NTEGRA Probe NanoLaboratory

Electrochemical measurements

Instruction Manual

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Read me First!

Observe safety measures for operation with devices containing sources of laser radiation. Do not stare into the beam. A label warning about the presence of laser radiation is attached to the measuring head (Fig. 1), laser sources.

![Laser Radiation Alert Label](https://example.com/laser_label.png)

**Fig. 1**

Before you start working with the instrument, get acquainted with the basic safety measures and the operation conditions for the instrument!

*If you are a beginner in scanning probe microscopy, we recommend you to familiarize with basic SPM techniques. “Fundamentals of Scanning Probe Microscopy” by V.L. Mironov gives a good introduction to the subject. This book is available on the Internet, [http://www.ntmdt.com/support](http://www.ntmdt.com/support).*

Feedback

Should you have any questions, which are not explained in the manuals, please contact the Service Department of the company ([support@ntmdt.ru](mailto:support@ntmdt.ru)) and our engineers will give you comprehensive answers. Alternatively, you can contact our staff on-line using the ask-on-line service ([http://www.ntmdt.com/online](http://www.ntmdt.com/online)).
User’s documentation set

The following manuals are included into the user’s documentation set:

- **Instruction Manual** – is the guidance for the preparation of the instrument and other equipment for operation on various techniques of Scanning Probe Microscopy. The contents of the user’s documentation set may differ in dependence on the delivery set of the instrument.

- **SPM Software Reference Manual** – is the description of the control program interface functions, all commands and functions of the menu and, also a description of the Image Analysis module and the Macro Language “Nova PowerScript”.

- **Control Electronics. Reference Manual** – is the guide to SPM controller, Thermocontroller and Signal Access module.

Some equipment, which is described in the manuals, may not be included into your delivery set. Read the specification of your contract for more information.

The manuals are updated regularly. Their latest versions can be found in the site of the company, in the section “Customer support” (http://www.ntmdt.com/support).
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1. Basic Information

1.1. Intended Use and Modes of Measurement

The NTEGRA EC configuration is designated for imaging the surface morphology in the course of chemical reactions. This configuration contains an electrochemical cell that provides control of the sample temperature in the range from –10 ° to +60 °C.

NTEGRA EC configuration enables the observation of the following processes and objects:

- formation of electrochemical adsorption layers;
- electrodeposition and electrodissolution of metals;
- electrocorrosion and electroreduction;
- oxidation of metals and other conductive materials;
- electrically active nanoscale centres, ions and molecules;
- mass transfer.

The instrument enables the measurements using the following modes and techniques:

- AFM: Contact AFM; Semicontact AFM; Lateral Force Imaging; Adhesion Force Imaging; Force Modulation Mode; Phase Imaging Mode; AFM Lithography (force).
- STM: Constant Current Mode, Constant Height Mode, Barrier Height Imaging, Density of States Imaging, I(Z) spectroscopy and I(V) spectroscopy.
### 1.2. Specifications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scanning measuring head for operation in liquid:</strong></td>
<td></td>
</tr>
<tr>
<td>Scanner</td>
<td>$100 \times 100 \times 10 , \mu m ,(\pm10%)$</td>
</tr>
<tr>
<td>RMS X, Y sensor noise in 300 Hz band</td>
<td>$\leq 0.3 , nm$</td>
</tr>
<tr>
<td>RMS Z sensor noise in 1000 Hz band</td>
<td>$\leq 0.07 , nm$</td>
</tr>
<tr>
<td>XY sensor linearity error</td>
<td>$\leq 2.0 %$</td>
</tr>
<tr>
<td><strong>EC STM Head</strong></td>
<td></td>
</tr>
<tr>
<td>Scanner</td>
<td>$100 \times 100 \times 10 , um ,(\pm10%); \ 3 \times 3 \times 2 , um ,(\pm10%)$</td>
</tr>
<tr>
<td>Preamplifier</td>
<td>$\pm 50 , nA$, noise $3 , pA$.</td>
</tr>
<tr>
<td><strong>EC Cell</strong></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Teflon, PEEK 1000</td>
</tr>
<tr>
<td>Volume of electrolyte</td>
<td>1.5 ml (without the temperature sensor and the Ag/AgCl electrode)</td>
</tr>
<tr>
<td></td>
<td>3.5 ml (if the temperature sensor is used and/or the Ag/AgCl electrode operates)</td>
</tr>
<tr>
<td>Sample positioning range</td>
<td>$1 \times 1 , mm$ (limited by the diaphragm)</td>
</tr>
<tr>
<td>Temperature range</td>
<td>from $-10^{\circ}$ to $+60 , ^{\circ}C$</td>
</tr>
<tr>
<td><strong>Electrodes</strong></td>
<td></td>
</tr>
<tr>
<td>Working (sample)</td>
<td>$\varnothing 10 \div 28 , mm$, thickness $0.1 \div 3 , mm$</td>
</tr>
<tr>
<td></td>
<td>wire of Cu, Pt, Au or another conductive material with diameter up to $1 , mm$</td>
</tr>
<tr>
<td>Counter</td>
<td>wire of Cu, Pt, Au or another conductive material with diameter up to $1 , mm$;</td>
</tr>
<tr>
<td></td>
<td>material depends on experimental conditions;</td>
</tr>
<tr>
<td></td>
<td>$-$ Ag/AgCl</td>
</tr>
<tr>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td><strong>Bipotentiostat</strong></td>
<td></td>
</tr>
<tr>
<td>Output Compliance Voltage</td>
<td>$\pm 15 , V$</td>
</tr>
<tr>
<td>Applied Voltage Range</td>
<td>$\pm 4 , V$ (stability $\pm 1 , mV$)</td>
</tr>
<tr>
<td>Current Ranges</td>
<td>$\pm 5 , mA; \pm 100 , \mu A; \pm 2 , \mu A$ (accuracy of measurement $\pm 0.1 %$ of the range)</td>
</tr>
<tr>
<td>Reference Input Impedance</td>
<td>$&gt; 10^{11} , Ohm$</td>
</tr>
</tbody>
</table>
1.3. **Instrument Components**

NTEGRA EC configuration includes the following basic systems and units:
- Base unit;
- Protective hood;
- Optical Viewing System;
- Vibration Isolation System;
- Controller;
- Computer;
- Electrochemical measurement unit:
  - Scanning measuring head (AFM or STM);
  - Electrochemical cell;
  - Bipotentiostat;
  - Preamplifier.

![Fig. 1-1. General view of PNL NTEGRA Aura configured for STM electrochemical measurements](image)

1 – base unit; 2 – optical viewing system; 3 – vibration isolation system; 4 – ES STM head; 5 – bipotentiostat; 6 – electrochemical cell; 7 – preamplifier
1.3.1. Electrochemical Cell

The electrochemical cell is designed for electrochemical measurements *in situ* or *ex situ* with STM and AFM techniques. The cell provides measurements in the range of temperatures from –10 °C to +60 °C. The cell can operate with the 3-electrode or with the 4-electrode system.

The cell is mounted on the base with the standard carriage (Fig. 1-2) that is fitted to the positioning device of the base unit.

The cell is fabricated either from Teflon® or from Ketron PEEK 1000.

The cell consists of the following parts (Fig. 1-3):

- cell housing;
- clip plate;
- clip ring;
- cover;
- ground wire with the connecting spring;
- outlets for feeding liquid/gas;
- gags;
- electrodes.
Electrochemical measurements. Instruction Manual

Fig. 1-3. Parts of the electrochemical cell
1 – cell housing; 2 – clip plate; 3 – clip ring; 4 – cover; 5 – ground wire with the connecting spring;
6 – outlets for feeding liquid/gas; 7, 8 – gags; 9 – electrodes

The sample is placed at the center of the bottom of the housing 1, pressed with the clip plate 2 that has a hole for the sample, and then fixed with the spring 3 that should be tightened in the cell housing with small effort. The connecting spring (pos. 5) made of Pt-Ir wire provides electrical contact of the sample. The clip spring presses the connecting spring against the sample and in addition protects side edges of the sample from exposure by electrolyte.

The electrodes are to be made of a conductive wire of diameter up to 1 mm. Besides, the delivery set of EC (electrochemical cell) provides the Ag/AgCl\(^1\) for the reference electrode.

The cell can be equipped with the following parts if necessary (Fig. 1-4):
- outlets for feeding liquid/gas (pos. 1, 2);
- Ag/AgCl electrode (pos. 4).

Fig. 1-4. Assembly of EC
1, 2 - outlets for feeding liquid/gas; 3 – temperature sensor; 4 - Ag/AgCl electrode

\(^1\) The delivery set of the electrochemical cell contains the Ag/AgCl electrode manufactured by Cypress system, Inc.
The wire electrodes and the ground wire pass slots at the top of the cell housing.

Heating/cooling the sample as well as maintaining it at the desired temperature is performed with Peltier elements that are placed at the cell base. To keep temperature of the cold faces of the Peltier elements, a flow system of water-cooling is used.

⚠️ **ATTENTION! Do not use the EC cell without water-cooling system in order to avoid damage to the cell.**

![Base of EC](image)

**Fig. 1-5. Base of EC**
- 1 - carriage;
- 2 - connecting pipes of the liquid cooling system;
- 3 - clips;
- 4 – fastening screw of the cell;
- 5 – contact of the auxiliary electrode;
- 6 – contact of the reference electrode;
- 7 – contact of the sample

Temperature is controlled with two sensors one of which is placed in the base and another is in the cell housing (see pos. 3 on Fig. 1-4).

The cell base is mounted on the standard carriage 1 (see Fig. 1-5) that is installed in the positioning device of the base unit.

Clips 3 serve for sealing the cell in experiments under controlled atmosphere. The screw 4 fastens the cell to the base. The base contains the transient contacts 5, 6, and 7 to connect electrodes to external contacts.

The connecting pipes 2 attach tubes of the cooling system.

The cell is universal in the sense that it could be used for electrochemical measurements both with AFM and STM techniques.

The EC can be used with the following models of measuring heads:
- scanning AFM head for operation in liquid (see description in i. 1.3.3 on page 13). Electrochemical measurements are performed with the 3-electrode scheme (see details in i. 1.4 «Principles of Operation» on page 18);
Electrochemical measurements are performed with the 4-electrode scheme (see details in i. 1.4 «Principles of Operation» on page 18).

The delivery set of the electrochemical cell contains:

- electrochemical cell in assembly;
- tubes of the cooling system;
- tube for supplying liquid/gas;
- cables kit for calibration of the bipotentiostat;
- kit of insulated tips for electrochemical measurements with STM.

### 1.3.2. Electrochemical Scanning STM Head

Scanning electrochemical heads of models SFS03ECNTF (scan range $3 \times 3 \times 3 \ \mu m$) and SFS100ECNTF (scan range $100 \times 100 \times 10 \ \mu m$) are designed for 4-electrode scheme of measurements (see details in i. 1.4 «Principles of Operation» on page 18).

General view of the electrochemical STM head (hereafter called EC STM head) is shown on Fig. 1-6.

EC STM head serves for STM measurements in chemical environment. Besides, it can be used in standard STM modes as well.

The EC STM head with scan range $100 \times 100 \times 10 \ \mu m$ (SFS100ECNTF model) is equipped with position sensors that provide fine adjustment over all three spatial directions.

The scanner is protected against corrosive environment with a fluoroplastic protector.
The head package includes a diaphragm (Fig. 1-7) that covers the cell tightly from the top during measurements thus providing leakproofness of the cell.

![Fig. 1-7. Diaphragm of the EC STM head](image)

### 1.3.3. Scanning AFM Measuring Head

This scanning measuring head is designed for 3-electrode scheme of measurement (see details in 1.4 “Principles of Operation” on page 18). The probe holder of this head is replaceable and so measurements are available both in STM and in AFM modes. The scanner of the measuring head is equipped with position sensors that provide fine adjustment over all three spatial directions.

General view and the main components of the scanning measuring head for operation in liquid are presented in Fig. 1-8.

![Fig. 1-8 Main components of the scanning measuring head](image)

1 – laser adjustment screws; 2 – photodiode adjustment screws; 3 – threaded supports; 4 – mirror; 5 – props; 6 – probe holder seat
**Probe holders**

The following replaceable probe holders are available for operation with the electrochemical cell:

- for AFM measurements in liquid (Fig. 1-9);
- for STM measurements in liquid (Fig. 1-10).

The STM probe holder expands capabilities of the measuring head by providing it with STM modes.

The sketch of the AFM probe holder is given in Fig. 1-11. It consists of disk 1 on the base of which glass pedestal 2 is mounted. The probe is fixed on the pedestal 2 by means of removable clip 3, the lower end of which is inserted in slot 4 in the base.
Chapter 1. Basic Information

The glass pedestal has two beveled sides 5 and 6 in its upper part serving as seats for the probe. The tilting angles of the sides differ, side 6 with the smaller angle being intended for the installation of the probe for operation in liquid, while side 5 with the larger angle is meant for operation in air and in gaseous media.

The clip spring is protected against corrosive environment during electrochemical measurements with polymeric covering.

For pressurizing the working area of EC, the probe holder is equipped with the diaphragm (Fig. 1-12). The diaphragm is made of silicon rubber and is fixed in metal ring 4.

Fig. 1-12. Probe holder inserted into the diaphragm
1 – probe holder; 2 – diaphragm; 3 – probe holder washer; 4 – ring

To prevent the diaphragm from damage while fixing the holder on the measuring head the fitting tool shall be used (Fig. 1-13). This fitting tool has two right sides for aligning the holder in set-up and working positions.

Fig. 1-13. Fitting tool

The holders are fixed on the measuring head by magnets (Fig. 1-14). Four ferromagnetic sectors are glued to the holder from below (Fig. 1-15). To avoid shocks when mounting the holder on the measuring head, the former is first positioned so that the ferromagnetic inserts fall between the magnets. Then the holder is turned until the inserts coincide with the magnets, thus providing magnetic clamping to the scanner tube.
Auxiliary mirror

The auxiliary mirror (Fig. 1-17) reflects image of the object under control to the objective lens of the optical microscope. The mirror is used for aiming the laser at the cantilever with the optical viewing system as well as for selecting the area to scan.

The mirror is mounted on the front supports of the AFM measuring head.

Observation is conducted normally to the sample surface using the viewing mirror of the measuring head and the auxiliary mirror (Fig. 1-17).
1.3.4. Bipotentiostat

The bipotentiostat is designed to control potential of the working electrode relative to the reference electrode or to drive the desired current of the sample. It can be operated in potentiostat and galvanostat modes.

Fig. 1-18 presents the location of counterpart connectors on the bipotentiostat back panel.

**Fig. 1-18. Location of the bipotentiostat connectors**

- **COM BP** – computer connection;
- **CELL** – preamplifier connection;
- **EXTENSION** – power supply connection;
- **TIP** – connection of EC STM head (STM only).
Preamplifier

The preamplifier (see Fig. 1-19) is mounted on the base unit. It is intended for the connection of electrodes to the bipotentiostat, as well as for the calibration of the latter.

Connectors CNT and REF are used in measurements. Other connectors serve for calibrating the bipotentiostat and for operations with the solution equivalent.

Designation of the connectors:

CNT – counter electrode connector;

REF – reference electrode connector;

TIP – tip potential measurement connector (used for STM only);

WRK – working electrode (sample) potential measurement connector;

100 M – equivalent tip resistance (used for STM only);

1 M – equivalent working electrode resistance in the currents range up to 2 µA;

20 K – equivalent working electrode resistance in the currents range up to 10 µA;

0.5 K – equivalent working electrode resistance in the currents range up to 5 mA;

R_D (Reference_Dummy) – equivalent reference electrode.

1.4. Principles of Operation

The main feature of operating SPM in electrolyte solutions as compared to the measurements in the air or in vacuum consists in instability of the solid-liquid interface. The composition and the structure of the transition layer depend on the nature and the structure of the sample (working electrode), the charge and the surface potential, the
electrolyte composition, temperature, solution stirring mode and the presence of admixtures in traceable quantity.

Thermodynamically, the possibility of an electrochemical reaction to take place is determined by the value of the potential that an external device (power supply or potentiostat) can set on the working electrode in the presence of the counter electrode, or by varying concentration C of the potential-determining ions in the solution.

Two basic connection schemes are used in operations with the electrochemical cells:

- **4-electrode**. Used in operations with the EC STM head.
- **3-electrode**. Used in operations with the AFM head. Potential applied to the tip (in STM modes) is not controlled by the bipotentiostat.

**4-electrode scheme**

Applying the polarizing current \( I_s \) to the “counter electrode” – “working electrode” system allows to maintain the required potential of the working electrode (the value of the polarizing current is automatically adjusted by the feedback loop of the potentiostat) and the potential \( E_s \) of the working electrode is measured relative the reference electrode. The potential \( E_p \) of the tip is set relative the common reference electrode, using the bipotentiostat. The current (velocity) of the electrochemical reaction and/or process of electron tunneling between the sample and the tip is then registered. To obtain a correct STM image, it is extremely important to maintain the Faraday current of the tip at much lower level than the tunneling one. This is the reason why only the tips almost completely insulated by non-conductive and chemically resistant material are used for electrochemical STM measurements. The working surface of the non-isolated apex of the tip usually comprises several square micrometers (the Faraday current is proportional to the area of the electrode surface).

![Fig. 1-20. 4-electrode scheme](image-url)

1 – sample; 2 – counter electrode; 3 – reference electrode; 4 – electrolyte; 5 – cell housing; 6 – tip
3-electrode scheme

The reference electrode, see Fig. 1-21, is used to measure the potential $E_s$ on the working electrode. Practically, the difference of potentials on the working and the reference electrodes is measured. The potential of the reference electrode must be known and shall be stable in time.

Applying the polarizing current $I_s$ to the counter electrode–working electrode system, the required potential of the working electrode is maintained, with the value of the polarizing current adjusted automatically by the potentiostat feedback loop. The potential $E_s$ of the working electrode is then measured relative to the reference electrode.

![3-electrode scheme diagram](image)

Fig. 1-21. 3-electrode scheme
1 – sample; 2 – counter electrode; 3 – reference electrode; 4 – electrolyte; 5 – cell housing

1.5. **Basic Safety Measures**

**General Safety Measures**

- Ground the instrument before operation!
- Do not disassemble any part of the device. Disassembling of the product is permitted only to persons certified by NT-MDT.
- Do not connect additional devices to the instrument without prior advice from an authorized person from NT-MDT.
- This instrument contains precision electro-mechanical parts. Therefore protect it from mechanical shocks.
- Protect the instrument against the influence of extreme temperature and moisture.
- For transport, provide proper packaging for the instrument so as to avoid its damage.
Electronics

− To reduce possible influence of power line disturbances on the measurements, we recommend supplying the instrument units with a surge filter.

− Before operation, set the power switch of the SPM controller to the position corresponding to value of the local electrical power line (this is only done with the controller being off!).

− Switch the SPM controller off before connecting/disconnecting its cable connectors. Disconnecting or connecting the cable connectors during operations may cause damage to the electronic circuit and disable the instrument. A warning label is attached to the SPM controller of the instrument (Fig. 1-22).

![Attention!](image1.png)

**Fig. 1-22**

Laser

− Observe safety measures for operation with devices containing sources of laser radiation. Do not stare into the beam. A label warning about the presence of laser radiation is attached to the measuring head (Fig. 1-23), laser sources.

![CAUTION](image2.png)

**Fig. 1-23**

Scanner

− Do not apply to the scanner forces bigger than it is necessary for installation of a probe or a substrate with a sample. Avoid impacts on the scanner and its lateral displacement. Remember that thickness of the scanner walls makes only 0.5 mm.

Electrochemical cell

− When operating with the electrochemical cell, wear on protective gloves resistant to acids and bases and a protective mask;

− Observe safety measures for operation with corrosive media.
1.6. **Operating Conditions**

The SPM should be installed in a room of total area larger 6 sq. meters that provides range of purity better 8 (by ISO 14644-1).

To provide for the normal operation of the device, it is recommended to observe the following conditions:

- environment temperature: \((25 \pm 10) \, ^\circ C\);
- temperature drift less than 1°C per hour;
- relative humidity at +25 °C less than (65±15) %;
- range of purity 8 (by ISO 14644-1);
- vibration amplitude in the band 1 ÷ 1000 Hz less 0.5 µm;
- atmospheric pressure 760 ±25 mm Hg;
- the work area should be supplied with a protective grounding circuitry and with grounded electric mains (110/220 V);
- electric mains:
  - voltage 110/220 V (+10%/-15%),
  - frequency 50/60 Hz;
- the room should be protected from mechanical vibrations and acoustic noises, either internal or external;
- vibration criterion VC-C, 12.5 µm/s (one-third octave band criterion);

- the device should be protected from the direct sun radiation impact;
- to provide solid stability against vibrations, SPM modules should be placed on self-leveling floor with marble covering alongside bearing components of the building (pillows, beams etc.).
the measuring unit of the instrument (the base unit with the measuring head) should be placed on a separate table away from computers and monitors, to eliminate electromagnetic interference;

- the table intended for installation of the measuring unit of the instrument must be stable and, whenever possible, massive.

The operation of the device is susceptible to heat flows, draughts and sudden alternations in temperature and humidity.

1.7. Storage and Transport Instructions

Storage Instructions

The instruments should be stored packaged in clean and dry premises with low ambient temperature variations:

- Acceptable temperature inside the premises is plus (20 ± 10) °C;
- Acceptable humidity inside the premises is < 80 %.

Electrochemical Cell Storage

Upon finishing operation disassemble the cell. Rinse all Teflon parts of the cell and the electrodes in running deionized water.

It is recommended that the Teflon parts of the cell and the protective cover plate are stored in a desiccator in inert atmosphere.

Transport Instructions

The instrument should be carefully packaged to avoid damage during transport.
2. Setup and Installation

Details of the procedure of setting up the instrument for electrochemical measurements depend on specific packaging. In general, the following operations may have to be performed:

1. Preamplifier Installation (if not performed by the manufacturer) (see i. 2.1 on page 24).
2. Electrical Connection (see i. 2.2 on page 25).
3. For electrochemical measurements with heating/cooling of the sample, the base of EC should be connected to the water-cooling system (see i. 2.3 on page 26).
4. For operation in electrochemical AFM modes, the probe holder should be inserted into the diaphragm that provides leakproofness of EC (see i. 2.4 on page 27).

A detailed description of the listed operations is given below.

2.1. Preamplifier Installation

1. Unscrew the screws 2 (Fig. 2-1) and remove the bars 1 from the exchangeable mount.

![Fig. 2-1.](image)

1 – bars to mount the auxiliary mirror; 2 – bar fixing screws; 3 – replaceable panel

2. Unscrew the three screws and remove the replaceable panel from the base unit of the instrument.

3. Take the replaceable panel with the preamplifier. Install the replaceable panel in the base unit and fix it with three screws (Fig. 2-2). Pass the preamplifier cable under the base unit with the bottom cover removed.
2.2. Electrical Connection

ATTENTION! Switch the controller off before connecting or disconnecting any instrument components. Connecting or disconnecting the components during the controller operation may damage the electronic circuitry.

1. Connect the components of the instrument according to the diagram, given in Fig. 2-3, following the captions on the sockets.

Fig. 2-2. Preamplifier installed in the base unit

Fig. 2-3. Instrument components connection diagram
2. Before operation, set the power switch of the SPM controller to the position corresponding to value of the local electrical power line (this is only done with the controller being off!).

3. Connect the controller to the power point.

⚠️ ATTENTION! SPM controller can be connected to an electrical power supply line of 110/220 V (60-50 Hz) after setting the voltage selection switch to the position corresponding to this power supply line. Not following this instruction may cause damage to the electronic components.

### 2.3. Connection of the Water-Cooling System

⚠️ ATTENTION! Do not use the EC cell without water-cooling system in order to avoid damage to the cell.

For connection of the water-cooling system and for gas supply, the base unit is equipped with a special spacer ring (Fig. 2-4). The spacer with its rubber seal down is placed on the metal rim of the base unit and then secured with special clamps.

![Spacer ring diagram](image)

**Fig. 2-4. Spacer ring**

1 – connecting pipes of the cell water-cooling system; 2 – outlets for feeding gas; 3 – grooving for placing the spacer on the base unit

Tubes of the water-cooling system are connected to the outlets from the outside of the spacer.

The cell base should be installed on the base unit before connecting the water-cooling system.
2.4. **Preparation of AFM measuring head**

For operation in electrochemical AFM modes, the probe holder should be inserted into the diaphragm that provides leakproofness of EC.

1. Remove the clip from the holder. To do this, take the clip with tweezers near the bend and pull it lengthwise along the base until the lower part of the clip releases from the guide slot in the base, Fig. 2-5.

![Fig. 2-5. Clip removal](image)

2. Take the diaphragm and turn it so that the side with the ring faces downwards to the holder. Put the diaphragm on the holder, with the glass pedestal passing through the hole in the diaphragm, see Fig. 2-6.

![Fig. 2-6. Diaphragm installation](image) ![Fig. 2-7. Diaphragm fixed on the holder](image)

3. Slightly stretching the diaphragm first from one side then from the other put it under the base flange, Fig. 2-7.

4. Wipe the holder with a napless tissue moistened in alcohol.

5. Mount the clip, Fig. 2-8. For operation in liquid the clip shall be inserted from the side with the smaller tilting angle relative to the horizontal plane.
NOTE. In order for the diaphragm to last longer avoid putting in on and off too often.
3. Preparatory Operations

Preparatory operations and performing measurements are explained on the example of the following experimental environment:

Working electrode (sample) – Au(111) single crystal;

Electrolyte – solution 50 mM H₂SO₄ + 1 mM CuSO₄;

Electrodes – made of copper wire of diameter 1 mm.

ATTENTION! When operating with the electrochemical cell, wear on a protective mask and protective gloves resistant to acids and bases.

Basic preparatory operations include the following:

1. Verification of Bipotentiostat (see i. 3.1 on page 30).
2. Cleaning (see i. 3.2 on page 31).
3. Sample Preparation (see i. 3.3 on page 32).
4. Mounting the Sample and Assembling the Cell (see i. 3.4 on page 33).
5. Mounting Cell on the Base Unit (see i. 3.5 on page 37).
6. Preparation of the measuring head and its mounting on the base unit:
   - for operation with the 3-electrode scheme (see i. 3.6 on page 38);
   - for operation with the 4-electrode scheme (see i. 3.7 on page 46).
7. Installation of a Protective Hood (see i. 3.8 on page 48).

A detailed description of these operations is given below.

NOTE. During preparatory operations store all components of the cell in the dessicator with inert atmosphere. Recall that the stability and the quality of the results obtained with the electrochemical cell are strongly dependent on the system cleanness.
3.1. **Verification of Bipotentiostat**

Calibration of the bipotentiostat is recommended to be checked every time before starting measurements. If the calibration appears invalid, the bipotentiostat should be recalibrated. The procedure on calibrating is explained in Appendix (see Appendix “Bipotentiostat Calibration” on page 92).

**To check calibration of the bipotentiostat, perform the following steps:**

1. Launch the Control program.
2. Select configuration of the controller (Fig. 3-1) regarding the desired measurement mode (*Tunnel Current* – for STM, *Contact* or *SemiContact* – for AFM).

![Fig. 3-1. Selecting configuration of the controller](image)

3. For STM modes, check commutation of the instrument block scheme. In the Auxiliary Operations panel, open the instrument block scheme by clicking the **Scheme** button. Move switches of voltages applied to the sample and to the tip so that the scheme reads as follows (see Fig. 1-4):
   - the tip connected to **Ex5**;
   - the sample grounded.

![Fig. 3-2](image)

4. In the Auxiliary Operations panel, go to the **ElectroChemistry** tab.
5. Switch the enabling button of the bipotentiostat (at the left of the Control panel) to the **On** position.
6. Set the switch of the bipotentiostat modes to **Potentiostat** position.
7. Switch on potential detection channels of the sample and of the tip: **Tnp ON**.
8. In the drop-down list of available conditions of the bipotentiostat operation, select operation with one of the equivalent resistances (e.g., 0.5 kΩ).

9. In the **Cycling** tab, define parameters of cycling, for instance:
   - **Cycle From** -100 mV;
   - **Cycle To** 100 mV;
   - **Cycle Rate** 15 mV/sec.

10. Select the sample potential as the object of cycling: **Cycling on Sample**.

11. Start cycling with the button.

12. Go to the **Graph** tab. Start measurements with the button. The oscilloscope is expected to display a triangular waveform. To avoid possible truncation of the graph, rescale the image with the button.

13. With the oscilloscope graph, check if the bipotentiostat calibration is correct.
   - The signal amplitude should be in the selected range (in our example, this range is from –100 to +100 mV) with accuracy ≤ 0.1 %.
   - The signal should be symmetric in shape (the times of rising and falling of the potential are equal).
   - In the **Measured Values** panel, observe how the sample potential $Smpl\ E$ varies. Variation rate of the potential should be equal to the selected value of **Cycle Rate**.

If necessary, recalibrate the bipotentiostat. The procedure on calibrating is explained in Appendix (see Appendix “Bipotentiostat Calibration” on page 92).

### 3.2. **Cleaning**

It is of high importance to remove organic contamination from all components of EC with careful washing before measurements.

Washing is especially necessary for the following components:
   - fluoroplastic parts of the cell;
   - Au(111) sample;
   - electrodes.
Details of the washing procedure are determined regarding specific features of the experiment.

When the Au(111) sample is measured, the cell, the electrodes, and the sample can be washed as follows:

1. Keep the components for 30 minutes in 1:1 mixture of concentrated sulphuric acid and concentrated aqueous solution of hydrogen peroxide.

   ATTENTION! The washing mixture is extremely caustic strong oxidant. Therefore, handle it with maximum care. When preparing the mixture, pour the acid in the peroxide solution with thin stream.

2. Wash the components in running deionized water (≥ 14 MΩ).
3. Dry the components in inert gas environment.

3.3. **Sample Preparation**

For Au (111) it is recommended to anneal the sample in the flame of a gas burner.

**Annealing procedure:**

1. Place the sample on a plate of fireproof material.
2. Bring a torch flame to the sample. Move the flame slowly over the sample surface so that the surface is annealed uniformly. Avoid overheating of the sample that is indicated by dark red glowing. The blue portion of the flame should contact the sample surface. Apply 3-4 complete passes of the flame over the surface.
3. If overheating happens, move the gas burner away from the sample for several seconds and wait until the sample cool down. Then resume the annealing procedure.

   ATTENTION! Avoid overheating the sample considerably, for it may deform, becoming unsuitable for the measurements.

On completion of annealing, place the sample in inert gas environment and wait until it cools down.
3.4. **Mounting the Sample and Assembling the Cell**

Fig. 3-4 presents components of the electrochemical cell.

![Fig. 3-4. Parts of the electrochemical cell](image)

1 – cell housing; 2 – clip plate; 3 – clip ring; 4 – cover;
5 – ground wire with the connecting spring; 6 – outlets for feeding liquid/gas;
7, 8 – gags; 9 – electrodes

**To mount the sample and to assemble the cell, perform the following steps:**

1. Place the sample at the center of the cell housing (Fig. 3-5).

![Fig. 3-5](image)

2. Pass the connecting spring through the hole in the inner wall of the cell housing so that it contacts the sample with one end (Fig. 3-6).

![Fig. 3-6. Connecting spring mounted](image)

![Fig. 3-7. Contact line of the working electrode mounted](image)
3. Insert the contact line of the working electrode (see pos. 5 on Fig. 3-4) into the hole at the top of the cell housing (Fig. 3-7). Use an ohmmeter to verify that the sample is in contact with the contact line.

4. Mount the clip plate observing the following conditions:
   - the connecting spring should be outside the collar on the bottom of the plate;
   - the connecting spring should be in contact with the sample surface;
   - the sample should overlap the hole of the plate completely. This condition provides protection of side edges of the sample against exposure to electrolyte.

5. Verify that the sample is in contact with the contact line.

6. Emplace the clip ring (Fig. 3-8). Outdents of the ring may not stay against the holes of the cell housing.

![Fig. 3-8. Clip plate and clip ring mounted](image)

7. If flowing gas or liquid is used in measurements, emplace tubes in holes of the cell. The tubes are mounted inside two holes that are at opposed ends of the cell diameter.

If the experiment doesn’t need a flowing agent, the holes are closed with gags (see pos. 8 on Fig. 3-4)

**To supply liquid:** the inlet tube hole should be lower than the outlet tube hole (Fig. 3-9). To achieve the desired difference in levels, turn the tubes to the necessary angle.

**To supply gas:** one of the holes is closed with a gag. The inlet tube is mounted so that its opening is above the electrolyte level (Fig. 3-10).

![Fig. 3-9. Mounting the liquid supply tubes](image) ![Fig. 3-10. Mounting the gas supply tube](image)

8. To use the Ag/AgCl electrode, place it as close to the sample as possible but avoiding any contact (Fig. 3-11).
9. Close all vacant holes of the cell housing.

10. Insert the auxiliary electrode and the reference electrode. When mounting, observe that these electrodes do not contact each other, the sample and conducting parts of the cell. Use pieces of wire of diameter up to 1 mm for electrodes to be involved in reactions. Shape of the electrodes is of no importance.

11. Close the cell with the cover.
12. To mount the cell on the base, pull off the front of the base slightly and place the cell so that the guide pin of the base comes into the groove on the bottom of the cell housing. Push the fastening screw (pos. 1 on Fig. 3-14) against the stop and turn it to 90° at any direction to fix the cell on the base.

![Fig. 3-14. Electrochemical cell assembled](image)

1 – fastening screw; 2 – contact of the sample; 3 – contact of the auxiliary electrode; 4 – contact of the reference contact

13. Connect the electrodes of the cell with the corresponding contacts of the cell base (Fig. 3-14).

14. Emplace the temperature sensor so that it projects a little inside the cell volume.

![Fig. 3-15. Hole for the temperature sensor.](image)

Temperature sensor
Black arrows show holes for the supplying outlets and for the Ag/AgCl electrode

15. Fill the cell with electrolyte so that the sample, the electrodes and the temperature sensor submerge. Electrolyte should fill the cell volume uniformly. Close the cell with the cover.

Assembly of the cell is now complete.
3.5. **Mounting Cell on the Base Unit**

1. Turn back the spring clips and insert the cell base into the positioning device of the base unit as shown on Fig. 3-16.

2. Make electrical grounding of the cell base with the ground wire (see pos. 1 on Fig. 3-16).

![Fig. 3-16. Electrical connections](image)

1 – grounding; 2 – contact of the auxiliary electrode; 3 – contact of the reference electrode

3. Connect the cell base to the sockets **CNT** and **REF** of the preamplifier with the connecting cables (Fig. 3-16).

4. Connect the cell base to the cooling system by coupling the connecting pipes of the cell base and the connecting pipes of the inside of the spacer ring with tubes (Fig. 3-17). The tubes should be inserted into the pipes against the stop.

![Fig. 3-17. Connecting the cooling system](image)

**NOTE. To remove a tube from a connecting pipe, use gentle pressure on the blue latch to push it inside the pipe.**

**ATTENTION! Do not use the EC cell without water-cooling system in order to avoid damage to the cell.**
3.6. Preparing AFM Measuring Head for Operation in 3-electrode Scheme

AFM and STM measurements in 3-electrode scheme use the SFC101LNTF model of the measuring head for operation in liquid. Depending on the desired mode, the head is equipped with the probe holder either for AFM or for STM.

Preparation of the measuring head for operation includes the following basic procedures:

1. Probe installation:
   - AFM (see page 38);
   - STM (see page 40).
2. Measuring Head Installation (see page 42).
3. Adjusting the System for Detecting the Cantilever Deflection (for AFM) (see page 44).

3.6.1. AFM Probe Installation

To install the probe:

1. Place the probe holder on a smooth surface.
2. To install the probe use the special wrench. Clench the clip with the wrench staple, Fig. 3-18.

![Fig. 3-18](image)

3. Using tweezers take a probe from the set. So not turn the chip over as the probes are placed with their tips pointing upwards.
4. By slightly pressing the wrench handle (see Fig. 3-19) unbend the clip and place the probe on the beveled side of the pedestal under the clip. The length of the chip part projecting above the polished surface of the pedestal shall be about 0.8 mm, i.e. the end of the chip with the cantilever shall be positioned above the center of the upper polished side of the pedestal.

⚠️ ATTENTION! To avoid deformation of the clip unbend it only on the minimum angle required.
5. Release the clip and remove the wrench.

6. Place the measuring head with its supports facing up on a smooth surface.

7. In order to prevent the diaphragm from damage, a special fitting tool was designed for fixing the holder on the scanning measuring head for liquid operation. Insert the holder in the fitting tool (Fig. 3-20) so that the clip goes into its slot.

8. Bring the holder to its seat on the head, holding the diaphragm with your fingers, see Fig. 3-21. The holder shall be rotated 45° relative to its working position (shown on Fig. 3-23).
9. Lower the holder into its seat, Fig. 3-22. The set ring on the lower part of the holder disk shall enter the scanner tip tube. The holder shall rest on the magnetic support evenly and without skew.

Fig. 3-22. Mounting position of the probe holder

Fig. 3-23. Working position of the probe holder

10. Turn the fitting tool with the holder 45 degrees clockwise. The right sides of the fitting tool shall be at the right angle to the front surface of the measuring head housing, see Fig. 3-23. This is the working position of the holder in which the measurements are performed.

11. Remove the fitting tool, Fig. 3-24.

Fig. 3-24. The probe holder mounted on the measuring head

3.6.2. STM Probe Installation

The package for electrochemical measurements contains the STM probes kit. If a home-made probe is used, it is recommended to apply one of electrochemical etching technique for probe sharpening, e.g., that of the paper “Electrochemical fabrication of cobalt and nickel tips for scanning tunneling microscopy” Cristiano Albonetti, Massimiliano Cavallini, Massimiliano Massi, Jean Francois Moulin, and Fabio Biscarini, J. Vac. Sci. Technol. B 23(6), Nov/Dec 2005.

ATTENTION! The procedure of electrochemical etching should be accomplished in a specially equipped room. All applicable safety regulations should be observed.
A sharpened W or Pt-Ir (10 ÷ 20 %) wire with the diameter of 0.25 mm is used as an STM tip.

To obtain a correct STM image, it is extremely important to maintain the Faraday current of the tip at much lower level than the tunneling one. Sharpening the probe with electrochemical etching provides a tip of well-defined shape with the Faraday current less 50 pA.

**To install the STM probe, perform the following steps:**

1. Place the measuring head on an even surface with the supports facing up.

2. Take an STM probe holder. The holder has a positioning mark. To prevent shocks when mounting the holder on the measuring head, the holder is placed initially so that the ferromagnetic elements come between the magnets. This placement needs that the mark on the holder is at the angle of 45° to the axes shown on Fig. 3-25. Lower the holder to its seat. The holder should insert into the magnetic fastener evenly without skewing.

3. Turn the holder to its working position (e.g., as shown on Fig. 3-26). This moves the ferromagnetic elements of the holder to the magnets of the fastener thus fixing the holder at the scanner tube.
4. Take the probe at its uninsulated part with sharp tweezers (Fig. 3-27). The uninsulated part is to be inserted into the holder and so it should be bent slightly to be fixed.

⚠️ ATTENTION! Take the probe only at its uninsulated part to prevent damage of the insulation covering.

Fig. 3-27

5. Insert the tip into the tip holder so as to make the insulated part of the tip protrude beyond the holder (Fig. 3-35).

Fig. 3-28. Tip installation

### 3.6.3. Measuring Head Installation

To operate the AFM probe, length of the measuring head supports should be adjusted to provide the distance between the probe and the sample surface not less than 2-3 mm. This procedure can be performed only once when the measuring head is installed for the first time. The adjustment procedure is described in the Appendix (see “Adjustment of the Length of Measuring Head Threaded Supports” on page 105).

If the optical viewing system is used, preliminary installation of the auxiliary mirror on the measuring head is necessary. Place the mirror on the measuring head and secure it with two screws (Fig. 3-29). Remove the protective cover of the mirror.

No adjustment of the mirror is needed.
To mount the measuring head proceed as follows:

1. Turning the approach knob clockwise, move the cell to its lowermost position. Remove the cover from the cell.
2. Place the measuring head so that the threaded supports rest on the seats of the exchangeable mount as shown in Fig. 3-30.
3. Adjust the sample location in XY plane. Use the micrometer screws of the positioning instrument to place the cantilever above the area to be observed.
4. Bring the sample to the cantilever at a distance of 0.5±1 mm by turning the approach knob counterclockwise.
3.6.4. Adjusting the System for Detecting the Cantilever Deflection (for AFM)

When using the AFM probe, adjustment of the detection system of the cantilever deflection should be performed before starting measurements.

The adjustment of the detection system is best performed with the optical viewing system. This way of adjustment needs the auxiliary mirror being installed on the measuring head. The adjustment of the detection system without using the video viewing system is described in the Appendix (see i. “Adjusting the Detection System without Videomicroscope” on page 107).

Proceed as follows:

1. Prepare the optical viewing system for operation for "scanning-by-probe" configuration as specified in Performing Measurements, Appendix.

2. Focus the videomicroscope on the cantilever.

3. Turning the approach knob and monitoring the sample position on the display (Fig. 3-31) bring the sample to the probe so that the edge of the glass pedestal with the probe dips in the liquid.

   If bubbles appear (see Fig. 3-31 b), remove the measuring head and carefully wipe the liquid off the probe and its holder using a napless tissue. Remount the measuring head on the exchangeable mount.

4. Bring the sample to the probe at the distance of 0.5 ÷ 1 mm by carefully turning the approach knob until the sample surface comes to focus.

5. Align the laser beam onto the cantilever using screws 1 and 2 (Fig. 3-32).
Further, precise alignment of the laser beam onto the cantilever tip shall be performed based upon the magnitude of the total photodiode signal. This procedure is implemented in the control program:

1. Switch the **Aiming** tab (the button ![Aiming](image) on the Main operations panel).

2. Carefully turning X, Y screws 1 and 2 for tuning the adjustment unit, achieve the maximum value of the **Laser** signal (15±20 nA).

   ![NOTE. If there is no signal on the photodiode indicator but the laser beam is aligned onto the cantilever, as could be seen on the optical viewing system display, then the photodiode might be in a position where the laser beam misses it. If this is the case, rotate the photodiode adjustment screws until the signal appears.](image)

3. Rotate photodiode adjustment screws 3 and 4 to center the laser spot on the photodiode indicator (Fig. 3-33). The values of **DFL** and **LF** signals shall be close to zero while the magnitude of the total Laser signal shall remain rather large.

   ![NOTE. If the **Laser** signal decreases to zero when turning any of the screws then it means that the laser beam hits the photodiode edge. In this event the corresponding screw shall be turned in the opposite direction.](image)
3.7. Preparing Electrochemical STM Measuring Head for Operation in 4-electrode Scheme

3.7.1. STM Tip Installation

The package for electrochemical measurements contains the STM probes kit. If a home-made probe is used, it is recommended to apply one of electrochemical etching technique for probe sharpening, e.g., that of the paper “Electrochemical fabrication of cobalt and nickel tips for scanning tunneling microscopy” Cristiano Albonetti, Massimiliano Cavallini, Massimiliano Massi, Jean Francois Moulin, and Fabio Biscarini, J. Vac. Sci. Technol. B 23(6), Nov/Dec 2005.

ATTENTION! The procedure of electrochemical etching should be accomplished in a specially equipped room. All applicable safety regulations should be observed.

A sharpened W or Pt-Ir (10 ÷ 20 %) wire with the diameter of 0.25 mm is used as an STM tip.

To obtain a correct STM image, it is extremely important to maintain the Faraday current of the tip at much lower level than the tunneling one. Sharpening the probe with electrochemical etching provides a tip of well-defined shape with the Faraday current less 50 pA.
1. Place the STM head on an even surface with the supports facing up.

2. Take the probe at its uninsulated part with sharp tweezers (Fig. 3-34). The uninsulated part is to be inserted into the holder and so it should be bent slightly to be fixed.

   ![Fig. 3-34](image)

   ATTENTION! Take the probe only at its uninsulated part to prevent damage of the insulation covering.

3. Insert the tip into the tip holder so as to make the insulated part of the tip protrude beyond the holder (Fig. 3-35).

   ![Fig. 3-35. Tip installation](image)
3.7.2. Mounting Electrochemical STM Head on Base Unit

To mount the EC STM head proceed as follows:

1. Turning the approach knob clockwise, move the cell to its lowermost position. Remove the cover from the cell.

2. Place the EC STM head so that the threaded supports rest on the seats of the exchangeable mount as shown in Fig. 3-39.

3. Adjust the sample location in XY plane. Use the micrometer screws of the positioning instrument to place the cantilever above the area to be observed.

4. Bring the sample to the tip at a distance of 0.5±1 mm by turning the approach knob counterclockwise.

3.8. Installation of a Protective Hood

It is recommended to work with a protective hood in the following cases:

a. if it is necessary to obtain a high resolution image in XY plane or along Z axis.

b. when carrying out temperature measurements.

c. for protection against temperature differences.

d. for reduction of acoustic noise level.
For installation of a protective hood execute the following actions:

1. Turn the videomicroscope support clockwise against the stop.

2. Take the protective hood with your left hand using handle 1, and with your right hand - using handle 2 (see Fig. 3-37).

3. Bring the hood to the stand so that plastic inserts on handle 1 of the hood (see pos. 3 in Fig. 3-37) rest against the stand, and the slot in handle 2 is located above the base unit frame (see Fig. 3-38).

4. Put on the hood so that the frame gets into the slot. The plastic inserts should slide along the stand.

After the installation of the protective hood turn on the Vibration Isolation System, see the Vibration Isolation System Manual for more details.
4. Preparation and Performing the Measurements

The measurement procedure includes the following basic operations:

1. Adjusting the Bipotentiostat Parameters (see item 4.1 on page 50).
2. Cyclic Voltamperometry (see pars. 4.2 on page 51).
3. Performing the Measurements:
   - Contact AFM (see item 4.4 on page 55);
   - Semicontact AFM (see item 4.5 on page 66).
4. Saving the Data (see item 4.9 on page 90).
5. Finishing the Operation (see item 4.10 on page 91).

⚠️ ATTENTION! When performing measurements, watch the level of electrolyte in the cell. The electrodes should be submerged into electrolyte. If the level of electrolyte drops in the cell, add it up.

Preparatory operations and performing measurements are explained on the example of the following experimental environment:

Working electrode (sample) – Au(111) single crystal;
Electrolyte – solution 50 mM H₂SO₄ + 1 mM CuSO₄;
Electrodes – made of copper wire of diameter 1 mm.

4.1. Adjusting the Bipotentiostat Parameters

Perform the following switching operations in the ElectroChemistry tab of the Additional operations panel (Fig. 4-1):

1. Switch the bipotentiostat activation button to On position.
2. Regarding the bipotentiostat operation mode, select either Potentiostat (for measuring potential) or Galvanostat (for measuring current).
3. Switch on the tip and the sample potentials registration channels by clicking on the Smpl ON and Tip ON buttons.

Fig. 4-1. Bipotentiostat parameters adjustment

4. Select Cell in the list of the bipotentiostat operating modes.
5. A value of current through the sample is displayed in the Smpl I box on the Measured values panel:
   - If 100 µA < Smpl I < 5 mA, switch the current measurement range to be 5 mA;
   - If the value in the Smpl I text box is below 100 µA, switch the current measurement range over to 100 µA;
   - If the value in the Smpl I text box is below 2 µA, switch the current measurement range over to 2 µA.

6. Select the value of 20 Hz in the list of potential digitizing frequencies.

### 4.2. Cyclic Voltamperometry

Electrochemical processes are often studied using the linear sweep of potential between the cathode and anode limits. This method is called cyclic voltamperometry and the dependence of current from the sample potential (E_s) is known as cyclic voltamperogramm (CVA). The location and the shape of the current peaks reflect the changes in the state of the electrode surface during different Faraday processes.

The cyclic voltamperometry with linear sweep of potential is one of the most widely spread methods to control the system cleanliness and to maintain the standard condition of the working electrode surface and the tip. Such dependencies are rather sensitive to the presence of admixtures and to any changes in the surface structure. Therefore, a number of CVA cycles is recorded right after the cell installation at the beginning of the experiment in order to monitor the system cleanliness using the shape and the height of the current peaks.

To monitor the system cleanliness and the condition of the working electrode surface the sample potential is usually cycled in an appropriate range between the measurement sessions.

A cyclic variation of the potential has another positive effect – for some systems such electrochemical processing provides cleaning of the electrode surface from adsorbed admixtures and allows prolonging EC AFM measurements in conditions of considerable system cleanliness.
To perform the cyclic voltamperometry, do the following:

1. Open the **Graph** tab.

2. Select the **Smpl I(E)** in the displayed signals selection list (Fig. 4-2).

3. Open the **Cycling** tab.

4. Select the **Cycling on Smpl** (cycling the sample potential) in the list of cycling objects selection (Fig. 4-3).

5. Set the parameters of cycling the sample potential. For the example under consideration (sample – Au(111), electrolyte – 50 mM H$_2$SO$_4$ + 1 mM CuSO$_4$) the following values of the cycling parameters are applicable (Fig. 4-3):

   - **Cycle From** 0 mV;
   - **Cycle To** 700 mV;
   - **Cycle Rate** 20 mV/s.

6. Start the cycling process by clicking on the **Start Cycling** button.

   As a result of this action, a voltage potential cyclically varying first from **Cycle From** to **Cycle To** and then from **Cycle To** to **Cycle From** is applied to the sample.

7. Open the **Graph** tab. The oscilloscope will display the dependence of the sample current on the potential.

   To balance the electrolyte-electrodes system, it is recommended to perform cycling for 15+20 minutes. The resulting voltamperogrampm for Au(111) will look like in Fig. 4-4.
8. Once the balance is achieved, open the Cycling tab and terminate the process by clicking on the Stop cycling button.

9. If the resulting voltamperogramm displays irrelevant peaks, indicating the presence of admixtures or insufficient system cleanliness, then cleaning the cell and sample again.

4.3. Controlling Sample Temperature

To change the sample temperature, perform the following steps:

1. Open the Additional operations area by clicking the button in the upper right corner of the program main window.

2. Power on the termocontroller by toggling the switch on its front panel. Upon turning it on the Thermostat button will appear in the Additional Operations panel.

3. Switch to Thermostat tab. In the Device list (Fig. 4-5) select the MP6LC(Gas) item.

![Fig. 4-5. Temperature Control panel for measurements in liquid]

| T1 = 27.03°C | T2 = 26.70°C | Heater power -0% |

T1 – readings of the sensor in the cell base.
T2 – current temperature of the liquid (the sensor is in cell housing).
4. In the text box enter the value of operating temperature.

**ATTENTION!** During sample heating the probe shall be detached from the sample surface at a distance of ~1 mm.

5. Turn on heating/cooling by clicking the button on the temperature control panel (Fig. 4-5).

6. Click on the toolbar of Temperature Graph panel (Fig. 4-6), to start plotting the temperature curve.

![Fig. 4-6](image)

Fig. 4-6

Fig. 4-7 shows the example temperature curve when the sample was heated from room temperature to 43.9°C. In this case the feedback is maintained using the temperature of the liquid.

![Fig. 4-7](image)

Fig. 4-7. Sample heating to 43.9 °C
1 – temperature of the sample; 2 – temperature of the liquid

Heating/cooling the probe may cause it to bend. So (when operating the AFM probe) verify positioning of the laser beam in the **Aiming** tab after the desired temperature is achieved. If necessary, readjust positions of the laser beam and of the photodiode.
4.4. **Contact AFM**

The measurements by the Contact AFM techniques will by discussed on the example of the Constant Force Mode which forms the basis for operating the instrument using other contact techniques (see *Performing Measurements*, chapter 3).

**Basic procedures performed when using contact AFM techniques:**

1. Approaching the Sample to the (see i. 4.4.1 on page 55);
2. Preparation for Scanning (see i. 4.4.2 on page 59):
   - Setting the Operating Level of the Feedback Gain Factor (see i. 4.4.2.1 on page 59);
   - Setting up the Scanning Parameters (see i. 4.4.2.2 on page 60);
3. Scanning (see i. 4.4.3 on page 63).

### 4.4.1. Approaching the Sample to the Probe

To approach the sample to the probe, do the following:

1. Switch the instrument to the operation in contact modes, by selecting **Contact** in the menu for choosing the controller configuration (Fig. 4-8).

   ![Fig. 4-8](image1)

   Once the configuration **Contact** is set, all switching sequences required to operate on contact techniques are performed automatically: DFL signal is applied to the feedback input, with the generator off and the required parameter values set.

2. Switch to the **Approach** tab (the **Approach** button on the Main Operations panel) (Fig. 4-9).

   ![Fig. 4-9](image2)
3. Check the position of the button for the automatic setting of Set Point parameter. Auto SetPoint button should be activated as shown on Fig. 4-9.

4. Start the approach procedure by pressing button.

The procedures above should yield the following results

- The value of Set Point parameter is automatically set exceeding the current value of DFL signal by two units (i.e. Set Point = DFL + 2);
- The feedback is switched on and Z-direction piezoscanner is protracted to the maximum. The protraction of Z-direction scanner is illustrated by the analog indicator of scanner protraction, located in the left lower corner of the program main window (Fig. 4-10). The degree of scanner protraction is characterized by the length of the color bar;
- The step motor is switched on moving the scanner with the sample towards the probe.

Watch the DFL signal changes in the oscilloscope during the approach procedure, while watching the progress of the scanner protraction indicator. Wait till the procedure is completed.

The approach parameters set correctly, the procedure is completed after some time, leading to the following:

- DFL signal increases to the value of Set Point parameter with the feedback maintaining Z-direction scanner in the position where DFL signal equals SetPoint with the position corresponding to approximately a half of the scanner protraction range;
- The length of the indicator’s color bar decreases and stops somewhere in the middle;
- The step motor stops;
- The increase of DFL signal to the value of Set Point parameter is represented on DFL(t) dependence on the oscilloscope (Fig. 4-11);
- The message "...Approach Done" will appear in the journal (pos. 2 in Fig. 4-11).
Special cases

Self-oscillations

In some cases, after the approach procedure is performed and DFL signal is increased to the value of Set Point parameter, DFL(t) dependence can demonstrate a considerable increase of the a.c. component of DFL signal (as shown in Fig. 4-12 for example). This means that a generation occurs in the feedback loop because the value of FB Gain parameter is too high. In this event, the value of FB Gain parameter should be decreased to 0.5–0.7 of the threshold level. The procedure of FB Gain parameter adjustment is described below in item 4.4.2 on page 59.
Selecting and setting up the Set Point parameter manually:

In order to manually enter the value of Set Point parameter:

- switch off the Auto SetPoint option;
- enter the Set Point parameter value in the text box in the main parameters panel.

The recommended initial value of Set Point parameter should be equal to the sum of the following: DFL signal plus 5÷10 % of Laser signal value (i.e. Set Point = DFL + (0.05÷0.1) * Laser).

When selecting an optimal value of Set Point parameter the considerations presented below should be taken into account:

- The difference between the value of Set Point parameter and the initial value of DFL signal defines the value of interaction between the apex of the tip and the sample surface. The larger is this difference, the greater is the value of cantilever deviation and the force of the tip-surface interaction. Thus, changing the value of Set Point parameter relative the initial value of DFL signal can result in modifying and setting a certain force of the tip-surface interaction, which enables to obtain surface topography images with certain levels of the tip-surface interaction;

- If the difference between the value of Set Point parameter and the initial value of DFL signal is too large, which corresponds to the tip-surface interaction of considerable force, it can result in the destruction of the tip, as well as the surface during scanning;
− The operation of the feedback system may prove unstable if the Set Point parameter value is too small;
− The value of Set Point parameter cannot be less than the value of the initial level of DFL signal and cannot exceed the value of Laser signal.

4.4.2. Preparation for Scanning

4.4.2.1. Setting the Operating Level of the Feedback Gain Factor

The larger is the gain factor value (FB Gain parameter), the higher is the rate of feedback processing. However, at a fairly large gain factor (known as threshold), the operation of the feedback system becomes unstable, with the DFL signal amplitude increasing considerably and self-generation starts. To provide stable operation of the system the gain factor level should be set below 0.6 ÷ 0.7 of the threshold value, at which self-generation starts.

To set the operating level of the feedback gain factor, do the following:

1. Double click the left mouse button in the text box of FB Gain parameter on the Main Operations panel (Fig. 4-13). Increase the FB Gain value using the popup slider, while observing the level of DFL signal by means of the software oscilloscope.

2. Determine the value of FB Gain factor at which the self-generation starts. The beginning of oscillation generation is registered by the abrupt increase of the a.c. component of DFL signal (Fig. 4-12).

3. Decreasing the FB Gain parameter set a value equal to 0.6 ÷ 0.7 of FB Gain value, at which the oscillation of DFL signal starts, as the operating one.
4.4.2.2. Setting up the Scanning Parameters

Switch to **Scan** tab (the button on the main operations panel) (Fig. 4-14).

**SPM Mode Setup**

Select the required operating mode (Contact Topography for Constant Force Mode) in the list **Mode** (scan mode list) of the control panel (Fig. 4-15). The instrument will be configured automatically.

**Selecting the area of scanning**

Recommendations for the selection of the initial size of the area of scanning:

- If any preliminary data on the sample surface properties is available, and there is confidence that the expected topography level difference is within the z-range of the scanner, it is possible to set the maximum area of scanning;

- In case of a sample with unknown surface properties, it is recommended to start the process from scanning a smaller area of about 0.5×1 μm for example. The optimal values of such parameters, as scan rate, **Set Point**, and **FB Gain** can be selected based on the results of scanning this small area. Then the size of the area of scanning can be modified.
By default, the **Scan Size** parameter is automatically set to maximum value. This is:

- for 100-micron scanner: $100 \times 100 \ \mu m^2$;
- for 3-micron scanner: $3 \times 3 \ \mu m^2$.

**To change the area size and to select another area within the limits of the maximum possible area, perform the following:**

1. Click the button in the Data Viewer toolbar (Fig. 4-16) to change the size and position of the area of scanning.
2. Change the area size and position using the mouse (pos. 1 in Fig. 4-16).

   **NOTE. Changing the scan area size will be automatically reflected in text box of Scan Size parameter (Fig. 4-14).**

3. Click the button. Make sure that the tip can touch the surface in any point within the selected area of scanning without "hitting" it anywhere. To do this, click the left mouse button and, move the cursor within the limits of the selected area, keeping the button pressed (pos. 2 in Fig. 4-16). The movement of the cursor reflects the actual displacement of the tip relative the sample surface. The degree of piezoscanner protraction should be controlled using the indicator at the bottom of the window.

![Fig. 4-16. Panel of 2D images of the scanning data](image)

1 – boundaries of the selected scanning area;
2 – cursor indicating the position of the tip relative the sample surface
Setting the scan size, the points number and the scanning step size

The size of the scanned image (Scan Size parameter), the number of points along X and Y axes (Point Number) and the scanning step (Step Size) are defined using the button for selecting the parameter, on which the corresponding parameter is shown, and the adjacent text boxes displaying the current value of the parameter. In the example in Fig. 4-17 the Scan Size parameter was chosen.

Fig. 4-17

When setting Scan Size, Point Number and Step Size parameters recall that:

- when changing Step Size:  Scan Size is changed;  
  Point Number remains the same;

- when changing Scan Size:  Step Size is changed;
  Point Number remains the same;

- when changing Point Number:  Scan Size is changed;
  Step Size remains the same.

Setting the Scan Rate

The recommended frequency of scanning the lines (the Frequency parameter) should be set within 0.5 ÷ 2 Hz (Fig. 4-17). The frequency of scanning is automatically set within this range at the program start, accompanied by loading of the standard parameters.
4.4.3. Scanning

As an example, let us consider the scanning of a sample in the form of a rectangular grating (standard TGZ-1 grating, scan step of 3 μm, with 3 μm pitch, and 19 nm step height).

4.4.3.1. Scanning Run

Once the preparatory operations are performed, the tip is landed to the sample, the Set Point is selected and the parameters of scanning are set, the process of scanning the sample surface can be started.

To start scanning click the Run button located in the left part of the Scan tab control panel (Fig. 4-18).

After pressing Run button:

- The scan of the sample surface by the probe begins and in the corresponding window the image of the surface being scanned starts to appear line by line, see Fig. 4-19. In our example an image of a rectangular grid is represented;
− In the window for viewing one-dimensional data the profile lines of the scanned surface appear, see (Fig. 4-20).

![Fig. 4-20](image)

− Some buttons on **Scan** panel are replaced with buttons **Pause**, **Restart**, **Stop** (Fig. 4-21).

![Fig. 4-21](image)

In case the scanning should be stopped for some reason, click **Stop** button.

### 4.4.3.2. Modifying the Parameters During Scanning

**Plane subtraction**

In the example shown above (Fig. 4-19, Fig. 4-20), the sample is slightly tilted in X direction.

The tilt can be subtracted directly during the scanning (i.e. in real time mode) using the **Subtract** button switch (Fig. 4-21). The button is set to **None** by default.

If this button is pressed, setting **Plane** position subtracts a plane and the previous image in Fig. 4-19 will approximately look like that in Fig. 4-22.
Correspondingly, in the window for viewing one-dimensional data the current scan profile line is also displayed with the tilt accounted for and subtracted (Fig. 4-23).

Other Subtract functions are described in the SPM Software, part 1.

NOTE. The changes made to the scanned image using Subtract function are not saved in the resulting frames.
4.4.3.3. Adjusting the Parameters During Scanning

The quality of the obtained image depends on various parameters, such as the scanning Velocity (Frequency of scanning), the value of Set Point, and Feedback Loop Gain (FB Gain). Any of these parameters can be modified during scanning.

The Pause button is specially intended for adjusting the parameters. When this button is activated, the scanning in the slow direction stops, whereas the scanning in the fast direction continues, going along the same line. This operation mode can be used to optimize parameters. The modification of the profile, corresponding to the scanned line resulting from the modification of a parameter, for example Velocity (or Set Point or FB Gain), can be monitored in real time.

Press the special Restart button to restart scanning.

Some Recommendations on the Optimization of the Scanning Parameters

The selection of the optimal scan rate value depends on the properties of the investigated object surface, on the scan size and on the environment conditions.

A surface with a smooth topography can be scanned with a higher velocity than a surface with a more pronounced roughness.

It is convenient to begin testing the sample at very low scan rate and then progressively increase it until the line profile becomes deformed: at this point the Frequency should be slightly decreased to obtain a high-quality image.

4.5. Semicontact AFM

Nitride cantilevers with in-liquid resonance frequency in the range of 10÷20 kHz are recommended for operation in liquid.

In semicontact mode of operation the piezodriver working frequency can be set both manually and automatically using a special macro. (see Appendices – Setting the Piezodriver Working Frequency in Automatic Mode on page 112). The procedures for the preparation of the instrument differ for the manual and the automatic mode.

Before using the procedure for setting the piezodriver working frequency in the automatic mode it is recommended to compare the resonance frequency values determined in both modes for a chosen cantilever type. If the results agree then the automatic procedure should be used for the cantilevers of the given type.
Chapter 4. Preparation and Performing the Measurements

The basic steps for the preparation of the instrument and performing the measurements of the piezodriver working frequency in the manual mode are:

1. Approaching the Sample to the Probe (see i. 4.5.1 on page 67).
2. Setting the Piezodriver Working Frequency (see i. 4.5.2 on page 69).
3. Preparation for Scanning (see i. 4.5.3 on page 73):
   a. Selection Set Point (see i. 4.5.3.1 on page 73);
   b. Setting the Working Level of the Feedback Gain (see i. 4.5.3.2 on page 75);
   c. Setting up the Scanning Parameters (see i. 4.5.3.3 on page 75).
4. Scanning (see i. 4.5.4 on page 75).

4.5.1. Approaching the Sample to the Probe

When applying semicontact microscopy techniques for operation in liquid the approach procedure for contact-mode measurements should be used.

Contact-mode approach procedure:

1. Select **Contact** in the menu for choosing the controller configuration on the main parameters panel (Fig. 4-24).

![Fig. 4-24](image)

2. Switch to **Approach** tab (the button **Approach** on the main operations panel) (Fig. 4-25).

![Fig. 4-25](image)

3. Check that **Auto SetPoint** button responsible for the automatic adjustment of the **Set Point** parameter is pressed (Fig. 4-26).

![Fig. 4-26](image)
4. Start the approach procedure by clicking **Landing** button.

5. Once the approach is finished, the message "...Approach Done" will appear in the journal (pos. 2 in Fig. 4-27). The scanner piezotube extension indicator shall advance on about half of its length.

A detailed description of the operations performed by the program during the approach is given in i. 4.4.1 “Approaching the Sample to the ” on page 55.
4.5.2. Setting the Piezodriver Working Frequency

Contrary to the cantilever resonance frequency response in air, the response in liquid contains many peaks. Hence, the determination of the cantilever resonance frequency is performed in a manual mode.

The procedure for setting the piezodriver working frequency is:

1. Turn off the feedback (button is not pressed in).
2. Select SemiContact in the menu for choosing the controller configuration on the main parameters panel (Fig. 4-28).

3. Switch to Resonance tab (the button on the main operations panel) (Fig. 4-29).

4. Set the range for measuring the frequency response of the cantilever oscillation amplitude (text boxes From and To) so that it contains the cantilever resonance frequency. It should be noted that the cantilever resonance frequency in liquid is 5-6 smaller than that in air. The recommended values are From=5 kHz, To=50 kHz.

5. In Options panel (Fig. 4-30) clear the Auto peak find check box (the option for automatic setting of the resonance frequency).
6. Set the maximum amplitude of the generator output signal (**Amplitude** parameter):
   a. On **Generator** panel select the gain for **Amplitude** parameter equal to 10 (Fig. 4-31);
   ![](image1)
   Fig. 4-31
   
   b. Double-click in **Amplitude** text box and, using the slider that appears, Fig. 4-32, increase the value of **Amplitude** to its maximum.
   ![](image2)
   Fig. 4-32

7. In the main parameters panel set **DFL** as a feedback input signal (Fig. 4-33).

   **NOTE.** Before switching the signal applied to the input of the feedback the latter shall be turned off (**FB** button is not pressed in).

   ![](image3)
   Fig. 4-33

8. Enter a value of **Set Point** parameter that exceeds the current **DFL** value by 1.5±2 nA.
9. Click Run button (on the left on the control panel) to obtain the frequency response of the cantilever oscillations amplitude (Mag signal). As can be seen in Fig. 4-34 the cantilever resonance curve in liquid contains numerous peaks.

![Fig. 4-34](image)

10. Select a range with the highest resonance peaks and input a new range for plotting the frequency response of Mag signal. This can be done by two ways:
- by changing the values of From and To on the control panel;
- using the markers that appear on the plot, see Fig. 4-34.

11. Click Run button to plot the resonance curve for the selected range.

![Fig. 4-35](image)

Fig. 4-35. Cantilever resonance curve in the free state
12. Click \[ \text{on} \] button to turn the feedback on. The piezotube will advance by half of its length, as can be seen on the piezotube extension indicator, and the cantilever will approach the sample surface.

13. Click \textbf{Run} button to repeat the resonance curve plotting procedure for the same range but with the feedback on. (Fig. 4-36).

![Fig. 4-36. Resonance curve for the cantilever propped to the sample surface.](image)

Compare the resonance curve corresponding to free cantilever with that for the propped cantilever. Some of the resonance peaks decreased significantly, others remained practically the same but some increased.

Any frequency at which the cantilever oscillation amplitude increases when the cantilever is propped can be chosen for the measurements. Select the peak for which the decrease is the largest.

14. Turn off the feedback ( \[ \text{off} \] button is not pressed in).
15. Replot the cantilever resonance peak in the free state ( \textbf{Run} button).

16. On the plot obtained find the selected peak. Set the piezodriver resonance frequency (\textit{Frequency} parameter) equal to that of the peak:

   a. In \textit{Frequency} parameter text box on \textbf{Generator} panel enter the value corresponding to the maximum of the selected peak. At this a marker will appear on the plot (see Fig. 4-37);

   b. Moving the marker (with the mouse left button pressed) set the frequency value related to the maximum \textit{Mag} signal for the selected peak. \textit{Frequency} text box will display a value at the current marker position.
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Fig. 4-37

NOTE. The resonance peak may have a flat top. In this case decrease the value of the Amplitude parameter.

Setting the piezodriver working frequency is complete.

4.5.3. Preparation for Scanning

4.5.3.1. Selection Set Point

1. On the main parameters panel select Mag as a feedback input signal (before switching make sure that the feedback is off) (Fig. 4-38).

Fig. 4-38

2. Input the value of Set Point equal to approximately half of the Mag signal value.

3. Switch to Approach tab (the button on the main operations panel).
4. Turn on the feedback (button on the main parameters panel). Once the feedback is on, \textbf{Mag} signal will fall to the level of \textbf{Set Point} (Fig. 4-39).

![Graph showing Mag signal](image)

\textbf{Fig. 4-39}

5. Verify that the probe was brought to contact with the sample surface by changing the value of \textbf{Set Point} in the range ±20\% using the slider and monitoring the piezotube extension on the corresponding indicator. Minor variations in \textbf{Set Point} shall not result in any piezotube displacement. Otherwise, repeat the approach procedure for a smaller value of \textbf{Set Point}:

a. Reduce \textbf{Set Point} by a factor of 0.5±0.7;

b. Deactivate \textbf{Auto SetPoint};

c. Start the approach procedure by clicking button.

Once the approach is finished recheck the piezotube behavior with variations in \textbf{Set Point}.

\textbf{NOTE. During retract from the surface Mag signal at a chosen frequency may drop making its use for another approach impossible. Otherwise, the same signal can be reused.}
4.5.3.2. Setting the Working Level of the Feedback Gain

1. Double click with the mouse left button in FB Gain text box located on the main operations panel. Using the slider that appears increase FB Gain while monitoring the Mag signal level on the software oscilloscope (in Approach tab).

2. Determine FB Gain value at which self-generation starts.

The beginning of self-generation is detected by a sudden rise in the Mag signal a.c. component (Fig. 4-40).

3. Set FB Gain equal to 0.6±0.7 of the value at which self-generation starts.

A typical FB Gain value in liquid is 0.6±1.2.

If the self-generation is still present after decreasing FB Gain to 0.2±0.3 try setting the piezodriver frequency on another peak. Also, the self-generation may result from poor fixing of the sample or the cell.

4.5.3.3. Setting up the Scanning Parameters

Setting up the Scanning Parameters are similar to those in contact AFM mode, see item 4.4.2.2 “Setting up the Scanning Parameters” on page 60.

4.5.4. Scanning

Scanning procedures are similar to those in contact AFM mode. See item 4.4.3 “Scanning” on page 63.
4.6. STM

4.6.1. Landing the Sample to the Tip

To maintain the feedback in EC STM measurements a current, flowing between the tip and the sample is used, determined by the value of the tunneling voltage $U_t$ which is equal to the difference between the potentials of the sample and the tip:

$$U_t = S_{mpl} E - T_{ip} E.$$

The value $U_t$ should not be too little, so as to prevent the tip hitting the sample. The control program can switch the feedback off if the difference between the potentials of the sample and the tip ($S_{mpl} E - T_{ip} E$) becomes less than 5 mV.

To approach the sample to the tip, do the following:

1. Switch to the Approach tab (the button on the main operations panel) (Fig. 4-9).

![Fig. 4-41](image)

2. In the input fields on the Steady State panel of the ElectroChemistry tab (Fig. 4-42), define potentials of the sample and of the probe according to the voltamperogram (see Fig. 4-4 on page 53). For Au(111) sample:

$$S_{mpl} E = 180 \text{ mV};$$
$$T_{ip} E = 50 \text{ mV}.$$

![Fig. 4-42](image)

NOTE. The potential difference between $S_{mpl} E$ and $T_{ip} E$ is analogous to the parameter $Bias V$ used in STM techniques.
3. Varying the Smpl E and Tip E values make the IprLow signal minimal.

4. Switch the AutoSetPoint off in the control panel of Approach tab (Fig. 4-43).

![Fig. 4-43](image)

5. Set the SetPoint value of 0.1 (Fig. 4-44) in the main parameters panel (this value defines the value of the tunnel current flowing through the probe I (see Fig. 1-21)).

![Fig. 4-44](image)

6. Close the feedback loop by clicking the button.

7. Launch the landing procedure by clicking the button.

As a result:
- The feedback will be switched on and Z-piezo-scanner will protract maximally. Z-scanner protraction will be represented on the scanner piezotube protraction analogue indicator, located in the lower left corner of the program main window. The length of a color strip characterizes the level of the scanner protraction;
- The step motor will start, moving the scanner with the sample to the tip.

After a while, if the parameters of approaching are set up correctly, the approaching will stop and the following will occur;
- IprLow signal will increase up to Set Point parameter value. The feedback will support the Z-scanner in a position, at which IprLow signal is equal to Set Point signal, this position corresponding approximately to one half of the scanner protraction range;
- The length of a color strip of the indicator will shorten, taking some intermediate position (Fig. 4-45);
- The step motor will stop;
- The increase of IprLow signal up to the value of Set Point parameter will be represented on IprLow (t) dependence in the program oscilloscope;
- The message "…Approach Done" will appear in the journal.
Origin of oscillation

It may happen that performing the approaching and increasing the \textit{IprLow} signal up to the \textbf{Set Point} parameter value leads to a substantial growth of the variable component of \textit{IprLow} signal (for example, as it is shown in Fig. 4-46). This means that there is an oscillation in the feedback system due to excessively big gain factor (\textbf{FB Gain} parameter). In this case it is necessary to reduce the \textbf{FB Gain} parameter value down to 0.5÷0.7 of the threshold one. Adjustment of \textbf{FB Gain} parameter is described below.
4.6.2. Setting the Operating Level of the Feedback Gain Factor

The more is the gain factor value (FB Gain parameter), the higher is the rate of feedback processing. However, if the gain factor is big enough (let us call this value a threshold one), the operation of the feedback system becomes unstable with the IprLow signal amplitude increasing considerably, i.e. "oscillation" starts.

To provide a stable operation of the system the gain factor level should be set to no more than 0.6÷0.7 of the threshold value, at which oscillation starts.

To set the operating level of the feedback gain factor, do the following:

1. Double click the left mouse button in the input field of FB Gain parameter on the basic operations panel. Increase the FB Gain value using the popup slider, while observing the level of IprLow signal by means of the program oscilloscope.

2. Determine the value of FB Gain factor, at which the oscillation starts. The oscillation onset is registered by the abrupt increase of the variable component of IprLow signal (Fig. 4-46).

3. Decreasing the FB Gain parameter set a value equal to 0.6÷0.7 of FB Gain value, at which the oscillation of IprLow signal starts, as the operating one.

4.6.3. Setting up the Scanning Parameters

There are two ways of obtaining scans during EC STM measurements:

1. Using Constant Current Mode, or;
2. Using Constant Height Mode.

The Constant Current Mode implies maintaining a constant value of tunnel current during scanning, using the feedback loop system. The feedback signal, fed to the scanner to accomplish the vertical drift, reflects the surface topography.

When using Constant Height Mode, the tip moves only in a plane so the changes of the current between the apex of the tip and the surface of a sample reproduce the surface topography.
4.6.3.1. **Constant Current Mode**

Switch over to the **Scan** tab by clicking the **Scan** button on the main operations panel (Fig. 4-14).

**Fig. 4-47**

**SPM Mode Setup**

To set up the operating SPM select the **Constant Current** mode in a drop-down **Mode** menu (Fig. 4-15). The device will be configured automatically.

**Fig. 4-48**

**Setting the size of the area of scanning, the number of points, and the scanning step**

Recommendations for the selection of the initial size of the area of scanning:

- If any preliminary data on the sample surface properties is available, and there is confidence that the expected topography level difference is within the z-range of the scanner, it is possible to set the maximum area of scanning;

- In case of a sample with unknown surface properties, it is recommended to start the process from scanning a smaller area of about 0.5÷1 μm for example. The optimal values of such parameters, as scan rate, **Set Point**, and **FB Gain** can be selected based on the results of scanning this small area. Then the size of the area of scanning can be modified.

**Selecting the area of scanning**

The maximal size of the area of scanning (**Scan Size** parameter) is set by default.

To change the area size and to select another area within the limits of the maximum possible area, perform the following:
1. Click the button in the Data Viewer toolbar (Fig. 4-16) to change the size and position of the area of scanning.

2. Change the area size and position using the mouse (pos. 1 in Fig. 4-16).

   NOTE. Changing the scan area size will be automatically reflected in input fields of Scan Size parameter (Fig. 4-14).

3. Click the button. Make sure that the tip can touch the surface in any point within the selected area of scanning without "hitting" it anywhere. To do this click the left mouse button and, move the cursor within the limits of a selected area, keeping the button (pos. 2 in Fig. 4-16). The movement of the cursor reflects the actual movement of the tip relative the sample surface. The degree of piezoscanner protraction should be controlled using the indicator at the bottom of the screen.

   Fig. 4-49. Data Viewer window
   1 – the limits of the selected area of scanning,
   2 – cursor indicating the position of the tip relative the sample surface

When setting parameters Point Number, Scan Size and Step Size, consider the following:

- While altering Point Number: 
  - Scan Size alters;
  - Step Size does not alter.

- While altering Scan Size:
  - Step Size alters;
  - Point Number does not alter.

- While altering Step Size:
  - Scan Size alters;
  - Point Number does not alter.
The values of the **Scan Size** (the size of the area of scanning), the **Point Number** (number of points on X and Y axes) and the **Step Size** (the step of scanning) parameters can be changed using the switch button displaying the selected option (Fig. 4-50) and the input fields, displaying the current value of the set parameter, which are located next to the switch button.

![Fig. 4-50](image)

Use one of the following methods to change a parameter value:

1. Double click the relevant input field and set the required parameter value using the popup slider.
2. Enter the required value into the input field using the keyboard.

**Setting the scanning velocity**

The recommended frequency of scanning the lines (the **Frequency** parameter) should be set within 0.5-2 Hz (Fig. 4-51).

![Fig. 4-51](image)

To change a parameter value use one of the following methods:

- Double click the relevant input field and set the required parameter value using the popup slider;
- Enter the required value into the input field using the keyboard.
4.6.3.2. **Constant Height Mode**

ATTENTION! When using the Constant Height Mode ("the flying apex") it is possible to scan only very smooth surfaces without any slopes, since the feedback during scanning is practically cut-out. Therefore the tip can "hit" the sample.

A surface topography, made while scanning in Constant Current Mode should be obtained prior to scanning in Constant Height Mode.

**Setting up the Scanning Parameters:**

1. Switch to the **Scan** tab (the button on the main operations panel).
2. Select the **Constant Height** mode in a **Mode** list (Fig. 4-52).

The device will be automatically configured to implement the selected mode:
- the feedback gain factor will be decreased to 0.01;
- the **lpr-Low** signal will be selected as the signal displayed during scanning. This can be checked by clicking **button of the scanning parameters setup, which opens **Scan Setup** dialog window (Fig. 4-53).

NOTE. When switching over back to measurements using the **Constant Current** mode, do not forget to increase the **FBGain** feedback gain factor value, since the former value will not be automatically assigned to this parameter.
3. Set the following parameters on the scanning parameters control panel (Fig. 4-54, Fig. 4-55):

Point Number = 128;
Step Size = 0.2-0.5 A;
maximal Frequency;
Plane subtraction.

NOTE. The linear dimensions of the area of scanning should not exceed several nanometers.

4. Set the analog-digital converter gain factor to 10. To do this:
   a. Click the Settings button.
   b. Select $x_{10}$ factor in the drop-down list of the Gain button in the dialog window Scan Setup (Fig. 4-56).
5. Select a flat area of the surface on the previously scanned image. To do this:
   a. Click the button of the scan area selection on the Data Viewer window toolbar (Fig. 4-57). Select **Active Frame** option in the drop-down list. The scanned image will occupy the maximum area of scanning available;

   ![Active Frame](image)

   **Fig. 4-57**

   b. Click the button to change the size and the position of the area of scanning;

   c. Moving the area selection frame and modifying its size select a smooth and flat area on the previously scanned image. The selected area should be located closer to the image center, if possible (Fig. 4-58).

   ![Selected Area](image)

   **Fig. 4-58**
4.6.4. Scanning

Scanning Start

To start scanning click the button located in the left part of the Scan tab control panel.

After the Run button is pressed:
− Line-by-line scanning of the sample surface is triggered and an image of the scanned area appears line-by-line in the panel of 2D images of the scanning data (Fig. 4-59);

![Fig. 4-59](image)

− The lines of the scanned surface topography profile will be displayed one by one in the panel of 1D images (Fig. 4-59).

Slope subtraction

It is evident that the sample in the above example (Fig. 4-59) has some slope along X axis.

The slope can be subtracted during scanning (i.e. in on-line mode), using the Subtract switch button. By default this button is in None state (Fig. 4-60).

![Fig. 4-60](image)

Clicking this button and selecting Plane in the drop-down menu will subtract the plane. A current line of the scanning profile displayed in the oscilloscope window will be modified accordingly.

Other Subtract functions are described in the “SPM Software”.
Chapter 4. Preparation and Performing the Measurements

Fig. 4-61 shows an exemplary Au(111) surface scan.

![Fig. 4-61 An example of Au(111) surface scan. The original scan is on the left, whereas on the right is the scan after plane subtraction.]

NOTE. The changes made to the scanned image using Subtract function are not saved in the resulting frames.

Scanning Parameters Setup

The quality of the resulting image of a surface depends essentially on such parameters as Frequency, the set point value Set Point, feedback gain factor FB Gain and constant voltage value BV. Any of these parameters can be modified directly during scanning.

When selecting the scanning parameters it is necessary to remember that the sharpness of the tip and the stability of the tip fixation in the holder are the primary factors, determining the quality of the resulting STM measurements.

The selection of the optimal scan rate value depends on the properties of the investigated object surface, the size of the area of scanning and the external conditions.

The surface with a smooth topography can be scanned with a higher velocity than the surface with a more steep topography and the considerable level differences.

The scan rate should be reduced when a slope of a projection or hollows located in the direction of scanning are not registered.
4.6.5. **Measurements in standard STM modes**

The EC STM head can be used to perform standard STM techniques. The difference in using the EC STM head as compared with other heads, included in NTEGRA components, lies in the fact that a direct voltage is supplied to the tip and not to the sample.

Thus, all preparatory operations, performed for using the EC STM measuring head in tunneling microscopy measurement mode should comply with the recommendations of the *Performing Measurements*, part 4 “Scanning Tunneling Microscopy”, except two points:

- When installing the sample, a voltage supply contact of the sample should be connected to the grounding socket on the base unit of the device;
- Once the device is in the tunneling microscopy measurement mode, the tip and sample voltage supply switches in the circuitry should be set as shown in Fig. 4-62.

![Fig. 4-62](image)

4.7. **Copper Sedimentation**

As an example we shall consider carrying out of the processes of sedimentation under a potential and dissolution of copper in a solution of 50 mM of H$_2$SO$_4$ + 1 mM of CuSO$_4$ using copper electrodes. Au (111) monocrystal is used as a working electrode.

1. Using the voltamperogramm (Fig. 4-63) set the range of the sample voltage variation (parameter *Smpl E*) for the case of equilibrium of the system electrolyte-electrode, and, also, of the dissolution and sedimentation areas (the procedure of cyclic voltamperometry is considered in **4.2 on page 51**).
2. Open the feedback loop (the button is not pressed in).

3. In the panel Steady State set the value of the sample potential $\text{Smpl E}$ that corresponds to the state of equilibrium in the system electrolyte-electrode.

   The value of parameter $\text{Smpl I}$, which is visualized in the panel Measured values, should be close to zero.

4. Using the voltamperogramm, determine the minimum current of sedimentation (parameter $\text{Smpl I}$). In the given example, (see Fig. 4-63) the minimum current is about $-60 \mu A$.

5. Open the tab Graph. Select $\text{Smpl I(T)}$ in the corresponding drop-down list.

6. To deposit copper, reduce $\text{Smpl E}$ so as to make the value of parameter $\text{Smpl I}$ to be equal to approximately half of the minimum. In the given example, the value of $\text{Smpl I}$ should be within the range $-30 \div -40 \mu A$.

7. In about 20 seconds increase the value of $\text{Smpl E}$ gradually so that the value of parameter $\text{Smpl I}$ would reach approximately a quarter of the minimum. This is done as follows:

   a. Use the top text box in the panel Predefined values to set the value of step resolution of the sample potential equal to 5 mV (Fig. 4-64).

   b. Observe variations of the sample current on the oscilloscope and, using the button $\text{↑} \prod \text{↑}$, increase the value of $\text{Smpl E}$ so that the value of $\text{Smpl I}$ becomes approximately equal to a quarter of the minimum. Wait until the current $\text{Smpl I}$ settles.
8. Close the feedback loop (the button \( \text{FB} \) is pressed in).

9. Take a scan of the sample surface. Dimensions of the deposited copper clusters depend both on the value of \( \text{Smpl I} \) and the duration of deposition. For this value of current, the size of copper clusters is minimum.

10. Open the feedback loop (the button \( \text{FB} \) is not pressed in).

11. Set the value of \( \text{Smpl I} \) equal to about 2/3 of the minimum for 20 seconds. Then increase the value of \( \text{Smpl I} \) to 1/2 of the minimum.

12. Close the feedback loop. Take a scan of the sample again. The size of the copper clusters should become large.

### 4.8. Copper Dissolution

1. Open the feedback loop (the button \( \text{FB} \) is not pressed in).

2. Using the voltamperogramm, determine the maximum current of dissolution (parameter \( \text{Smpl I} \)). In the given example (see Fig. 4-63) the maximum current is about 150 μA.

3. Open the tab Graph. Select \( \text{Smpl I(T)} \) in the corresponding drop-down list.

4. To dissolve copper, set the value of \( \text{Smpl E} \) so as to make the value of parameter \( \text{Smpl I} \) to be approximately equal to 1/3 of the maximum. In this example the value of \( \text{Smpl E} \) should be about 260 mV. Note that the value of \( \text{Smpl I} \) must be positive.

5. Observe the graph \( \text{Smpl I(T)} \) and make sure that the current decreases.

6. In 15–20 seconds after the sample current has settled, close the feedback loop and take a scan of the sample surface.

   If the clusters do not become smaller, increase the value of \( \text{Smpl I} \) by 20–30 μA. Take another scan.

### 4.9. Saving the Data

Once the sample surface is scanned, the resulting surface image is stored in RAM.

To save the obtained data to a hard disk:

1. Choose File → Save in the Main menu panel.

2. Enter the filename in the dialog box and click Save button. The data will be saved in the file with *.mdt extension. A separate frame corresponds to each scanned image of a surface. Indexing of frames corresponds to the order of their acquisition.
4.10. Finishing the Operation

1. Remove the sample from the probe for 2+3 mm. To perform this, do the following:
   a. Switch to the **Approach** tab (click the **Approach** button on the Main Operations panel) (Fig. 4-65).
   
   ![Fig. 4-65](image)

   b. Set the Moving value for the Backward to 2+3 mm and click on the Fast button.

2. Open the feedback loop by clicking on the Feedback button.

3. Perform the following switching operations in the **ElectroChemistry** tab:
   a. Switch the sample and the tip potential registration channels off by clicking on the **Sample OFF** and **Tip OFF** buttons.
   b. Switch the potentiostat over to the equivalent resistance (20 kOhm) operation mode (Fig. 4-66).

   ![Fig. 4-66](image)

   c. Set the bipotentiostat activation button in the Off position.

4. Switch the SPM controller off.

5. Switch the vibration isolation system off.

6. Exit the control program.

**Operation to be fulfilled after finishing the work with the cell**

Disassemble the cell and remove the protective cover plate from the measuring head. Rinse all Teflon parts of the cell, the protective cover plate and the electrodes in running deionized water.
APPENDICES

1. Bipotentiostat Calibration

Calibration is required to ensure correct operation of the bipotentiostat. The calibration process involves the comparison of the assigned values of potentials with the actual (measured) ones.

A digital voltmeter and the connecting cables from the electrochemical installation kit (see Fig. 1-1) are required to perform the calibration.

Calibration can be applied to all channels of the bipotentiostat or to a certain channel selected by the user:

**Complete calibration.** This procedure calibrates all channels of the bipotentiostat successively in the sequence defined in the program. Calibration of the next channel in the sequence starts with clicking the **START** button.

**Individual calibration.** A channel of individual calibration is selected in the drop-down list form the top of the **Bi Potentiostat Calibration** window (Fig. 1-2).
Appendix 1. Bipotentiostat Calibration

The complete procedure of the bipotentiostat calibration includes the following basic operations:

1. Switching the bipotentiostat on.
2. Calibrating the sample potential measurement channel (Sample potential).
3. Calibrating the Tip Potential Measurement Channel (only for EC STM).
4. Calibrating the +/-2 µA range current measurement channel.
5. Calibrating the +/-100 µA range current measurement channel.
6. Calibrating the +/-5 mA range current measurement channel.
7. Calibrating the Tip Current Measurement Channel (only for EC STM).
8. Calibration in the SWEEP mode.
9. Saving the calibration results.

**Switching the Bipotentiostat on**

1. Switch the computer on.
2. Start the control program.
3. Using a switch button on the front panel, turn on the SPM controller.

⚠️ **ATTENTION! Fix all the connectors before switching the instrument on. Any disconnections during the instrument operation may result in damage of the electronic components.**

4. Click the button for choosing the controller configuration and in the menu that opens select (Fig. 1-3):
   - **Contact**, for measurements using contact mode. At this, **DFL** signal will be chosen as the feedback input;
   - **SemiContact**, for measurements using semicontact mode. At this, **Mag** signal will be chosen as the feedback input;
   - **Tunnel Current** for measurements using STM. At this, **Ipr-Log** signal will be chosen as the feedback input.

 ![Fig. 1-3](image)

5. Open the Additional operations panel by clicking on button in the upper right corner of the main program window.
6. Open the Block Scheme by clicking on the **Scheme** button. Verify the position of the switch for applying voltage to the sample: the sample must be grounded, the probe connected to **Ex5** see Fig. 1-4.

![Fig. 1-4](image)

7. Open the electrochemical cell operations tab by clicking on the **ElectroChemistry** button (Fig. 1-5).

![Fig. 1-5](image)

8. Switch the bipotentiostat activation button to **On** position (Fig. 1-6).

![Fig. 1-6](image)

**Calibration of the Sample Potential Measurement Channel**

1. Connect the **CNT** and **REF** connectors (Fig. 1-7) using the auxiliary cable.
2. Open the bipotentiostat calibration menu by clicking on the button. A **Bi Potentiostat Calibration** dialog box shall appear (Fig. 1-8).

3. Connect the preamplifier and the voltmeter as shown in Fig. 1-8.

4. The dialog text box displays a value of the potential to be applied from the bipotentiostat to the sample. Replace it with the actual potential value measured by the voltmeter.

5. Once you click on the **START** button the polarity of potential applied to the sample inverts and the calibration window will look like shown in Fig. 1-9.

6. Enter the voltmeter readings.
NOTE. The sign of the can be ignored when entering the voltmeter readings.

**Calibrating the Tip Potential Measurement Channel**

This calibration is available only for 4-electrode scheme (when operating the electrochemical STM measuring head). For experiments in the 3-electrode scheme, calibration of the tip potential channel should be skipped.

1. Once you click on the **START** button the calibration window will look like in Fig. 1-10. The **Tip potential** will be selected in the calibration parameter list. When calibrating the bipotentiostat for AFM measurements this stage is skipped.

![Fig. 1-10](image)

2. Connect the auxiliary cables and the voltmeter as shown in Fig. 1-10.

3. The dialog box entry field displays a value of potential to be supplied from the bipotentiostat to the tip. Replace it with the actual value of potential, measured by the voltmeter.

4. Once you click on the **START** button the polarity of potential supplied to the tip changes and the calibration window will look like in Fig. 1-11.

![Fig. 1-11](image)

5. Enter the voltmeter readings.
Calibrating the +/-2 µA Range Current Measurement Channel

1. Click the START button or (for the 3-electrode scheme) select the **Current range ±2 µA** item in the list of calibrated parameters (see Fig. 1-12). The dialog window will become similar to that shown in Fig. 1-13.

![Fig. 1-12](image1.png)  
![Fig. 1-13](image2.png)

2. Connect the preamplifier sockets using the auxiliary cables as shown in the dialog box in Fig. 1-13:
   - Connect the CNT and REF using the cable;
   - Connect the WRK and 1M using the second cable (Fig. 1-14).

![Fig. 1-14](image3.png)

3. Click on the START button to display the dialog box like in Fig. 1-15. The table lists the ideal and measured values of the currents and the potentials for the bipotentiostat, operating in the potentiostat mode.
4. Click on the **START** button to calibrate the bipotentiostat for the galvanostat mode (Fig. 1-16).

![Fig. 1-15](image1) ![Fig. 1-16](image2)

**NOTE.** The difference between the ideal and the actual values of the currents and the potentials shall not exceed 0.1 % of the upper limit of the current range (≤ 0.002 µA in this case). Otherwise, repeat the calibration procedure.
Calibrating the +/-100 µA Range Current Measurement Channel

1. Click on the **START** button.

![Fig. 1-17](image)

2. Connect the preamplifier sockets using the auxiliary cables as shown in the dialog box in Fig. 1-17.

3. Click on the **START** button to display the dialog box like in Fig. 1-18. The table lists the ideal and measured values of currents and potentials for the bipotentiostat, operating in the potentiostat mode.

![Fig. 1-18](image)  ![Fig. 1-19](image)

4. Click on the **START** button to calibrate the bipotentiostat for the galvanostat mode (Fig. 1-19).
Calibrating the +/-5 mA Range Current Measurement Channel

1. Click on the **START** button to display the dialog box shown in Fig. 1-20.

![Fig. 1-20](image)

2. Connect the preamplifier sockets using the auxiliary cables as shown in the dialog box in Fig. 1-20.

3. Click on the **START** button to display the dialog box shown in Fig. 1-21. The table lists the ideal and measured values of currents and potentials for the bipotentiostat, operating in the potentiostat mode.

![Fig. 1-21](image)

4. Click on the **START** button to calibrate the bipotentiostat for the galvanostat mode (Fig. 1-22).

![Fig. 1-22](image)

5. Click on the **START** button. For the next item in the calibration parameter list, **Tip current** will be offered. When calibrating the bipotentiostat for AFM measurements this stage is skipped.
Calibrating the Tip Current Measurement Channel

This calibration is available only for 4-electrode scheme (when operating the electrochemical STM measuring head). For experiments in the 3-electrode scheme, calibration of the tip potential channel should be skipped.

1. Click the START button. The program will suggest Tip current (Fig. 1-23) as the next channel to calibrate. This item should be skipped when calibrating the bipotentiostat for AFM measurements.

![Fig. 1-23](image)

2. Connect the 100M preamplifier socket with the measuring head tip holder, using the tip calibration cable (Fig. 1-24).

![Fig. 1-24 EC STM head calibration connection](image)

3. Click on the START button to display the dialog box like in Fig. 1-25. The table lists the ideal and measured values of currents and potentials.
Calibration in the SWEEP Mode

In the calibration parameter list choose **Sweep mode calibration**.

A dialog box shown in Fig. 1-26 will appear.

For some time the window will display the recent value of the potential. The instrument is calibrated to equalize the direct and the reverse potential SWEEP speeds.

After some time the calibration shall be finished.

NOTE. Once the calibration is complete it is recommended to perform a check calibration of the selected channels.
Saving the Bipotentiostat Calibration Parameters

Click on the **Save** button in the **Bi Potentiostat Calibration** window to display the **Save Calibration** window.

![Save Calibration Window](image)

**Fig. 1-27**

Select a folder for saving the bipotentiostat calibration parameters. Enter a file name and click on the **Save** button.

Loading the Bipotentiostat Calibration Parameters

The **Bipot.cfc** file is loaded by default when operating the bipotentiostat.

In case you want to load a different file, do the following:

1. Enter the bipotentiostat calibration menu by clicking on the **Load** button.
2. Click on the **Load** button in the **Bi Potentiostat Calibration** window that appears.

![Open Window](image)

**Fig. 1-28**

3. In the **Open** window that appears select and load the required file with ***.cfc** extension.
Verifying the Calibration

Upon finishing the calibration procedure you may want to verify the calibration in the range of interest. This stage is optional.

An example of calibration check in the current range of 2 μA is given below.

Perform the following switching operations in the ElectroChemistry control panel:

1. Switch on the tip and the sample potentials channels by toggling the \text{Tip ON} and \text{Smpl ON} in ON position.

2. Switch the potentiostat to the cell mode by selecting the \text{Cell} item in the list, see Fig. 1-29.

3. Connect CNT and REF contacts by a cable. Use the second cable to connect WRK and 1M contacts as shown in Fig. 1-30.

4. In \text{Steady state} panel enter the sample potential equal to: Smpl E = 100 mV, see Fig. 1-31.

The values close to the previously assigned shall display on the \text{Measured values} panel Fig. 1-32.
2. Adjustment of the Length of Measuring Head Threaded Supports

This procedure is accomplished at the initial set-up of the measuring head or when changing the cell.

The length of the measuring head threaded supports shall be sufficient to provide at least 2-3 mm gap between the sample and the probe when fixing the measuring head on the exchangeable mount. To reduce undesired tilting during scanning the measuring head base surface shall be parallel to that of the sample stage (providing the object to be observed is nearly parallel-sided.)

To adjust the threaded supports length proceed as follows:

1. Fix the cell with the sample in the positioning system of the base unit, see Fig. 2-1.
2. Turning the approach knob clockwise move the cell to its lowermost position.
3. Check the distance between the sample and the probe holder:
   a. Put the measuring head front supports fixed by the lock-nuts in their seats 1 (see Fig. 2-1) without letting down the rear support.
   b. Looking from a side, carefully lower the rear support of the measuring head. If the gap between the holder and the sample is less than 2 mm then remove the measuring head.
   c. Loosen the lock-nuts and unscrew the threaded supports on the required length.
4. Place the measuring head on the exchangeable mount. The gap between the sample surface and the probe holder shall be at least 2-3 mm.
5. Verify that the measuring head base is parallel to the sample stage surface:
   a. Measure the distance between the exchangeable mount surface and the measuring head base near each of the tree supports.
   b. Adjust the length of the supports so that these distances are equal. A ruler with one-millimeter-point scale would provide the adjustment accuracy of 0.5 mm which usually suffices.
   c. Fix the lock-nuts on the front supports.

This finishes the adjustment of the measuring head supports length.
3. Adjusting the Detection System without Videomicroscope

3.1. Laser Beam Alignment onto the Cantilever

1. Power on the computer and start the control program.
2. Turn on the Scanning Probe Microscope controller.
3. The laser switching-on and switching-off is controlled by button (to the right on the main parameters bar). The laser is automatically switched on upon starting the control program.
4. Take the measuring head and lift it about 10-15 cm above a sheet of paper using the latter as a screen for observing the shape of the laser spot (Fig. 3-1).

![Laser spot](image)

Fig. 3-1

Three are three possibilities here:

a. Undistorted image of the laser spot is observed on the screen (Fig. 3-2). This means that the laser beam hits neither the cantilever nor the probe tip.

b. The image of the laser spot is distorted. The beam partly hits against some part of the design or the cantilever (Fig. 3-3). It should be noted that quite a variety of images is possible (as, for instance, in Fig. 3-3).

c. No image of the spot is seen on the screen. This means that the laser beam hits either the chip (Fig. 3-4) or the probe holder and cannot leave the measuring head.
Moreover, the design of the measuring head allows visual examining the cantilever and the surrounding parts thus enabling the determination of the approximate location of the laser beam.

**To align the laser beam onto the cantilever the following steps are required:**

1. Rotating screw 2 (Fig. 3-5) achieve the undistorted shape of the laser beam. Generally, the laser spot would appear in position 1 (see Fig. 3-6).
2. Rotating screw 2 move the beam at the right angle to the front edge of the chip (1→2 in Fig. 3-6) until the laser spot becomes distorted again.

![Diagram](image)

**Fig. 3-6. Moving the laser spot in general case**

3. Rotating screw 1 move the beam parallel to the front edge of the chip. The two alternatives are possible:
   a. The laser spot moves along the edge of the holder (2→3): in this case the spot disappears when it hits the chip;
   b. The laser spot moves along the edge of the chip (4→5): in this event, when the beam hits the cantilever an interference pattern is observed (Fig. 3-7). Now the laser beam is at the base of the cantilever. Move it towards the cantilever tip. The laser beam alignment onto the cantilever is complete.

4. When the spot disappears rotate screw 2 moving the laser beam towards the end face of the chip (3→4) until the laser spot reappears. Now the laser beam is at the edge of the chip (position 4).

5. Use screw 1 to move the beam along the front edge of the chip (4→5) until an interference pattern is observed (Fig. 3-7). Now the laser beam is at the cantilever base.

6. Move the laser beam towards the cantilever tip.

![Images](images)

**Fig. 3-7. Image of the spot when the laser beam hits the cantilever**

The laser beam aligned, put the measuring head on the desk with the threaded supports up.
3.2. **Accurate Alignment of the Detection System**

After lowering the cantilever in liquid adjust the detection system using the readings of the photodiode signal indicator.

Adjustment procedure:

1. Switch to the **Aiming** tab.
2. Turn screw 2 (see Fig. 3-8) 10 – 25° **clockwise** (this causes the laser spot to move towards the chip) until some **Laser** signal appears.
3. Then turn screw 1 **clockwise** while observing the variation in the **Laser** signal. A criterion for hitting the cantilever is the presence of maximum in **Laser** signal when turning screw 1. In case of a triangular cantilever the laser beam hits one of its arms.
4. Turn photodiode adjustment screws 3, 4 to achieve the maximum increase in **Laser** signal.

![Fig. 3-8. Scanning measuring head](image)
1, 2 – laser adjustment screws;
2, 3 – photodiode adjustment screws

**NOTE.** When adjusting the photodiode position it is important to make sure that turning the photodiode vertical displacement screw causes the vertical motion of the laser beam and similarly for the horizontal screw. If the laser beam moves arbitrarily and **Laser** signal decreases to zero it means that the laser beam hits the photodiode edge. In this event the corresponding screw shall be turned in the opposite direction.

5. Move the laser beam in the direction away from the chip by alternately turning the adjustment screws. Tune on the maximum value of **Laser** signal (15-20 nA).
6. Turn photodiode adjustment screws 3 and 4 (Fig. 3-8) center the laser on the photodiode indicator. The values of **DPL** and **LF** signals shall be close to zero while the magnitude of the total **Laser** signal shall remain fairly large.
Appendix 3. Adjusting the Detection System without Videomicroscope

For triangular cantilever it is recommended to check whether the laser beam hits the tip of the triangle or one of its arms. To do this:

1. Shift the laser beam closer to the chip without changing the laser horizontal position in order to reduce Laser signal approximately twice. The laser adjusted correctly, the laser beam now passes between the cantilever arms reflecting to some extent from both of them.

2. When turning the laser horizontal displacement screw left and right two maxima of Laser signal shall be observed corresponding to the two arms of the triangular cantilever.

3. To return the laser beam to the triangle tip position the laser beam between the arms to obtain minimum Laser signal and then move the laser beam from the chip to the triangular tip.

A criterion for the right alignment of the laser beam onto the triangular cantilever tip is that the Laser signal decreases upon turning the laser adjustment screws.

When using the procedure described above for multy-beam probes the laser beam is likely to be aligned onto an outer beam. For more precise laser beam positioning use the optical viewing system. Moreover, the laser beam can be aligned onto the required probe beam by moving the former along the front edge of the chip and noting the number of maxima in the Laser signal, each of which corresponds to an arm of the triangular cantilever or to a rectangular cantilever.
4. Setting the Piezodriver Working Frequency in Automatic Mode

Nitride cantilevers with in-liquid resonance frequency in the range of 10–20 kHz are recommended for operation in liquid.

Before using the procedure for setting the piezodriver working frequency in the automatic mode it is recommended to compare the resonance frequency values determined in both modes for a chosen cantilever type. If the results agree then the automatic procedure should be used for the cantilevers of the given type.

Basic stages of preparation for measurements when setting the piezodriver working frequency automatically:

1. Setting the Piezodriver Working Frequency (see i. 4.1 on page 112).
2. Approaching the Sample to the Probe (see i. 4.2 on page 116).
3. Preparation for Scanning (see i. 4.3 on page 118):
   a. correction of the working frequency;
   b. selection of Set Point;
   c. setting FB Gain.

Scan parameters settings (selection of SPM mode, scan area and scan speed) and scanning itself are similar to that in contact AFM mode, see items 4.4.2.2–4.4.3 of Contact AFM Section.

4.1. Setting the Piezodriver Working Frequency

Prior to determining the resonance frequency in the automatic mode the probe shall be manually brought to the sample surface at a distance of 1–2 mm. The optical viewing system can be used for this purpose. With the videomicroscope focused on the cantilever, proceed with manually approaching the sample to the probe until the sample surface comes to focus.
To set the piezodriver working frequency proceed as follows:

1. Switch to **Resonance** tab (button on the Main Operations panel) (Fig. 4-1).

![Fig. 4-1](image)

2. Set the range to perform search for the resonance frequency (text box From, To).
   
   In the case when the resonance frequency in liquid is unknown for the given probe, define an approximate frequency range by measuring thermal noise of the cantilever. This is done as follows:
   
   a. Disable the feedback loop (the button is not pressed in).
   
   b. Set the following parameters from the control panel of the tab **Resonance** (Fig. 4-2):
      
      - Clear the check box Auto peak find;
      - Average ≈ 20;
      - Point N ≈ 3000;
      - Amplitude 0;
      - Gain 100;
      - Gain coefficient of the synchronous detector \( \times 10 \).

![Fig. 4-2](image)

   c. Using the Block Scheme of the instrument, set the key into the position where voltage from the generator is applied to the probe (Fig. 4-3).
d. Set a frequency range to measure thermal noise:
   - From $\approx 5$ kHz;
   - To $\approx 300$ kHz.

![Fig. 4-3](image)

e. Click the button **Run** to build a frequency dependence of the cantilever oscillation amplitude.

f. Set the range of values **From**. **To**, which is used to perform search for resonance frequency, so that it would contain the peak of thermal noise corresponding to the first harmonic.

3. In the main menu select subsequently **Tools** $\rightarrow$ **Script** $\rightarrow$ **Scripts** $\rightarrow$ **Res_Liq_Find** (Fig. 4-4).

![Fig. 4-4](image)

Upon choosing **Res_Liq_Find**, the automatic determination of the cantilever resonance frequency for operation in liquid will be performed:
Appendix 4. Setting the Piezodriver Working Frequency in Automatic Mode

- cantilever thermal noise will be measured (Fig. 4-5);

![Fig. 4-5](image)

- the frequency response of the cantilever oscillation amplitude (Mag signal) will be obtained in the range corresponding to the maximum of thermal noise;

- finally, the frequency response of Mag signal will be plotted near the maximum (Fig. 4-6).

![Fig. 4-6](image)
The search for resonance frequency results in the following:

- the piezodriver working frequency will be adjusted to a peak optimal for the operation in the semicontact mode;
- the operating level SetPoint will be selected;
- the feedback loop will be enabled.

If required, once the automatic tuning is done, manual tuning of the generator and the synchronous detector is possible.

4.2. Approaching the Sample to the Probe

1. Switch the instrument in the semicontact AFM measuring mode by selecting SemiContact (Fig. 4-7) in the menu for choosing the controller configuration on the Main Parameters panel.

![Fig. 4-7](image)

2. Switch to Approach tab (the button on the main operations panel) (Fig. 4-8).

![Fig. 4-8](image)

3. Check that the option for the automatic setting of SetPoint parameter is activated. Auto SetPoint button shall be pressed as shown in Fig. 4-9.

![Fig. 4-9](image)

4. Click Landing button to start the approach procedure.
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Once the approach has completed, the message "...Approach Done." will appear in the journal (Fig. 4-10). The scanner piezotube extension sensor shall advance on about half of its length.

![Fig. 4-10](image)

A detailed description of the operations performed by the program during the approach is given in Performing Measurements, part 3, section “Semicontact AFM Measurements”.

A criterion for finishing the approach, i.e. for the contact between the probe and the sample surface, is the sudden drop of the Mag signal value (a nearly vertical line in Fig. 4-11).

![Fig. 4-11](image) ![Fig. 4-12](image)

The absence of a sharp dip on the plot, as in the example shown in Fig. 4-12, is the evidence that the approach was incomplete. In this event the value of Set Point shall be decreased:

1. Switch to the Resonance tab.
2. Turn off the feedback (button on the main parameters panel).
3. Click Run button to plot the resonance curve.
4. Using the marker fine-tune the piezodriver working frequency.
5. Switch to Approach tab.
6. Check that the option for the automatic setting of Set Point parameter is disabled (button is not pressed in).
7. Decrease Set Point by a factor of 0.5 ÷ 0.7 (at this the scanner shall advance on its full length).
8. Start the approach procedure by clicking button.
Once the approach procedure in liquid is finished, it is recommended to verify that the probe has actually approached the sample:

1. Double-click in **Set Point** text box.
2. Using the slider that appears change the value of **Set Point** in the range \(\pm 0.5 \pm 1\) nA, while observing the piezotube extension by the indicator.
   
   The indicator shall not change its position. Otherwise, the approach shall be performed with a smaller value of **Set Point**.

4.3. **Preparation for Scanning**

**Correction of the piezodriver working frequency**

Near the surface the shape of the resonance peak can change hence after finishing the approach the piezodriver working frequency shall be corrected:

1. Switch to **Resonance** (\(\text{Resonance}\)) tab on the main operations panel).
2. Turn off the feedback (\(\text{FB}\)) button on the main parameters panel).
3. Click **Run** button to plot the resonance curve.
4. Using the marker correct the piezodriver working frequency.

**Selecting the Set Point**

The working point for scanning shall be chosen 0.8-0.9 of the cantilever free-oscillations amplitude measured after the approach.

The amplitude curve shall be measured (Mag(z) function) in order to determine the maximum amplitude of **Mag** signal:

1. Switch to **Curves** tab (\(\text{Curves}\)) button on the main operations panel).
2. In the control panel of **Curves** tab (Fig. 4-13) select **Mag** (\(f_1(a)\) parameter) and **Height** signal as its argument (\(a\) parameter).

![Fig. 4-13](image)

3. Set the height variation range (\(\text{Land}\) and \(\text{Lift}\) parameters) from \(-10\) nm to \(+100\) nm.
4. Using the cursor select a point in the scanning region where Mag(z) function is to be measured.
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5. Click **Run** button. Once the measurements are finished an additional window appears displaying the measured response.

6. Carefully adjust the height variation range to obtain a curve similar to that in Fig. 4-14.

![Fig. 4-14](image)

7. Assign **SetPoint** a value $0.8 \div 0.9$ of the maximum **Mag** signal amplitude.

A typical value for the maximum **Mag** signal amplitude is within the range of 5-10 nm.

**Setting the working level of FB Gain**

Set the feedback gain as described in 4.5.3.2 on page 75.

A typical value for **FB Gain** is $0.6\div1.2$. If self-generation is still present after reducing **FB Gain** to $0.2\div0.3$ then either the sample or the cell are not fixed properly.

Setting up the scanning parameters and scanning are similar to those described in 4.5 “Semicontact AFM” on page 66.