# SOFTWARE FOR DETERMINATION OF SURFACE TENSION WITH SESSILE DROP METHOD

MYKHAILO LYTVYN

*Ivan Franko National University of Lviv*
*8 Kyrylo and Mephodiy Str. 79005 L'viv, Ukraine*

(received: 25 November 2016; revised: 22 December 2016; accepted: 28 December 2016; published online: 13 January 2017)

**Abstract:** The sessile drop method was implemented to calculate the values of the surface tension coefficient of liquid metals. Appropriate software was developed to increase the data processing efficiency and the accuracy of the obtained results. This paper provides information on the structure and applications of the designed programs as well as the underlying mathematical models used during computations. Since the determination of the surface tension coefficient in this study is based on the recognition of drop outlines from a digital image, the problems of calibration and appropriate photography mode adjustments are mentioned in this paper. In addition, the methods of controlling the research equipment using Arduino shields are described. Finally, the research results are presented in the form of graphs which show the temperature dependence of the studied parameters of metallic samples and compared with the literature data.

**Keywords:** sessile drop method, surface tension calculation, Young-Laplace equation

**DOI:** https://doi.org/10.17466/tq2017/21.1/k

## 1. Introduction

Several different methods such as the sessile or hanging drop methods, the spinning drop method and the du Nouy ring method are used to determine the surface tension of liquid metals. In this paper we focus on the sessile drop method, since it allows experimental measuring of volumes, densities and contact angles of samples at high temperatures.

An experiment requires the axial symmetry of the studied sample and the horizontal positioning of the substrate which are difficult to provide. Errors occurring while adjusting a unit of research equipment often lead to an irregular shape of the drop. The drop outlines obtained in such cases cannot provide any valid information about the values of the measured parameters.

Obviously, the choice of a suitable calibration constant for conversion of digital photo pixels into a metric measurement system is an important factor which has a considerable influence on the final result of calculations. The correct determination of this coefficient plays an important role in the measurements of the volume and consequently all the other sample parameters obtained using its value. It can be achieved with the help of a calibration device of a known and constant size placed inside the chamber.

Processing the images obtained during such an experiment without appropriate software would be challenging and time-consuming. It would also require a high level of concentration and might generate additional imprecision of the final results. Thus, an optimal solution was to create a program which would increase the efficiency and accuracy of the calculations mentioned in the paragraphs above.

This task was managed using a Qt development environment, and in particular the QGraphics and QCustomPlot libraries which allow the program to open and edit images, and appropriately estimate the obtained data during the processing.

## 2. Logical structure of calculations – main mathematical functions

The values of density and the surface tension coefficient are calculated in a few successive stages. The first stage involves determination of the substrate position and the point-to-point recognition of the drop outline, basing on the differences in the pixel brightness.

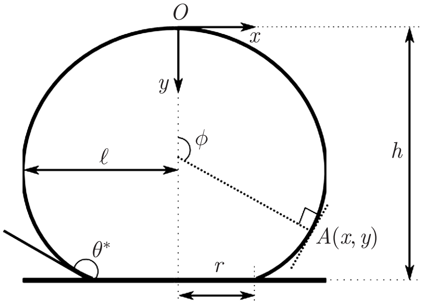


**Figure 1.** Scheme of coordinate system positioning

The drop volume is given by the formula:

$$V = \int_{0}^{h_{\max}} \frac{\pi}{4} R^2 dh = \int_{0}^{h_{\max}} \frac{\pi}{4} (x_R - x_L)^2 dh \tag{1}$$

where $x_L$, $x_R$ are the $x$-coordinates of points lying on the left and right sides of the outline appropriately at a given height. Since a set of discrete points has been selected and the value of $dh$ in pixels is equal to one, the equation assumes the following form:

$$V_{\text{pt}} = \sum_{i=0}^{i_{h\max}} \frac{\pi}{4}\left(x_{R[i]} - x_{L[i]}\right)^2 \tag{2}$$

We can use the following relation to convert the size of the sample from pixels to millimeters

$$V = \frac{d^3_{C\,\text{mm}}}{d^3_{C\,\text{pt}}} \cdot V_{\text{pt}} \tag{3}$$

where $d^3_{C\,\text{mm}}$ and $d^3_{C\,\text{pt}}$ are the parameters of the calibration device.

Several different methods can be used to find the surface tension coefficient $\sigma$. According to [1] $\sigma$ is given by the formula:

$$\sigma = d^2 \rho g \frac{1}{H} \tag{4}$$

where $d$ is the drop diameter, $g = 9.81$ m/s$^2$, $\rho$ is the density of the sample, $\frac{1}{H}$ is the function $\frac{1}{H} = f(\frac{d}{2\cdot h})$ given by the table. In order to carry out the calculations the table of function values was interpolated by a polynomial and hardcoded as a function.

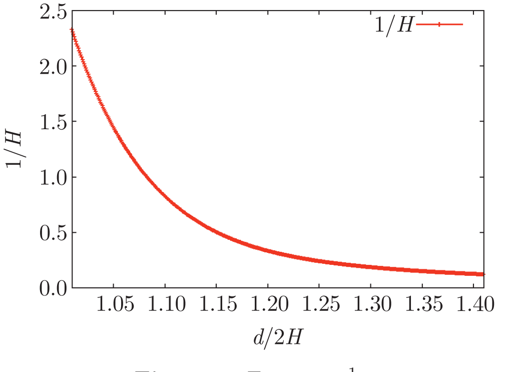


**Figure 2.** Function $\frac{1}{H}$

An essential advantage of this method is the possibility to perform the required calculations using a data set consisting of three points only. However, the set of points might be selected inappropriately if there are defects in the image. This implies that the method is suitable for manual processing, though it can generate errors in the automatic mode.

The method described above is a simplification to calculate the surface tension coefficient for a given value of the contact angle.

According to [2], the following formula can be obtained using the sessile drop method:

$$\sigma = \frac{g\rho h^2}{2\cdot\left(1+\cos(\theta)\right)} \tag{5}$$

In this case the contact angle can be determined as the arctangent of the coefficient $k$ present in the equation $y = kx + b$. The coefficient itself is obtained

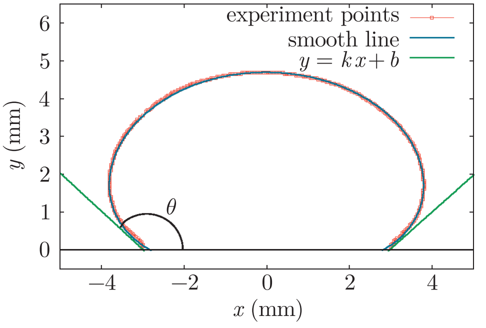


**Figure 3.** Distinguished outline

during the linear interpolation of outline points in the range of $x$ corresponding to the values of $h \in [0; \frac{h}{10}]$. In order to increase the accuracy of the experiment the angle is determined for both sides of the drop outline and the average value is calculated. Additionally, information on the temperature dependence of the contact angle can be obtained.

Another method of calculating the surface tension coefficient involves solving the Young-Laplace equation [3]:

$$\sigma\left(\frac{1}{R_x} + \frac{1}{R_y}\right) = \Delta p \tag{6}$$

where $R_x$, $R_y$ are the orthogonal radii of the drop surface curvature, $\Delta p$ is the pressure difference across the liquid-gas interface. Equations used to determine the radius of curvature $k_x = \frac{1}{R_x}$ can be expressed in several different forms:

$$k_x = \frac{1}{R_x} = \frac{y''}{\left(1 + \left(y'\right)^2\right)^{3/2}} \tag{7}$$

$$k_x = \frac{1}{R_x} = \left|\frac{\rho^2 + 2\left(\rho'\right)^2 - \rho\rho''}{\left(\rho^2 + \left(\rho'\right)\right)^{3/2}}\right| \tag{8}$$

Equation (7) [3] is given in Cartesian coordinates. The function used to determine the radius of the curvature, which is described with the mentioned equation, has breakpoints as its first derivative approaches infinity. Thus, it is necessary to convert the equation to a polar form in order to avoid such complications. Derivatives in polar coordinates can be calculated in the following way:

$$\begin{aligned} \rho(\phi) &= \sum_{i=0}^{n} A_i \cdot \phi^i \\ \rho'(\phi) &= \sum_{i=1}^{n} A_i \cdot i \cdot \phi^{i-1} \\ \rho''(\phi) &= \sum_{i=2}^{n} A_i \cdot i \cdot (i-1) \cdot \phi^{i-2} \end{aligned} \tag{9}$$

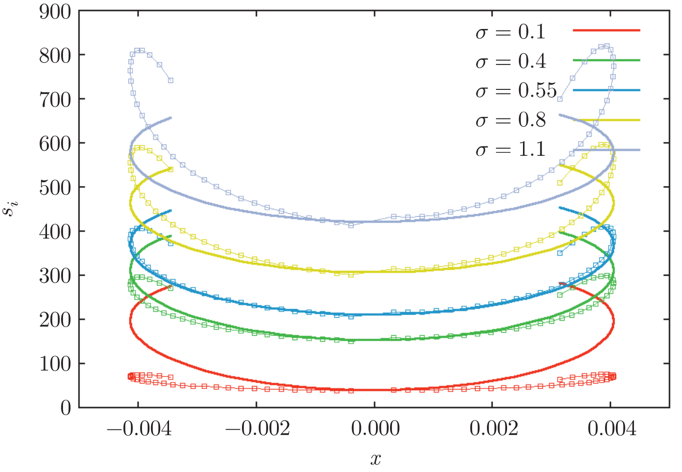


**Figure 4.** Values $s_i$ for different values of $\sigma$

where $n$ is the order of the fitting polynomial.

The curvature $k_y$ is given by [3]

$$k_y = \frac{1}{R_y} = \frac{y'}{x \cdot \left(1 + \left(y'\right)^2\right)^{1/2}} \tag{10}$$

It can be rewritten in polar coordinates as:

$$y' = -\frac{\rho\cos(\theta) + \sin(\theta)\rho'}{\rho\sin(\theta) - \cos(\theta)\rho'} \tag{11}$$

The function (10) has a single breakpoint $x = 0$.

As a result of substituting the expressions (8) and (10) into Equation (6) we get:

$$\sigma\left(\left|\frac{\rho^2 + 2\left(\rho'\right)^2 - \rho\rho''}{\left(\rho^2 + \left(\rho'\right)\right)^{3/2}}\right| + \frac{y'}{x \cdot \left(1 + \left(y'\right)^2\right)^{1/2}}\right) = \frac{2\sigma}{b} - \rho g y \tag{12}$$

where $b = \frac{1}{y''(0)}$.

The last equation is satisfied for each $\phi$-value, $\phi_i$ value. The values of $s_i$ for various values of $\sigma$ are shown in Figure 4.

The optimal value of $\sigma$ can be calculated from:

$$S = \sum_{\phi=-\frac{\pi}{2}}^{\frac{\pi}{2}} s_i(\phi) = \sum_{\phi=-\frac{\pi}{2}}^{\frac{\pi}{2}} \left[\sigma_i\left(\left|\frac{\rho(\phi)^2 + 2\left(\rho'(\phi)\right)^2 - \rho(\phi)\rho''(\phi)}{\left(\rho(\phi)^2 + \left(\rho'(\phi)\right)\right)^{3/2}}\right| + \frac{y'(\phi)}{x(\phi) \cdot \left(1 + \left(y'(\phi)\right)^2\right)^{1/2}}\right) - 2\sigma y''(0) + \rho g y(\phi)\right] \tag{13}$$

## 3. General information and application of the software – means of development

The experimental data processing program has been designed to calculate the values of volume, density, contact angles and the surface tension coefficient of a sample within a sessile drop experiment. The program's interface consists of a main window and output data display windows.

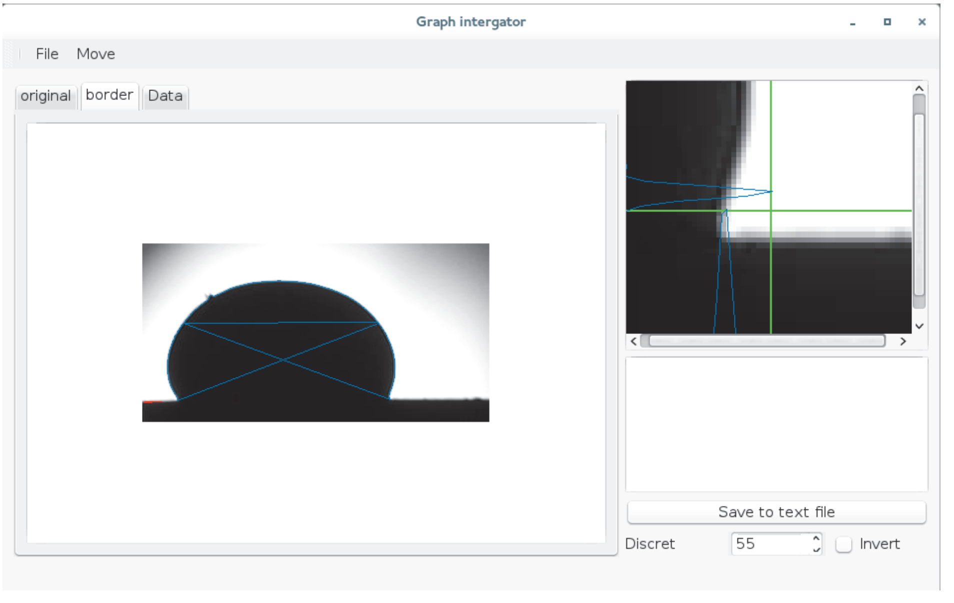


**Figure 5.** Program main window

The main window has a QTabWidget containing three tabs. The first tab displays the image to be processed as well as a magnification field for the area of the image which can be selected with the cursor. Furthermore, the magnification field shows the curves which represent the color intensity distribution. This additional feature enables the user to evaluate the quality of the image as well as take the possible outline blur and minor roughness of the drop profile into account.

The second tab holds a field which displays a substrate line and a drop contour line plotted over the image. This display area gives a possibility to estimate whether the outline is distinguished correctly. The outline of the drop itself can be found as a result of comparing the color intensity of adjacent pixels of the image. Since the difference in the pixel intensity can vary for different images depending on the lighting brightness, the shutter speed of the camera and the temperature of the sample, the option to alter the lower level of the intensity difference is available in the program.

Although images taken at low temperatures depict a dark sample on an illuminated background, it often is more convenient to set the inverse photography

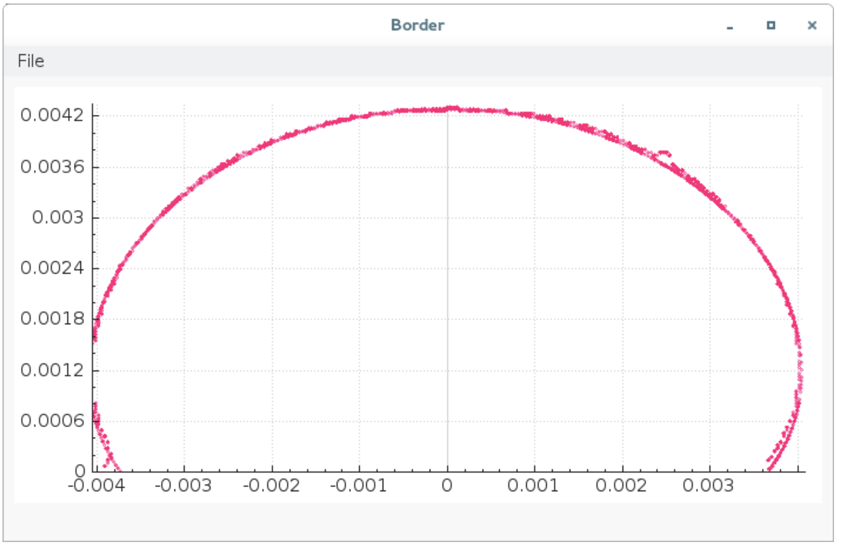


**Figure 6.** Additional display window

mode while picturing samples at high temperatures ($T > 900°\mathrm{C}$) and distinguish an outline of a glowing sample on a dark background. In this case it is necessary to set up the program to the inverted image processing mode. The drop outline obtained in the way described above is calibrated into the metric system and displayed on an individual window as a graph (Figure 6). A line obtained during the interpolation of the outline using the least squares method is also plotted over the graph. Such a way of output data representation gives a possibility to estimate the real size of the sample, its symmetry and correctness of calibration.

A QGraphicView object is used to display images and additional lines. It contains QGraphicsScene with appropriate objects (`addPixmap()`, `addLine()`, `addPolygon()`). The `addPixmap()` function is applied to put an image on the appropriate field followed by the addition of cursor lines and a polygon contour on the appropriate tabs. Since the cursor control is essential for determination of the magnification area, new methods have been developed to provide the ability to use control keys in order to move the cursor on the image area. Simultaneously the cursor centre coordinates are displayed in the status bar of the program. This allows measuring the distances between two points of the image in pixels.

The third tab of the program's main window holds an input area for the calibration device parameters and the mass of the sample. In order to determine the calibration coefficient it is necessary to provide the values of the size of the object measured in pixels using the program and its real size (in mm) as the input data. The output area for the data obtained as a result of the program implementation is also located at this tab. The output is carried out using the QTextEdit widget and separates the data into appropriate columns: temperature, contact angle (in radians), volume (in $\mathrm{mm}^3$), density (in $\mathrm{g/cm}^3$) and the surface tension coefficient. The data displayed in the output text field can be saved into a file.

The Command items of the “File” menu provide access to the functions which are applied to open images, distinguish outlines of the images and perform a complete image analysis with the data output. An “Open file list” item calls a function which allows simultaneous opening of an image array for complete analysis. The results of this analysis are plotted in an additional display window as a graph which represents the temperature dependence of density and the contact angle. The outline display area on the graph in the additional window is set clear of the data as a new image is opened. The main menu “Move” item contains cursor control functions for the first tab. These functions can also be accessed using key shortcuts.

## 4. Results of software tests

A series of images of samples was taken at a given temperature with different exposure times to test the program.

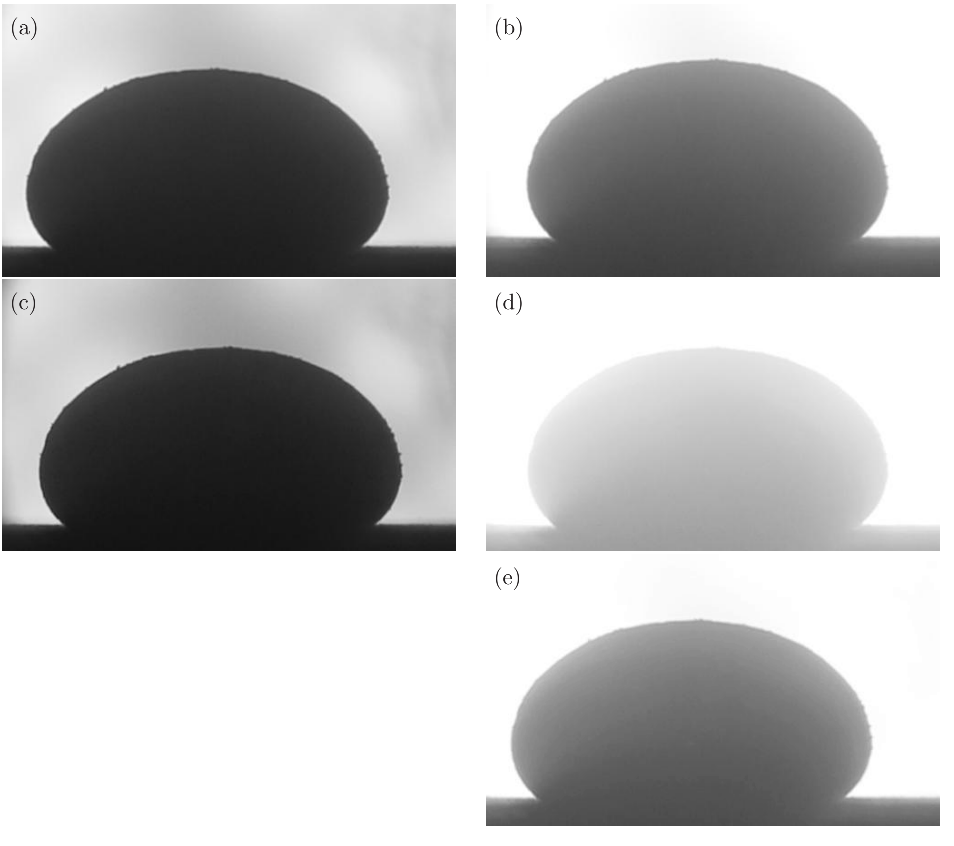


**Figure 7.** Photos of drops taken with different exposure times

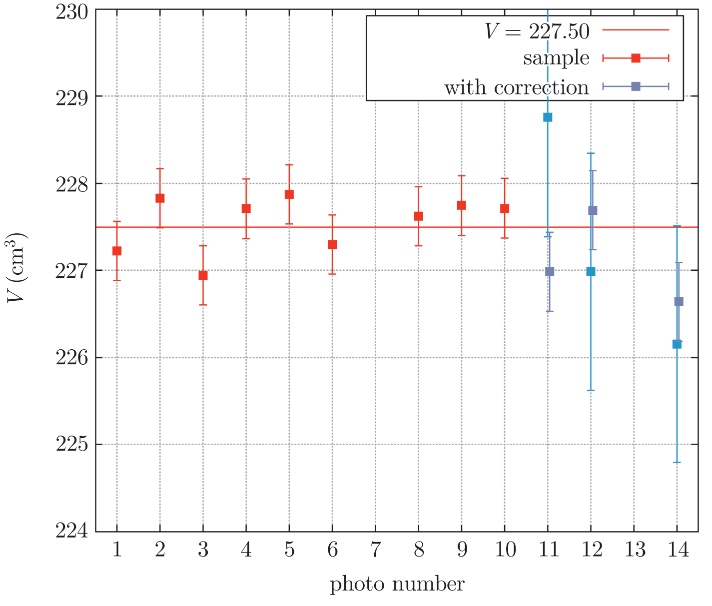


**Figure 8.** Drop volume calculated for different images

The results of this picturing are illustrated in Figures 7 (a)–(e). Image (a)[1] was taken with an optimal set of parameters of the camera, for images (b), (d), (e) the shutter speed was set too high, for image (c) – too low.

It can be concluded from Figure 8 that the volume computed for picture (a) closely approaches its real value, while the deviations for low-quality pictures of the same sample are much more noticeable.

The values of the volume obtained from the images of different quality (Figure 7) with the same image processing settings are marked with red and blue, while magenta is used to depict the values obtained for the altered brightness difference, which increases the accuracy of the outline recognition. As we can conclude from the figure the program handles the problem of dim lighting (point 12 Figure 8). However, excessively highlighted images cannot be recognized in an adequate way.

Figure 9 shows a graph of the temperature dependence of the volume for a stainless steel bead of the diameter equal to 6.350 mm. From the linear interpolation we get the following values of the studied parameters: $V_0 = 134.5$ mm $\beta = 6.06 \cdot 10^{-5}$ K$^{-1}$ Such results match the table values for steel ($V_0 = 134.06$, $\beta = 5.94 \cdot 10^{-5}$).

The temperature dependence of the studied parameters of metallic samples compared with those given in literature. After comparing the results of the samples of pure metals with the literature data we can say that there is good coincidence of our data with the data from previous studies (Figure 10, Figure 11).

1. One of a set of ten images is presented in Figure 7 a).

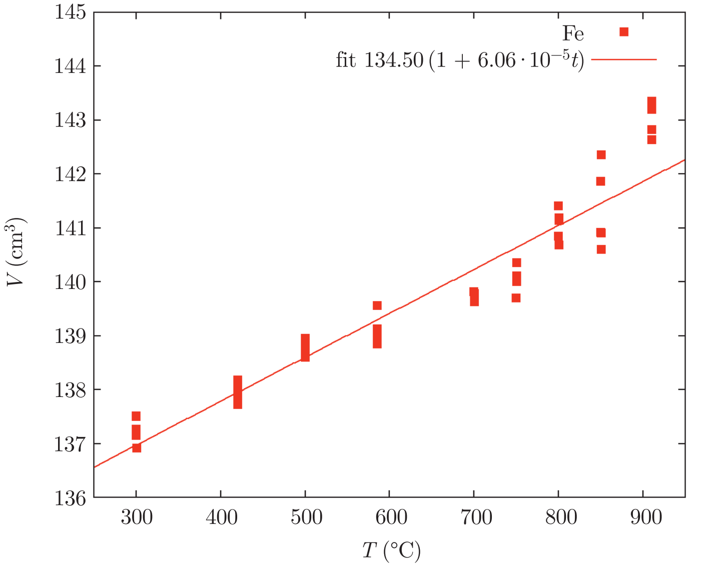


**Figure 9.** Temperature dependence of metal bead's volume

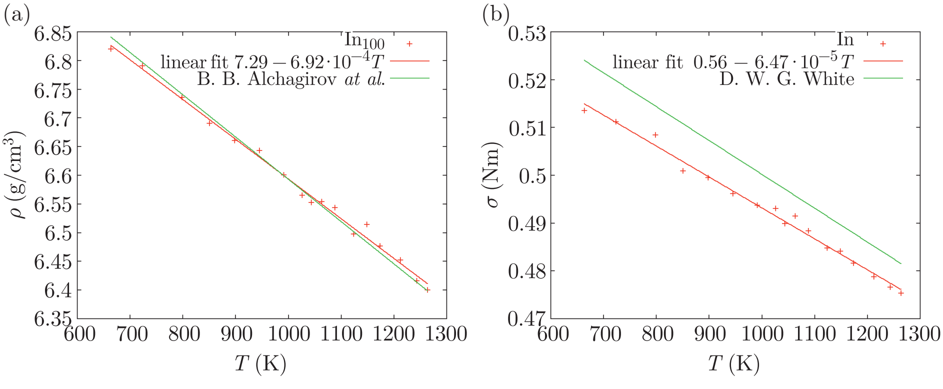


**Figure 10.** Temperature dependence of density (a) and surface tension coefficient (b) of pure indium compared to the data provided in the literature

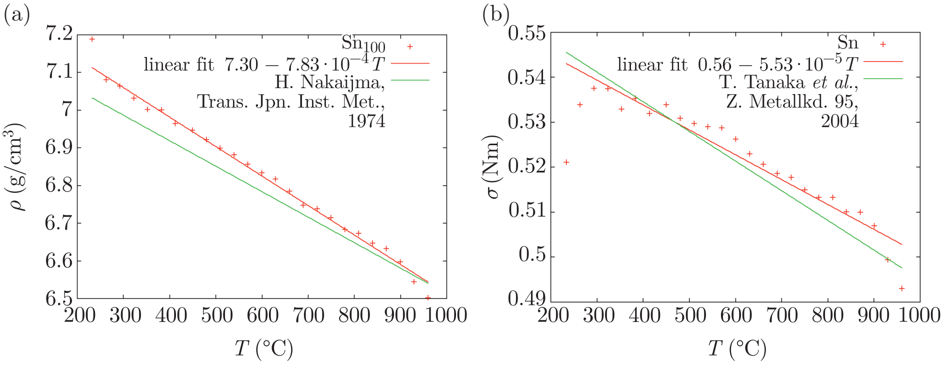


**Figure 11.** Temperature dependence of density (a) and surface tension coefficient (b) of pure tin compared to the data provided in the literature

## 5. Additional software

A unit of research equipment is operated with the help of an additional program. It was designed to enable the user to control the temperature of the sample and operate the camera. The temperature is measured using a thermocouple. Afterwards the obtained data is passed to the computer with the help of the Arduino shield to start its processing. Depending on the data obtained from the measuring device using PWM Arduino the power of the heater is set according to the PID regulation law. The time dependence of temperature is displayed as a graph.

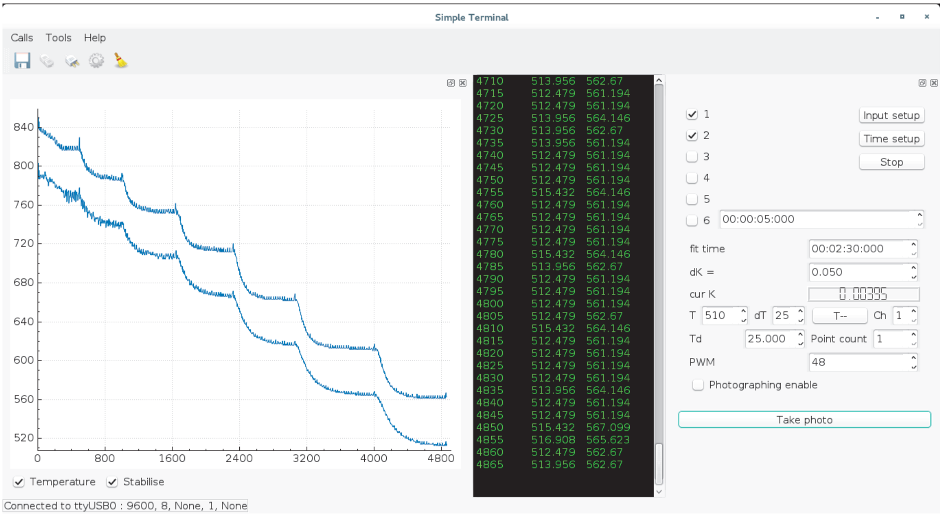


**Figure 12.** Main window of the program

Additionally the program outputs values of a time derivative of temperature, which gives a possibility to track the temperature stabilization. The camera control is based on signals to take an image generated in a relay operated with the same Arduino board.

Arduino itself is operated via a virtual serial port by sending command codes.

The QSerialPort library is used to provide a data exchange. It allows the user to send and receive data via a serial port. QCustomPlot and QTextEdit objects are used to display data. In addition, the data is dynamically written to a text file.

Additional programs were also created for the purposes of the preprocessing image edition which includes cropping images to the standard size and renaming files. Cropping an image decreases its size and consequently increases the speed of analysis. The image files are renamed in order to match an image with appropriate temperature at which it was taken. The file names are later read by the final data processing program and used during the output data formation process. QDir and

QFile libraries are used to manage all the mentioned operations, while files are chosen and displayed using QFileSystemModel and QTreeView.

## 6. Conclusions

A new, original package of programs was created to conduct an experiment implementing the sessile drop method and to simplify the processing of the obtained data. Experimental data closely coincides with the values of the studied parameters provided in the literature which shows a high accuracy of the implemented method.

### *References*

[1] Koshevnyk A Yu, Kazakov M M, Lubman N M 1953 *Journal of Physical Chemistry* **27** (12) 1887

[2] Chow T S 1998 *Journal of Physics: Condensed Matter* **10** (27), L445

[3] Bashforth F, Adams J C 1892 *An Attempt to Test the Theory of Capillary Action*, Cambridge