic acid (preparation see 4.2)

4.2. General rules of operation

Open the cover of the module of the titration cell. Measure about 30 ml of the titration electrolyte and take care to have the levels of the electrolyte in the central vessel and in both side arms the same.

Respect the recommended composition of the titration electrolyte:

For the determination of halides: 12 ml 8.7% w/v $NaClO_4$ and 18 ml acetic acid (99 w %) (6.3.)
Preparation: Dissolve 50 g $NaClO_č.H_2O$ in about 400 ml of deionized water and dilute to 500 ml.

Preparation: dissolve 0.1 g KI, 0,1g NaN_3 and 1.1 g $K_2SO_4.H_2O$ in about 80 ml of deionized water (better - freed from oxygen by the flow of pure N_2 or Ar), add 0.5ml 99% CH_3COOH, mix and dilute to 100 ml by water.

Use reagent grade chemicals and prefer chemicals with declared lowest level of chlorides. Use $NaClO_4.H_2O$ with declared low level chlorides and perchlorates (6.3.)! Current concentration of acetic acid may change after opening the bottle. Change time worn electrolyte for a new one!

ATTENTION! Acetic acid may cause by spilling and staining very serious burns. Use protective gloves and glasses!

Check the level of electrolyte in the titration cell. All electrodes should be immersed by their active parts in the electrolyte.

Put magnetic stirrer into the central part of the titration cell, place the cell on the center of the electromagnetic agitator and fix it by the clamp on the stand. Close the central part by the PTFE cover and insert clean electrodes in the proper placings (see part 2.9.).

Check always if the electrodes are quite immersed by their active surfaces into the electrolyte and that there are no bubbles in/on the electrolytic bridge of the reference electrode!

Switch on the apparatus LTX Unique and the electromagnetic agitator. Set the speed of rotation of the stirrer onto the second unit of the scale (corresponds to the setting 12 on the clock dial). Open the program ENGINE LT, Then push the button *Ebias*. Automatic generation of Ag^+ or iodine will follow to set the selected Ebias. **Ebias = -102 mV for the determination of halides** Even concentration Ag^+ or I_3^- in the side arm of the reference electrode by repeated hitching up and pushing down the reference electrode in the joint. Then repeat Ebias set up. When Ebias stabilizes start measurement of drift of the indication cell (button *Drift*). Drift of the indication cell voltage, measured after several minutes, should be max. 0.15 mV/min. and actual values of the measured voltage should not vary more than ± 0.1 mV.

4.3. Confirmation of the coulometer calibration

Hydrochloric acid of the concentration 0.1 mol/l is recommended in standards and procedures stated in the chapter 1. It is possible to use also standard solution of NaCl corresponding to 1.000g/l Cl^-.

Select in the menu the project of the type *Chlorides*. Check the settings of the time intervals for titration delay in the method *calibration verification*. The interval is set by the producer to 20s. Edit sample file with the sample type *analytical* and the task for this measurement. 1 up to 50 µg Cl^- is the proper range to confirm accuracy. Optimal value is 10 µg Cl^- in the case of the use of the only one point for confirmation. Sample carefully microvolume of the solution 0.1 mol/l Cl^- or 1 g/l Cl^- corresponding to the set value of chlorides. Push the button *Go* and sample the selected volume into the titration cell. Repeat measurement of the calibration solution with different amounts of chlorides. Plot the regression straight line of the measured/sampled amount of chlorides. **Correlation coefficient should be greater than 0.999 and regression coefficient should be in the interval 0.97 - 1.03.**

Use only micropipettes with adequate confirmation to confirm the calibration of the microcoulometer. **Sampled volume should not exceed 50 µl.** Accuracy and precision of the confirmation of the calibration is determined usually by the precision and accuracy of dosing the microvolumes of chloride solution.
Precision and accuracy most micropipettes of the volume 1 - 20µl is characterized by the relative standard deviation 0.5 - 1.0%.

4.4.Determination of chlorides

Determination of chlorides in the microvolume samples is done in the same way as the confirmation of the microcoulometer. Edit the project of the type *Chlorides* and the sample file. Specify *Liquid* state of the sample and enter the sampled volume. Optimum volume is 0.020 ml of the sample. Sampled volume 0.050 ml causes already dilution of the electrolyte and decrease of the potential of the indication electrode. It is possible to use blank correction (e.g. in used demineralized water to obtain leachates or to dissolve solid samples etc.) when the determination of chlorides is performed in the mode of analytical samples. The measurement is identical with the described in the previous paragraph.

Microcoulometric determination is suitable for samples containing more than 20 mg/l Cl^- and sampled volume 20 µl. The optimum range is 200 - 2000 mg/l Cl^-.

4.5. *Determination of AOX*

Select first the project of the type AOX and edit sample file containing samples you are to measure. Connect the analyzer to the oxygen cylinder, set on the pressure control valve the output pressure 0.15 MPa. Set the outer oxygen flow to 75 counts.

Pour about 5 ml of conc. sulfuric acid into the absorber and check tightness of the discharge faucet.

Leave glass beaker permanently below the discharge cock to catch possible drops of sulfuric acid. Pour sulfuric acid into the absorber after running oxygen through the apparatus.

ATTENTION! Sulfuric acid can cause serious burns!!! Therefore use always rubber gloves and protection glasses during handling with sulfuric acid!!!!!!!

Switch on power to the furnace, and set possibly the requested temperature of the combustion furnace by the controls of the regulator CAL 3200.

For the determination of AOX use 950 °C as combustion temperature.

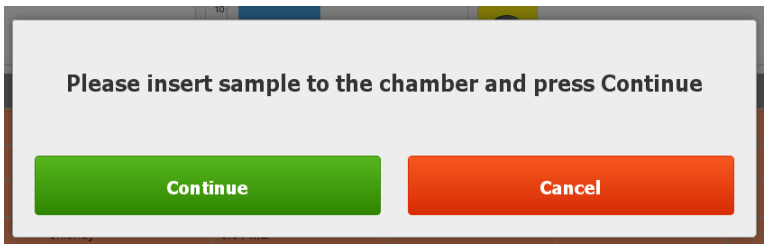
Requested temperature will be reached during approx. 30 min. Prepare titration cell and set Ebias during this time, as described in part 4.12. Carry out also the confirmation of the function of the microcoulometer by an everyday procedure described in par. 4.2. Measurement of a single point in the center of the working range of the microcoulometer (e.g. 10 µg Cl^-) is normally adequate.

Check the flow of gas into the titration cell. Clean mechanically rest of ash from the boat.

4.5.1. Determination of blank value

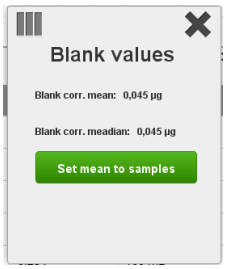
It is a good practice to determine several blanks before the measurement of analytical samples. Use the same project and method selected for the measurement. Change the *Sample file* to contain also samples of the type *Blank*.
Left mouse button marks the sample that we want to analyze (Blank.). The sample designation appears in the status bar. Left-click the start icon to start the analysis. The chamber opens and the pull rod moves to the position where the boat can be inserted.

After the boat is loaded, the analysis starts with the continue button, then the analysis is automatically controlled by the software.



After the measurement is finished, the results are stored in the database. Add the correction value into further measured samples. Select the bookmark *Results* and the results of the blank measurements. Click on the *STASTICS* icon to display the calculated Blank correction mean window. Enter this value to all programmed samples of *Analytical type* by selecting *Set mean to samples.*

Figure 21 - Blank test window



NOTE: It is a good analytical practice to give attention to the content of organohalides determined not only in the complete analytical procedure, but also to individual contributions to the final blank (activated charcoal, PC filters, used chemicals, demineralized water used to prepare solutions, lab atmosphere etc.)

4.5.2. Determination of recovery

It is very useful to verify the recovery after determination of blank value. Standard solution of 4-chlorphenol or 2,4,6-trichlorphenol is used conventionally for the recovery test. In the menu *Sample* select the type *Recovery*. Fill out the amount of the organically bound chlorine [µg] in the box *Value*. Select the form for blank correction in the task. It is recommended to correct by the mean value of blank in the case of normally distributed individual measurements or after excluding outliers.

Update and possibly test the selection of measured values of blanks in the menu *Results* and *Blanks* for outliers before choice of the correction by the mean value of blank.

Measure the sample of the recovery test as described above.The calculated coefficient of recovery will be displayed after titration terminates.

4.5.3. Analysis of the routine analytical samples

Assemble a sample file, enter and check the recovery value (default value 1), and the blank correction value. In the Sample type select the Analytical. Enter the sample state (liquid or solid) and charge of the measured sample (volume or weight).
Use the left button to mark the first sample and start measurement as described above. Upon finishing, another sample is automatically offered for analysis. The name of the sample currently being measured is listed in the status bar. All information about already measured samples is stored in the database and can be viewed in the RESULTS bookmark.

4.6. Determination of EOX

Remove the module AOX and the combustion tube for AOX and install the module EOX including also the combustion tube as described in par. 5.3. Connect input tubings of gases - oxygen and argon to the couplings in the rear panel of the instrument.

Check always agreement of the input markings of oxygen and argon on the rear panel and the tubings of individual gases. Oxygen is introduced by the hosing 6 mm o.d. and argon by the hosing with 8 mm o.d. to prevent confusion.

ATTENTION !!!

Transposition of argon and oxygen inputs can lead to the explosion !!!!

Prepare the titration cell and carry out the calibration of the coulometer as described in par. 4.2 and 4.3. Set the argon flowrate (by the valve of the flowmeter in the right side) to 40 mm of the scale and the flowrate of oxygen (by the valve on the left hand flowmeter) to 55 mm of the scale. Pour approx. 5 ml of conc. sulfuric acid into the absorber of water vapor. Open project type EOX. Set the titration delay to 490 s and the run out time of the graph to 20 s in EOX method. Compile the sample file with the sample of the type *Blank*. Titration delay can be proportionately reduced in the case of sampling less than 250 µl. Check the switch of the pump to be in the position on. Release the drive of the pump and shift it along the spindle quite to the right.

Fill gastight syringe (with the needle of 110 mm length) by the used solvent (e.g. hexane purity "for pesticide anal." with low content of Cl) accurately to the volume 250 µl (be careful to expel all, even small bubbles, from the syringe and needle). Place the syringe with the sample into the guide groove of the linear pump and fix it by the spring clamp. Shift the drive close to the piston rod. Move the pump in the guideline to the left and run through the middle of septum. Start the measurement sequence by the button *Go* in the dialogue panel *Measurement* and slide slowly entire needle into the evaporation part of the combustion tube (linear pump is then shifted quite to the left to the furnace and to the stop) and switch the pump on. Switch off the power to the pump when the sampling has been finished (terminal switch is switched off). Shift the pump about 40 mm to the right and wait about 1 min. to cool the tip of the needle. Then you can pull the needle out of the septum, release the drive and take the syringe out.

Leave the needle to cool to the ambient temperature before filling the next sample. Always flush the syringe by the next sample. Recharge regularly the absorber of water vapor. Foaming of sulfuric acid after about 10 injections of 250 µl of hexane indicates the proper time to recharge acid in the absorber.

It is a good practice, prescribed in majority of standards, to determine blank of the whole analytical procedure in addition to the blank of the used solvent(s) and to verify recovery of the standard compound (e.g. 5 - 10 µg Cl using aldrin). Then you can analyze the routine samples.

4.7. Turn off the instrument

Turn off the instrument after completion of measurements in this sequence:

- Switch off the electromagnetic stirrer
- Discharge sulfuric acid from the absorber into the beaker and release the hemispherical ground joint connecting the absorber with the outlet of the combustion furnace to prevent the rest of sulfuric acid in the transport path to suck into the hotter parts and to the furnace.
- Close the gas supplies
- Switch off the instrument LTX Unique
- Switch off SW ENGINE LT and PC

Maintenance of the analyzer and exchange of modules

Chapter 5

5.1. Maintenance of electrodes and the titration cell

At the normal frequency of measurements carry out maintenance of the electrodes daily and once or twice a week change of the electrolyte for halides including cleaning of the titration cell. It is necessary to take out both silver electrodes and the reference electrode from the titration cell and close the cell cap by stoppers of silicone rubber NZ 14 and NZ 10 after each working day. Rinse the electrodes with distilled water. Silver electrodes should be kept dry till the next measurement. Put a rubber cap on the tip of the reference merkurosulfate electrode; alternatively keep the reference electrode upright with the tip immersed into the solution of saturated solution of K_2SO_4. Platinum electrode can be left alternatively in the titration cell.

Remove daily, before measurement, the coating of AgCl from the generation electrode (e.g. by dissolution in the solution of ammonia). Repolish the surface of the generation anode and the indication electrode by finely ground limestone on a soft cloth, rinse by a stream of water and then dry. Check the inner part of the reference electrode for absence any bubbles and other defects (e.g. paucity of inner electrolyte: saturated solution of K_2SO_4). Clean occasionally fritted ceramic in the tip of the reference electrode by an emery paper.

Many failures of the indication cell are caused by the malfunction of the reference electrode. Pay attention to the service of the reference electrode, possibly replace it. Check always quite immersion of the active parts of all electrodes in the electrolyte and absence of bubbles on electrodes and interfaces.

Rinse the titration cell and the magnetic stirrer by a solution of ammonia and then by diluted HNO_3. Clean in this way also both side arms of the cell, especially the fritted glass in the arm and the platinum cathode. Rinse the cell with water and then leave it to dry.

5.2. Servicing other parts of the instrument

Routinely check the state of glass parts of the apparatus, couplings and seals.

Quartz sampling boat should be cleaned frequently from the ash of the used charcoal and rests of combusted samples. Ash contains salts of alkaline metals, which gradually damage quartz glass. Ash can be removed mechanically. Do not forget to anneal the boat after any contact with foreign material before the analysis of the next sample. Replace the worn boat for a new one.

Exchange of the combustion tube: Lifetime of the quartz combustion tubes is under normal operation conditions several years. Nevertheless, visual inspection of the tube from time to time and to clean from the condensate which may be formed inside the tube, especially in the entrance port

and in the exit capillary, is strictly recommended. Follow the instructions for the exchange of the tubes as described in par. 5.3 for the exchange of the AOX and EOX modules. Soot can be settled particularly in the exit capillary of the tube in the case of imperfect combustion of some liquid samples, especially aromatics. It is necessary to remove soot and the products of pyrolysis by shifting the contaminated part of the tube into the hot zone of the furnace and annealing in the oxygen flow.

Check the state and tightness of the plastic tubings in the couplers in the rear panel, in the chamber(s) of the module(s) and the side arm of the combustion tube. Lubricate slightly O-rings by a silicone grease before inserting the glass and quartz tubes into the steel adapters. Lubricate slightly also the hemispherical ground joint combustion tube(s) with the water vapor absorber. Do not grease neither the PTFE discharge cock of the absorber nor the ground glass cap of the absorber.

Do not leave sulfuric acid in the absorber after finished measurement. Open the gas flows through the system before pouring a new portion of sulfuric acid into the absorber. So, you can prevent overheating of sulfuric acid in the inlet capillary causing fuming of the sulfuric acid. Frequently check the tightness of the connection silicone rubber hoses over the PTFE tubing coupling absorber and the titration cell.

Exchange septa in the sampling adapter for EOX if required. Lifetime of septa is about 50 injections. Drawing out hot needle reduces the lifetime of septa.

5.3.Exchange of the sampling modules

Attention! Combustion furnace should be always switched off during the exchange of the modules and combustion tubes. Ceramics of the combustion furnace is conductive at higher temperatures and touching it can cause injure by electricity.

5.3.1. Installation of the module AOX

- Insert the combustion tube for AOX into the furnace from the right hand side (Fig. 6.)
- Slide AOX module to the control unit to be in the axis of the furnace.
- Keep the sampling module AOX by the right hand and insert the combustion tube by your left hand turning it slightly into the "O-rings" in the sampling cell
- Shift the whole module with the tube to the left a fix it by central screw
- Connect one connectors to socket on side wall of the main unit
- Put together the hemispherical ground joint of the combustion tube and the water vapor absorber and fix it by the spring clip

Demount the module in the reverse order.

Attention! Combustion tube may be still hot when it is taken out from the furnace! Do not touch the hot parts of the tube and do not lay it on the surface not enough thermally resistant.

5.3.2. Installation of the module EOX

- Insert the combustion tube for EOX into the furnace from the right hand side (Fig.)
- Slide EOX module to the control unit to be in the axis of the furnace.
- Keep the sampling module EOX by the right hand and insert the combustion tube by your left hand turning it slightly into the "O-rings" in the sampling cell
- Shift the whole module with the tube to the left a fix it by central screw

- Connect connector to socket on side wall of the main unit
- Put together the hemispherical ground joint of the combustion tube and the water vapor absorber and fix it by the spring clip
- Connect connector of the linear pump to socket on side wall of the main unit

Demount the module in the reverse order.

5.3.3. Installation of the structure for POX

- Insert the EOX combustion tube from the right-hand side into the furnace
- Slide the part of the EOX module with the sampling adapter from the right-hand side into the leading grooves
- Keep the sampling module EOX by the right hand and insert the combustion tube for AOX by your left hand, turning it slightly, into the "O-rings" in the sampling adapter
- Shift the above part of the module with the combustion tube to the left, fix it by inserting the arresting pins into the holes in the guide bars and put together the hemispherical ground joint of the combustion tube and the water vapor absorber and fix it by the spring clip
- Pull the hose with outer gas into the snap coupler (Φ = 4 mm)
- Pull the hose with inner gas - connection with output from the scrubber in the thermostat - into the snap coupler (hose Φ = 6 mm)
- Install thermostat and leave it to reach the set temperature

Demount the structure in the reverse order.

List of consumables

Chapter 6

Consumable material to assure run of the LTX Unique analyzer consists of glass parts of the apparatus, hoses, coupling material and sealing elements, electrodes etc..

6.1.General Consumables

	AOX
L019888	Combustion tube AOX-UNIQUE+
L009358	Silica boat
L009360	Silica rood UNIQUE
L006252	Nucleopore Polycarbonate membrane AOX = 25 mm, size18 ; 0,45 micron
L001359	Activated Carbon AOX Batch 50g (filters)
L001357	Activated Carbon AOX Batch 50g (frits)
	EOX
L015119	Combustion tube EOX-UNIQUE
L011638	Steel needle for syringe
L012383	Syringe
L014718	Septum silicon BTO 1/2" pckg/10pcs

6.2. Consumables for AOX and EOX method

L009835	Magnetic stirrer
L009837	Magnetic stirring bar
L015518	Clamp of the spherical-ground joint
L016070	Titration cell
L017713	Cover of the titration cell PTFE
L005378	Indication Ag electrode (PTFE) incl. O-ring
L005374	Generation Ag electrode (PTFE) incl. O-ring
L005377	Generation Pt electrode NZ 10 (white)
L005381	Reference electrode Hg/Hg2SO4
L014949	Glass gas connection taper joint for titration cell
L018332	Taper joint topping
L000646	Absorption cell incl. heating element
L011415	O-ring 17x2,5 Silicon 70 (red)
L011423	O-ring 9x2 Silicon 70
L011421	O-ring 35x3 Silicon 70
L007896	Silicon tube 1 m
L007895	PTFE tube 1 m
L008641	Sodium perchlorate

Consumables and service of the instrument LTX-Unique support:

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