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AUTOMATIZACE VYHODNOCOVÁNÍ DAT TDS
AUTOMATIZATION OF TDS DATA EVALUATION

BAKALÁŘSKÁ PRÁCE
BACHELOR'S THESIS

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BRNO 2012

ABSTRAKT

Tato práce se zabývá automatizací vyhodnocování dat termální desorpční spektroskopie (TDS). Teoretická část pojednává o procesích adsorpce a desorpce atomů a molekul a teplotní závislosti desorpce. Součástí práce je také kvantitativní analýza signálu měřícího přístroje. Hlavním cílem praktické části bylo vytvoření počítačového programu na automatizaci vyhodnocování dat TDS. Popis programu a uživatelská příručka jsou také součástí práce. Proběhlo testování programu na předchozích měření a kinetické parametry desorpce byly zjištěny u několika vzorků.

KLÍČOVÁ SLOVA

Termální desorpční spektroskopie, tepelně řízená desorpce, automatizace vyhodnocování dat.

ABSTRACT

This bachelor thesis is focused on automatization of post-processing and evaluation of thermal desorption spectroscopy (TDS) data. The theoretical part discusses the processes of adsorption and desorption of atoms and molecules on surfaces and the thermal dependence of the latter. This work also provides a quantitative analysis of the measured signal from the instrument. The main objective of the practical part is to create a computer tool for automatization of TDS data evaluation. Description of the program, as well as a user guide, is included in the work. Comprehensive tests of the created program were concluded on previously measured TDS spectra and the kinetic parameters of several samples were determined.

KEYWORDS

Thermal desorption spectroscopy, temperature programmed desorption, data evaluation automatization.

BADIN, V. Automatizace vyhodnocování dat TDS. Brno: Vysoké učení technické v Brně, Fakulta strojního inženýrství, 2012. 29 s. Vedoucí bakalářské práce Ing. Michal Potoček, Ph.D.

Acknowledgements

CONTENTS

1 INTRODUCTION

Mass spectroscopy nowadays is a very common technique in analytical laboratories that study physical, chemical, or biological properties of a great variety of compounds. It is an analytical technique that measures the mass-to-charge ratio of charged particles. Mass spectroscopy measurements are a source of great amount of data. Instead of direct measuring of molecules the measured data are affected for example by molecule fragmentation during ionization or different ionization probabilities. Moreover, thermal desorption spectroscopy (TDS) is limited by the fact, that it isn't able to record the whole spectrum, only a few selected masses can be measured. The presence of a certain molecule on the observed surface can be confirmed by the correlation of desorption rates of different signals.

The main goal of this bachelor's thesis is to create a computer software for calculation of correlation coefficients from measured TDS data. This program will be tested on previously measured data. Furthermore, TDS measurements of variously treated silicon samples will be evaluated using the created program.

Chapter 2 discusses the main physical principles related to thermal desorption spectroscopy. It also gives a detailed description of the instruments used in TDS measurements as well as a description of mechanisms responsible for signal degradation and their possible corrections.

In chapter 3, the created program is presented. In section 3.1, the output file structure of the measure instrument is analyzed, as the program reads measurement data from this file. Description of the created program and a user guide are also included in this chapter. Additionally, a sample analysis of previously measured spectra is provided taking advantages of the created program in section 3.3.

2 THEORETICAL PART

2.1 Fundamental principles

2.1.1 Adsorption

Adsorption takes place when the attractive interaction between a particle and a surface is strong enough to overcome the disordering effect of thermal motion. When the attractive interaction is the result of van der Waals forces then physisorption takes place. Physisorptive bonds are characterized by desorption energies (E_d, figure 2.1) below approximately $50 \, \text{kJ/mol}$ [1]. Physically adsorbed molecules are not bound to a specific location on the surface and may therefore diffuse along the surface. Chemisorption occurs when the overlap between the molecular orbitals of the adsorbed particle and the surface atoms allow the formation of chemical bonds, which are characterized by desorption energies exceeding $50 \, \text{kJ/mol}$. The formation of a chemisorptive bond often requires overcoming of an activation barrier. Figure 2.1 shows potential diagrams for different particles. Figure 2.1a shows the dependance of potential on distance for a monoatomic particle whereas figure 2.1b demonstrates the dependance for a diatomic molecule.

Physically adsorbed molecules may form multiple layers. Chemisorption usually only proceeds as long as the adsorbtive (the molecule prior to being adsorbed) can make direct contact with the surface, hence a single layer is formed. Both physisorption and chemisorption may take place on the surface simultaneously – molecules may be physically adsorbed to an underlying chemisorbed layer. The same surface can display physisorption at a certain temperature and chemisorption at a higher temperature. For example, at $77 \, \text{K}$ nitrogen gas will adsorb physically to an iron surface but at $800 \, \text{K}$ the thermal motion of nitrogen atoms makes it impossible to form physical adsorption bonds, hence nitrogen will adsorb chemically and form iron nitride [2].

2.1.2 Desorption

Desorption is the opposite process of adsorption (or sorption, generally) – a phenomenon where a particle is released from a surface. That is, the attractive interaction between the particle and the surface becomes weaker than the disordering effect of thermal motion. The desorption rate is usually expressed as

$$ r = \nu_l n^l \exp\left(-\frac{E_d}{kT}\right), \tag{2.1} $$

where $r = -\text{d}n/\text{d}t$ is the desorption rate, n is the concentration of adsorbed molecules, ν_l is a material-dependent preexponential factor, l is the the kinetic order of desorption, E_d is the desorption energy of an atom (molecule), k is the Boltzmann-constant and T the thermodynamic temperature. The preexponential factor, the desorption energy and the desorption order are often called the kinetic parameters of desorption. For first-order kinetics, i.e. $l = 1$, n can be replaced by the surface coverage Θ in monolayers without any changes in the preexponential factor;

(a)

(b)
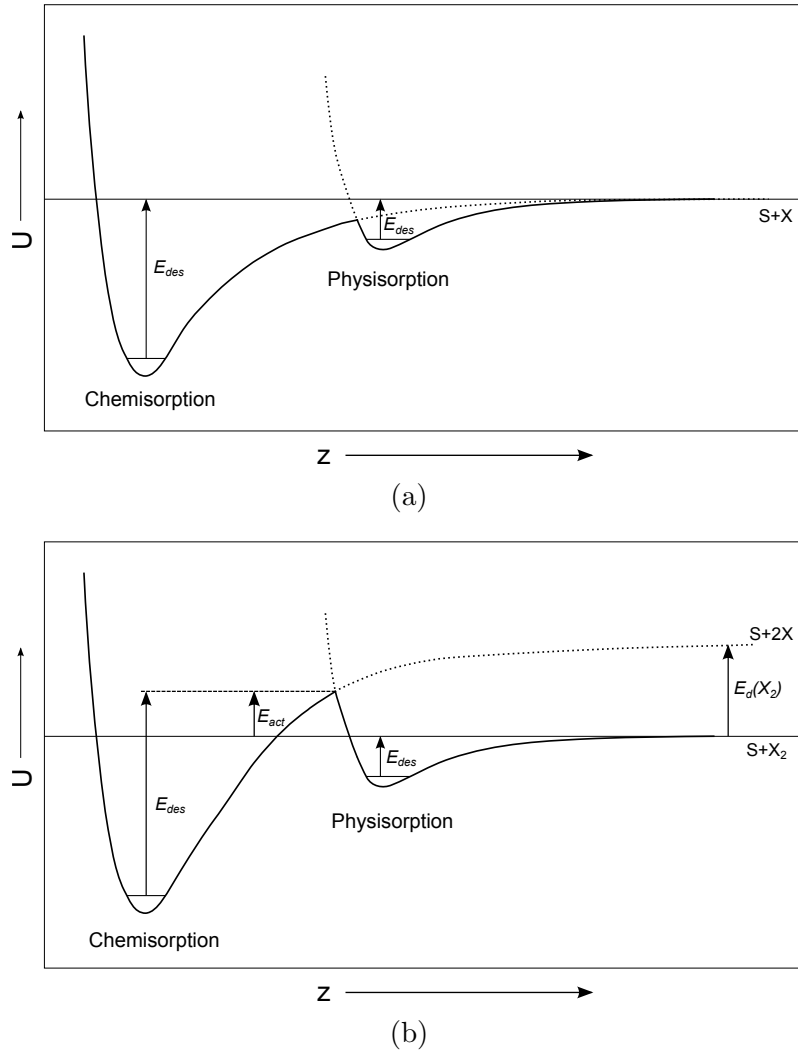
Figure 2.1: Dependance of potential diagram on distance for an atom X (a) and a diatomic molecule X_2 (b) that approaches a surface S along the z-axis. E_{des} denotes the desorption energy, $E_d(X_2)$ is the dissociation energy needed to break the X−X bond and E_{act} is the activation energy necessary for chemical bond formation. The physisorption potential has been assumed to be a Lennard-Jones potential, whereas chemisorption is described by a Morse potential.
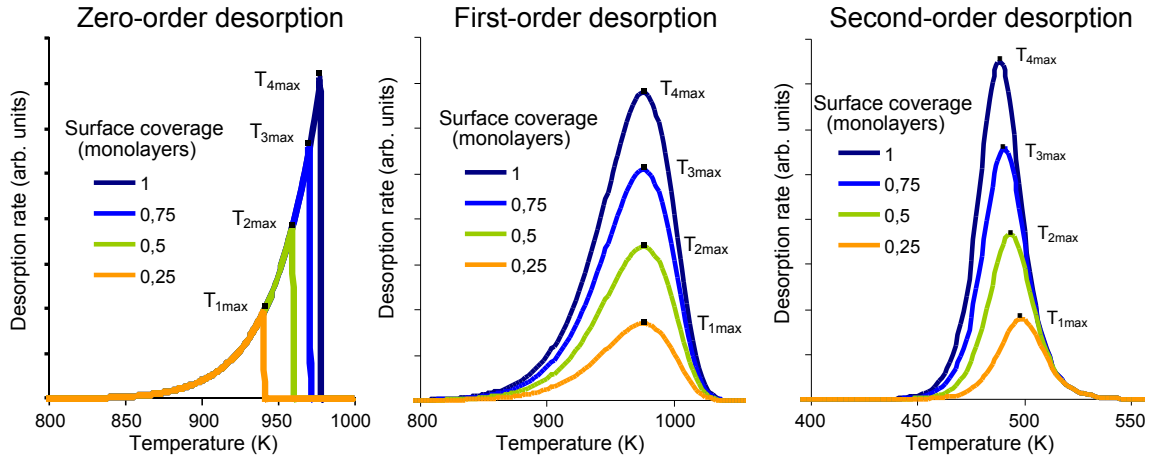
Figure 2.2: Typical desorption rates of zero-, first- and second-order desorption. Peak intensity is a function of initial surface coverage [4].

the desorption rate is then defined as $r = -\mathrm{d}\Theta/\mathrm{d}t$. Equation (2.1) is often referred to as the Polanyi-Wigner equation [3]. Figure 2.2 shows typical desorption rates of zero-, first- and second-order desorption. The desorption energy and the preexponential factor are usually determined experimentally from desorption spectra using various curve-fitting algorithms.

2.2 Thermal desorption spectroscopy

Thermal desorption spectroscopy (TDS) also known as *temperature programmed desorption (TPD)* is often used to determine the kinetic parameters of desorption: energy of desorption, preexponential factor and order of desorption. Though other methods have been developed as well (such as XPS[1], AES[2], LEIS[3]), some even more sensitive or more precise, TDS is among the most attractive ones for this purpose. The main advantage of TDS is its simplicity and applicability to a wide range of samples.

2.2.1 Development of TDS

The progress made in ultra-high vacuum (UHV) techniques in the 1950s led to a rapid increase in research focused on studying interactions at metal surfaces. J.A. Becker at Bell Labs and G. Ehrlich at General Electric developed the *flash-filament* method to study adsorption of gases on metal surfaces: a refractory metal sample (usually a polycrystalline wire at that time) was cleaned by heating in UHV conditions and a sample gas was allowed to adsorb on its surface. The sample was then heated in a desirably programmed way and the resulting pressure changes were recorded.

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[1]XPS – X-ray photoelectron spectroscopy.
[2]AES – Auger electron spectroscopy.
[3]LEIS – Low-energy ion scattering spectroscopy.

Reaction rate measurement at continuously changing temperatures was first described by Urbach in 1930 and had been used many times to study chemical kinetics. The flash-filament method for adsorption kinetics studies was proposed by L. Apker in 1948 and further developed by J.A. Becker and H.D. Hagstrum at Bell Labs in the early 1950's. G. Ehrlich showed how the thermal desorption spectra could be analyzed to obtain data on surface coverage in various adsorbed phases and the parameters of their desorption kinetics. P.A. Readhead and G. Carter independently published two manuscripts in 1962 extending Ehrlich's work and leading to identical conclusions. Furthermore Redhead's paper demonstrates remarkably useful calculations of the desorption parameters from different forms of the desorption spectrum. Later, Redhead's paper becoming a *Citation classic*, he defines thermal desorption spectroscopy as

> *"The heating in vacuum of a solid sample, on which gases have been previously adsorbed, results in a spectrum of pressure changes"* [5].

2.2.2 A TDS measurement

As stated earlier, ultra-high vacuum conditions are necessary for desorption measurements; the pressure is maintained using a vacuum pumping system. The analytical chamber *Žeryk* (figure 2.3) of vacuum vessel *Antonín* is used for TDS measurements at the Institute of Physical Engineering (IPE) in Faculty of Mechanical Engineering, Brno University of Technology. Ultra-high vacuum is maintained using a combination of an ion pump (pumping speed $200\,l/s$) and a titanium sublimation pump (not shown in figure 2.3) attached to the main chamber where the samples are being held in a sample holder during TDS measurements. A quadrupole mass spectrometer (QMS) is connected to the main chamber via a secondary chamber with separate pumping system – a smaller ion pump ($50\,l/s$) and a smaller titanium sublimation pump. This setup enables base pressure around $5 \times 10^{-8}\,Pa$ which is measured with a Bayard-Alpert hot-cathode ionization gauge.

Using a combination of manipulation rods the sample with adsorbed particles on its surface is put into the UHV chamber and placed in a sample holder. It is then heated with a desired rate by means of resistive heating, i.e. by applying voltage to the sample[4]. The current temperature of the sample is measured simultaneously by two different instruments: a Syscon pyrometer which is calibrated for temperatures above ca. 300 °C (used between 300–1400 °C) and a thermocouple which is able to measure temperatures below the limit of the pyrometer.

Quadrupole Mass Spectrometer

The main instrument used in TDS is the quadrupole mass spectrometer. A first technically realizable variant of a QMS was described in 1953 by W. Paul and H. Steinwedel [6, p. 9]. The chief functional components of a mass spectrometer are:
- analyzer unit with ion source, rod system and detector;
- HF generator;

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[4]Usually silicon with high boron or phosphorus doping level. Resistivity of the sample is in the 10^{-3}–$10^{-1}\,\Omega\cdot cm$ region.
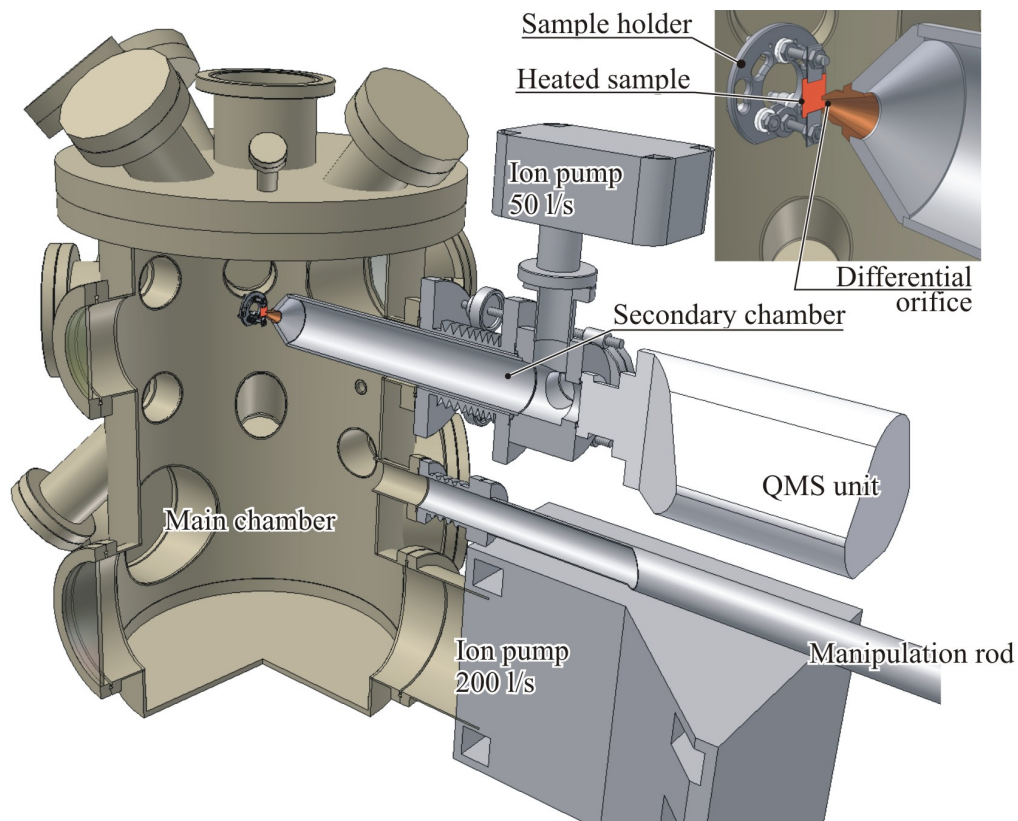
Figure 2.3: The analytical chamber *Žeryk* which is used for TDS measurements at the Institute of Physical Engineering. The sample is placed in a sample holder in the main chamber. Desorbed particles pass through a differential orifice ($\varnothing 3\,\mathrm{mm}$) into the secondary chamber where the QMS unit is located. Picture by Ing. M. Potoček, Ph.D.

- electrometer preamplifier or pulse preamplifier;
- control unit with the quadrupole electronics;
- power supply for the ion source and the hight voltage power supply for a SEM detector and the computer interfaces;
- control and evaluation software.

Figure 2.4 shows a schematic arrangement of these components. This work only discusses the analyzer component – the Quadrupole Mass Analyzer (QMA).

The QMA unit consists of three parts, each characterized by a specific process: ionization, mass separation and ion detection. The next sections discuss these parts in detail. A schematic of the arrangement of QMA parts is shown in figure 2.5.

The ionization process

A small fraction of the atoms and molecules present in the gas phase (residual atmosphere with desorbed particles) are brought into an ionized state by bombarding them with low energy electrons. This produces singly and multiply charged ions. The energy of the collision electrons has a strong effect on the number and on the
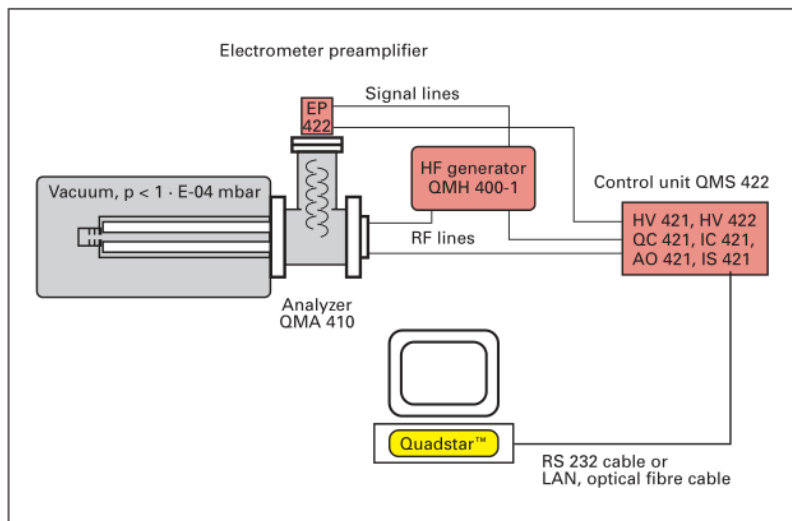
Figure 2.4: Schematic of the component arrangement of a Pfeiffer Vacuum quadrupole mass spectrometer [6].
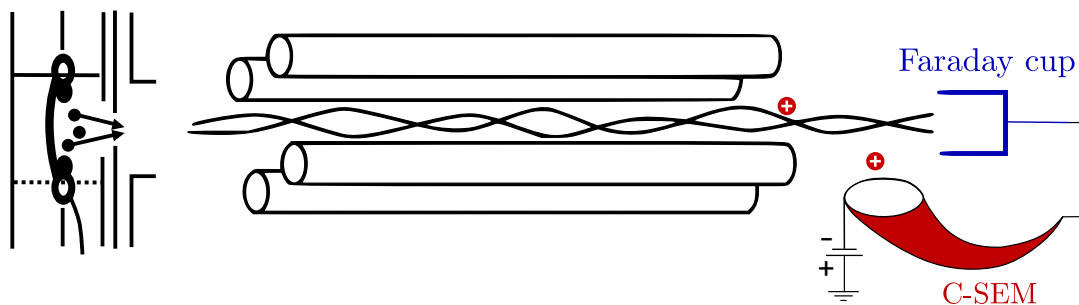
Figure 2.5: Arrangement of a QMA with a Faraday cup and a C-SEM installed. Ionized particles that pass the rod system are detected by the Faraday cup unless their trajectory is deflected towards the C-SEM using a strong electric field.

type of ions which are produced. Figure 2.6 shows the amount of ionized atoms as a function of the electron energy.

For molecule ionization, the number of possible types of ions rapidly increases with increasing complexity of the molecules. Fragment ions appear in addition to singly and multiply charged molecular ions.

$$
\begin{aligned}
\mathrm{ABC} + \mathrm{e}^- \rightarrow \ & \mathrm{ABC}^+ + 2\,\mathrm{e}^- \\
& \mathrm{ABC}^{++} + 3\,\mathrm{e}^-
\end{aligned} \tag{2.2}
$$

$$
\begin{aligned}
& \mathrm{AB}^+ + \mathrm{C} + 2\,\mathrm{e}^- \\
& \mathrm{A}^+ + \mathrm{BC} + 2\,\mathrm{e}^- \\
& \mathrm{C}^+ + \mathrm{AB} + 2\,\mathrm{e}^- \\
& \mathrm{B}^+ + \mathrm{A} + \mathrm{C} + 2\,\mathrm{e}^-
\end{aligned} \tag{2.3}
$$
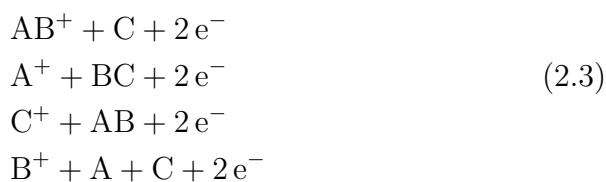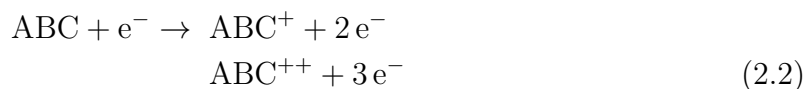
The appearance and relative abundances of the individual species of ions are characteristic for a certain kind of molecule and serve as important clues for identifying the
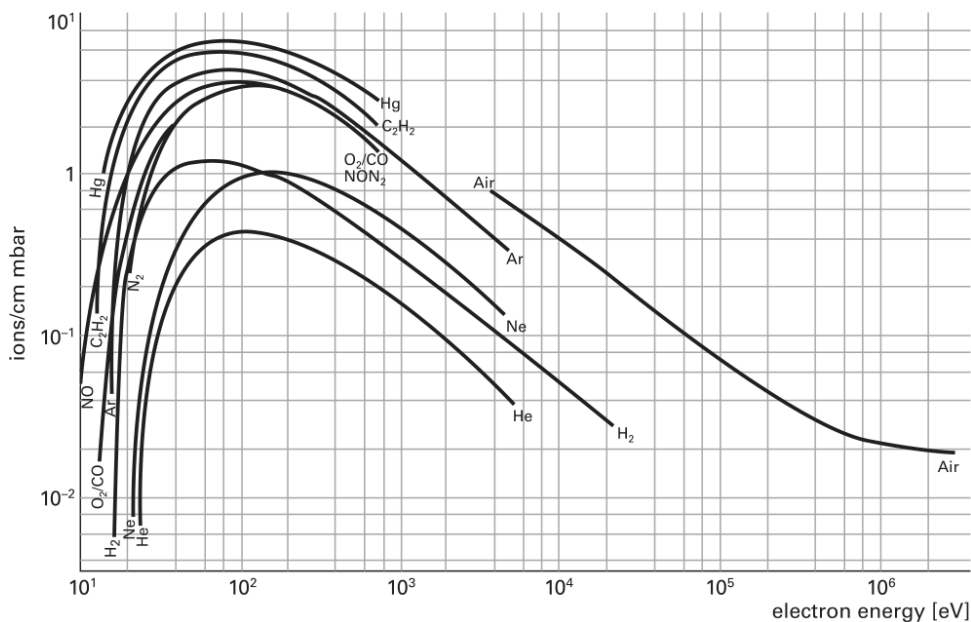
Figure 2.6: Produced ion density as a function of impacting electron energy. The number of ions produced increases rapidly with increasing energy, reaching a maximum at 50–150 eV depending on the type of the gas, then falling slowly as the energy is further increased [6].

molecule and thus, also for qualitative gas analysis. Figure 2.7 shows the distribution of fragments of CO_2 recorded with 70 eV electron energy.

Operation of ion source

The neutral particles arriving in the ionization space (formation space) are ionized by the electrons which are emitted by the filament and accelerated in the formation space. Tungsten, rhenium and yttrium oxide coated iridium is used as filament material. The produced positive ions are accelerated out of the formation space into the mass separation part.

Mass separation

Ions can be separated according to their mass-to-charge ratio (m/q, usually expressed in unified atomic mass units/multiples of elementary charge) in a high frequency quadrupole field ideally produced with four hyperbolic rod electrodes. Because of the technical difficulties involved in making hyperbolic electrodes of sufficient quality, cylindrical electrodes are used in most commercial applications. A combination of direct voltage U and high frequency alternating voltage with amplitude V and angular frequency ω is applied to the electrodes as shown in figure 2.8a. The equations of motion for ions injected into the electric field (of the quadrupole) are described by the Mathieu differential equations. These equations allow the ions two different types of motion: stable oscillations result in flying through between the quadrupole rods, unstably oscillating ions on the other hand collide with one of the electrodes and are neutralized, thus not reaching the detection module. The
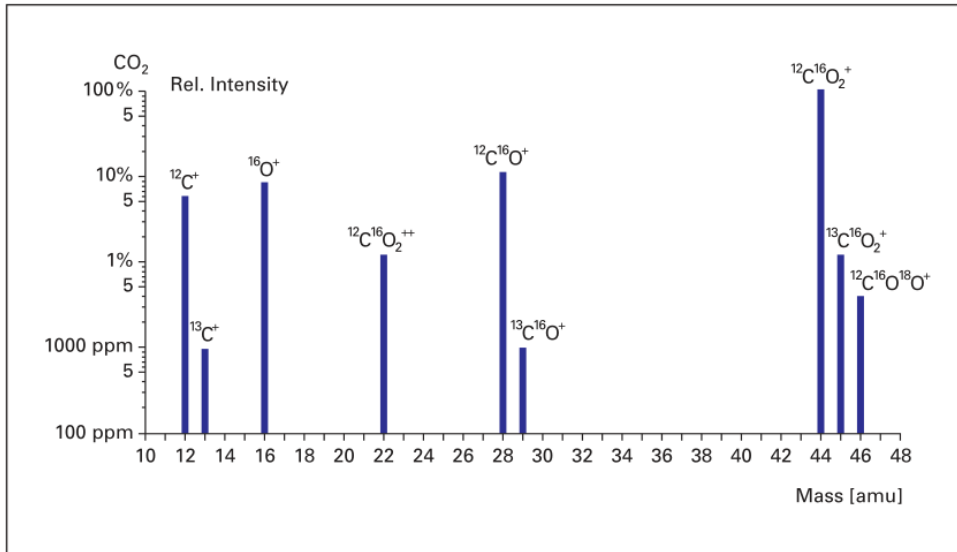
Figure 2.7: Fragment distribution of CO_2. The main reason of multiple peaks is molecule fragmentation during the ionization process (2.3) and the mass difference of oxygen isotopes [6].

$$U + V cos(\omega t)$$

(a)   (b)
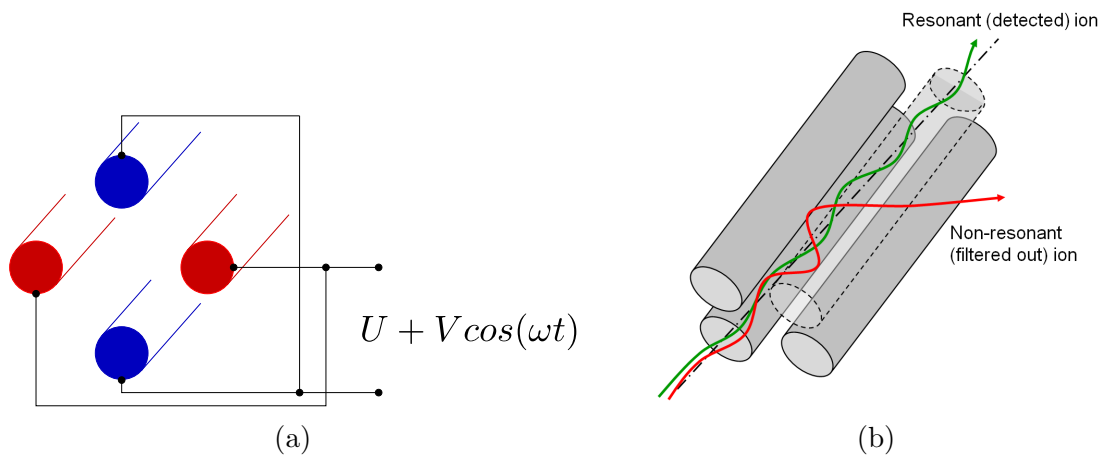
Figure 2.8: A combination of direct voltage U and high frequency alternating voltage with amplitude V applied to the electrodes (a) results in either stable or unstable oscillations of ions (b) depending on their mass-to-charge ratio [7].

parameters of the system (geometry, U/V ratio and ω) determine the mass/charge ratio interval of the unfiltered ions.

Ion detection

The ions, which have been separated according to their mass/charge ratio in the rod system, can be electrically detected by various types of detectors (figure 2.9):

- Faraday cup,

- continuous dynode secondary electron multiplier (C-SEM) and

- discrete dynode secondary electron multiplier (SEM).

The choice of the detector is primarily based on the required detection speed and detection sensitivity. Other aspects, such as thermal and chemical stability and the amount of available space should also be taken into consideration.

In the first case the ions hit a Faraday cup (figure 2.9a) where they are neutralized. A sensitive current/voltage converter converts the resulting current into a voltage signal proportional to the ion current. The signal is not affected by degradation or mass-discrimination effects at the detector. A Faraday detector also has long-term stability and high thermal resistance. It is integrated into most of quadrupole mass analyzers.

A more sophisticated solution is the usage of a continuous dynode secondary electron multiplier (C-SEM) (figure 2.9b). C-SEM is a vacuum-tube structure that multiplies incident charges in a process called secondary emission. An ion or electron can, when bombarded on the active layer of the C-SEM, induce emission of roughly 1 to 3 electrons. These electrons may be accelerated towards the next surface by an electric field where they induce secondary emission of still more electrons. This can be repeated a number of times, resulting in a great number of electrons collected by a metal anode. The amplification ratio is approx. 10^6 and is limited by the dark current in the active layer. The C-SEM is usually placed somewhat off the central axis of the rod system. The positive ions can be deflected by applying a negative potential to the mouth of the C-SEM as shown in figure 2.5. The advantage of this configuration is that it is simple and the selection between the two detectors can be done quickly.

If the ion current is very low and high measuring speed is required, a discrete dynode secondary electron multiplier (SEM, figure 2.9c) can be used as the detector in a 90°off-axis arrangement. This arrangement is useful to minimize the contribution of impacting photons, soft x-rays or fast neutral particles which are also coming form the direction of the rod system. The ions leaving the mass separation system are accelerated to several keV. They are then deflected by an electrostatic field so that they hit the first dynode of the SEM. Similarly to C-SEM, here they induce secondary emission of multiple electrons which are then multiplied in a series of further dynodes. The amplification ratio of a SEM is approx. 10^8.
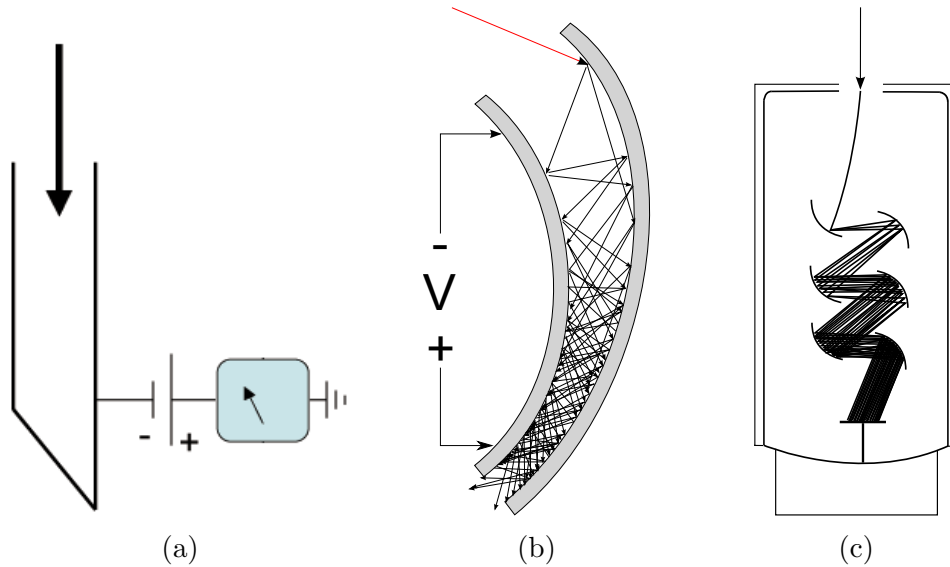
Figure 2.9: Various types of detectors that can be used in a quadrupole mass spectrometer: Faraday cup (a) [8]; continuous dynode secondary electron multiplier – C-SEM (b) [9]; discrete dynode secondary electron multiplier – SEM (c).

2.2.3 Quantitative analysis of the QMS signal

Measurement techniques using QMS-RGA (Residual Gas Analysis) do not offer direct information on the quantity of residual gas particles in the vacuum chamber. As discussed in section 2.2.2 the measured particles undergo a series of processes before they are detected and transformed into a current signal.

In order to make quadrupole mass separation possible, desorbed particles need to be ionized. Fragmentation of molecules may occur during the ionization process contributing to peaks of other masses or creating new peaks in the mass spectrum (2.3). Too high energies of the ionizing electrons may result in multiply charged ions further modifying the measured spectrum (2.2). Ionized particles then travel through a quadrupole mass filter which is a source of significant attenuation of the signal. Another important process is the detection of ions e.g. using a C-SEM.

To obtain partial pressures from the QMS signal, a quantitative analysis needs to be performed. It consists of the following steps [4]:

a) subtraction of the background signal,

b) consideration of signal attenuation dependance on ion mass,

c) multiplication of the measured intensity matrix $I(m)$ by calibration factors of the observed particles,

d) calculation of the ratio of the vacuum chamber pressure and the sum of modified intensities,

e) conversion of QMS signal to partial pressures,

f) conversion of partial pressures to number of particles.

The following paragraphs discuss steps a) to f) in detail.

a) Real values of signal intensities $I(m)$

Prior to every TDS measure, the background signal H_{sig} is measured for a duration of usually 30 s. Averaging this signal one gets the background signal intensity for each mass/charge ratio $H_{background}(m)$. The real values of signal intensities can be obtained by subtracting the background signal from the measured signal

$$H(m) = H_{sig}(m) - H_{background}(m). \qquad (2.4)$$

b) QMS sensitivity

The sensitivity of the spectrometer is affected by the transmission ratio of the given instrument which depends, among others, on the radii of the quadrupole rods. The sensitivity decreases exponentially with increasing mass of particles [[10]]. QMS manufacturers usually provide the transmission ratio of their products for xenon atoms($m/z = 110$). Assuming transmission ratio for hydrogen atoms($m/z = 1$) to be 100 %, one can easily calculate the transmission ratio function of the given instrument by fitting the provided value to an exponential $e^{-\alpha m}$ function. For the QMA200 analyzer used at IPE $\alpha = 0.0209$ [4]. The corrected intensity vector is

$$I(m) = \frac{H(m)}{e^{-\alpha m}}. \qquad (2.5)$$

c) Calibration factors matrix

To compensate the effect of mass interference caused by fragmentation during the ionization process, the measured data have to be multiplied by a matrix of calibration factors for the observed elements. These calibration factors are available in the NIST online database (National Institute of Standards and Technology, `http://webbook.nist.gov/chemistry`) or in [6]. Fragmentation is especially influenced by the energy of the ionizing electrons.

By multiplying the calibration matrix with the measured intensity vector, a vector of the concentration of observed elements (molecular intensity) can be obtained.

$$C(g) = S(m, g)I(m), \qquad (2.6)$$

where g is the index of the observed element and $S_{m,g}$ is the calibration factor of element g and measured mass m.

d) Determining the ratio of the vacuum chamber pressure and the sum of modified intensities

To calculate the partial pressure of the present gases, the sum of signals of all masses and the total pressure p_{total} in the main chamber where the sample is located have to be compared. The calculation should be performed in a temperature interval where the two compared quantities show good correlation, e.g. in figure 2.10 the temperature interval $[200; 350]$ °C would be ideal.
The ratio k_{PC} is given by

$$k_{PC} = \frac{p_{total}}{C_{total}}, \qquad (2.7)$$

$$\text{where } C_{total} = \sum_g C(g).$$
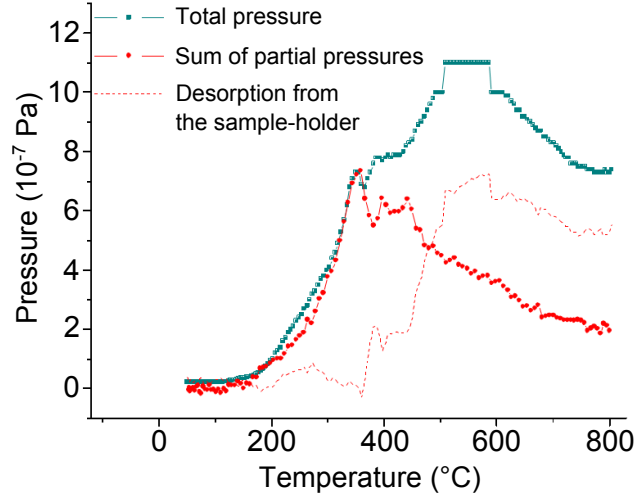
Figure 2.10: Comparison of total pressure and the sum of partial pressures of desorbed particles [4].

e) Conversion of QMS signal to partial pressures

Partial pressures of desorbed particles can be easily obtained by multiplying the element concentration vector $C(g)$ with the calculated pressure-intensity ratio

$$p_c(g) = k_{PC}C(g). \tag{2.8}$$

f) Converting partial pressures to number of particles

By substituting the obtained partial pressures into

$$N_c = \frac{p_c(g)V}{k_B T} \tag{2.9}$$

one gets the number of desorbed particles N_c. In equation (2.9) V is the volume of the vacuum chamber and k_B is the Boltzmann constant.

3 PRACTICAL PART

The main objective of this thesis is to create a computer software for automatization of TDS data evaluation – *TDS data evaluation tool*. Such program would need to get raw measurement data as input. The simplest solution is to read the file generated by the QMS unit, therefore, it is necessary to investigate the structure of the QMS output file.

3.1 QMS output file structure

The QuadStar™ software shipped with the Prisma series spectrometers offers exportation of measured data as an ASCII text file (*.asc). This option suits best the needs of this work as it contains string representations of the measured data in a user-friendly table/matrix form. The file structure is illustrated below.

```
ASCII SAMPLE CYCLES :          20101210 desorption PMMA
DATE :  10.12.2010   TIME :  14:37:16
CONVERTED CYCLES :             381

Number of stored cycles       381
Printed start cycle           1
Printed end cycle             381
Number of stored datablocks   1

Datablock 0     Ion Current [A]
'0/0'   2.00    min:  5.81999E-011  max:  4.12974E-010
'0/1'   4.00    min:  2.01429E-012  max:  6.74526E-011
'0/2'   12.00   min:  -7.61361E-012 max:  7.4881E-010
    .
    .
    .
'0/50'  168.00  min:  2.54279E-013  max:  1.00551E-012

Cycle  Date         Time        RelTime[s]  '0/0'        '0/1' ...
1   10.12.2010  14:37:16:00  0        6.58597E-011  7.39656E-012 ...
2   10.12.2010  14:37:25:67  9.679    7.4839E-011   8.41441E-012 ...
    .
    .
    .
381 10.12.2010  15:36:44:08   3568.09 1.85595E-010  3.35055E-011 ...
```

The file consists of four parts separated by blank lines. The header part of the file (lines 1–8) contain the following data: name, measure date and time, number of measured cycles etc.

In the next part (starting with "'0/0'") each line indicates the mass/charge ratios (from now on referred to as "masses") measured on each channel of the QMS. These lines also contain maximum and minimum values of the measured current for each mass.

The last table contains the measured data. As the table header indicates, the individual columns from left to right represent the number of the measured cycle, date, time, relative time (time elapsed from the measure initialization). The next columns contain measured values of current, one column for each mass.

3.2   TDS data evaluation tool

TDS data evaluation tool was created in MATLAB environment.

3.2.1   Program flow

A simple flowchart of TDS data evaluation tool is shown in figure 3.1.
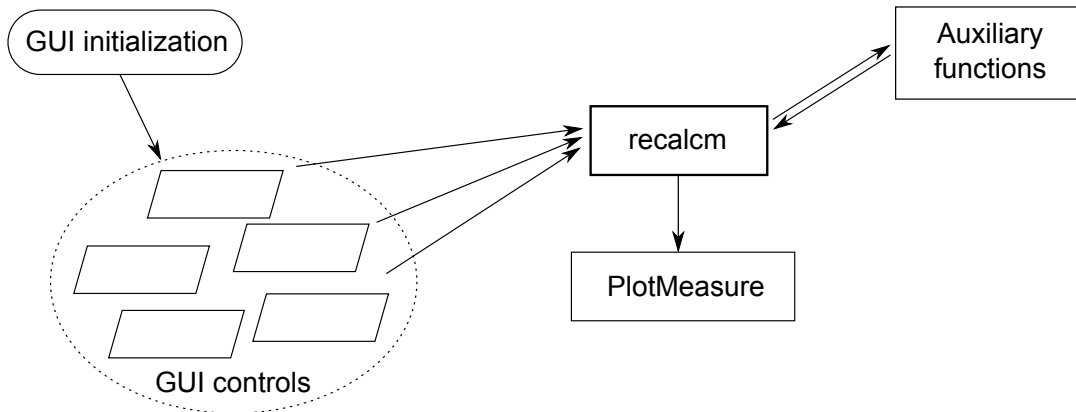
Figure 3.1: Flowchart of TDS data evaluation tool. After starting the program it waits for a user action. The user may interact with the program via the GUI controls (buttons, etc.). These call the central function `recalcm` which provides the calculations. Plotting of the calculated data is done by the function `PlotMeasure`.

Firstly, the GUI controls are initialized: drawing of the main figure, buttons, checkboxes, text fields, etc. as seen in figure 3.2 and the matrix $S(m, g)$ (equation (2.6)) is read from file 'peaks.csv'. After that, the program waits for user interaction which can be done by pressing a button, editing a text field or a similar action. These actions are called events in event-driven programming and they trigger callback functions. A callback function is a piece of code which is executed after the specific user action. For example, the callback function of the 'Open ASCII file' button, triggered by clicking the button, asks the user to specify the file to be opened. Subsequently, it starts to read the file line by line and searches for specific data. The function reads and stores the date and time of the measurement, number of cycles recorded by the QMS unit, which masses were measured and lastly the measured values of current. The date and time of measurement, as well as the number of converted cycles, are then shown in static text boxes (non user-editable text fields) whereas a vector of measured masses and a matrix of measured values are stored in global variables (namely *masses* and *measureOrig*) so that all functions can access them.
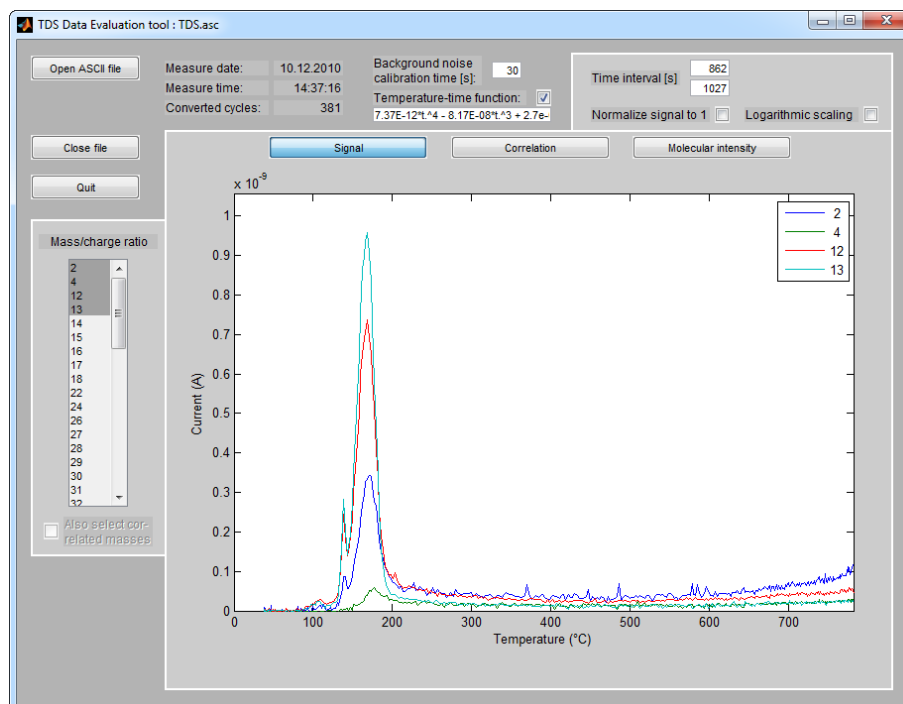
Figure 3.2: Screenshot of TDS data evaluation tool Signal tab. Signals of masses 2,4,12,13 are selected and plotted as a function of temperature. Data taken from measurement of poly(methyl methacrylate) desorption from silicon surface by Ing. M. Potoček, Ph.D.

Other callback functions (most of GUI control callbacks) evaluate the causing event and call the central function (`recalcm`, standing for recalculate the measurement) with new user-input parameters as arguments. These arguments are processed by the `recalcm` function which stores them in persistent variables[1] and performs necessary calculations. These calculations include subtraction of the background from the measured signal according to equation (2.4), normalization of measured values and calculation of correlation matrices or molecular intensities (equation (2.6)). They are either computed directly by the function itself or by use of other functions (such as `nonoise` for subtraction of the background signal, `normal` for normalization and `calcMI` for the calculation of molecular intensities).

After all of the necessary calculations had been carried out, `recalcm` either calls function `PlotMeasure` to plot desired data such as signal or molecular intensity, or fills calculated correlation values in the correlation coefficient table, according to the currently active tab.

A list of key TDS data evaluation tool functions is given in section 3.2.2.

---

[1]Persistent or static variables' lifetime extend across the entire run of the program; they are not deallocated once parent function terminates. Static variables are similar to global variables but they are available only in their parent function.

3.2.2   List of functions

A list of key TDS data evaluation tool functions created by the author, as well as input and output arguments and a short description of each function, is given in this section.

Callback functions

Callback functions have access to the GUI controls, they can read or change their properties. All callbacks have *hObject* and *eventdata* input arguments. The former is the handle of the invoking control while the latter contains event-related data if any exist. Button callbacks are triggered by clicking the button or by pressing the ⟨space⟩ or ⟨enter⟩ key while the button has focus.

btn_OpenFile_Callback(hObject, eventdata, file) Callback of the 'Open ASCII file' button. The functions reads data from the ascii file specified either by the *file* input argument or by a select file dialog.
Read data are saved in *masses* (measured masses) and *measureOrig* (measured current values) global variables.

bg_main_SelectionChangeFcn(hObject, eventdata, tag) Callback of the tab selection buttons. The selected tab is either passed to the function in the *eventdata* or as the *tag* argument. The function sets the visibility property of the unnecessary controls to 'off' and of necessary controls to 'on'. The function also informs recalcm of the new active tab.

Functions with access to GUI controls

ResetGUIelements Sets all gui controls to their default values, clears variables *measureOrig* and *masses*.

recalcm(var, val, nocalc, noout) The main function of TDS data evaluation tool. Most of GUI control callback functions pass their parameters to recalcm. It stores incoming arguments in persistent variables and performs necessary calculations. Switches *nocalc* and *noout* can be used if just the update of persistent variables is needed (no calculations have to be performed or no output has to be displayed).

PlotMeasure(measureMatrix, cr, type) This function is responsible for plotting graphs on the Signal as well as Molecular intensity tab. Type of the graph is specified by the *type* argument.

Other functions

[ret, measureDate, measureTime, cCycles] = ReadHeader(file) and

cellArray = ReadMatrix(i, file) are the functions responsible for reading measure file header, measured masses and measured values of current. These functions are called by btn_OpenFile_Callback.

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`[measureout, k] = nonoise(measurein, int)` subtracts background signal from *measurein* and returns the result *measureout*.

`measurenorm = normal(measurein, inv)` normalizes measured values. Inverse normalization also implemented but not used.

`MIcell = calcMI(measureMatrix, MIpeaks, masses)` calculates molecular intensities from input arguments according to equation (2.6). Returns a cell array *MIcell* of molecular intensities.

3.2.3   User guide

Features

Let a quick summary of TDS data evaluation tool main features serve as the beginning of this user guide:

- subtracting of the background signal from measured data,
- plotting desorption intensity as a function of time or temperature for single or multiple masses,
- calculating correlation between desorption of different mass/charge signals,
- estimating the relative quantity of desorbed atoms and molecules,
- exporting calculated data, saving graphs as images.

Starting the program

The program was created as a function in MATLAB environment (MATLAB R2011a, version 7.12.0; tested on versions R2007a+), therefore, MATLAB needs to be installed to be able to use it. To start TDS data evaluation tool, run MATLAB and change its current folder to point to the m-file of the program (*TDS.m*) then pop up the context menu by right-clicking on the file and select run. Typing "TDS" in the command window (without quotation marks) after changing the current directory yields the same result. A few moments later the main figure of TDS data evaluation tool will open with the Signal tab (figure 3.2) active. There are three different tabs in the program: Signal, Correlation and Molecular intensity. Switching between them is achieved by clicking on the corresponding buttons.

The next step is to load a measurement file which is done by pressing the 'Open ASCII file' button and selecting the desired file. The file must be exported from QuadStar™ as an ascii text file as discussed in section 3.1. The program then reads the file and displays its contents such as the date and time of measurement, etc.

The file is now loaded, let the calculations begin. TDS data evaluation tool automatically subtracts the average intensity from each mass signal calculated over the first n seconds of measure where n is set by the user in the 'Background noise calibration time' text field. Its default value is $30\,\text{s}$. In order to display measured data as a function of temperature rather than time, the temperature-time function must be set either by typing it in the corresponding text field of the main figure or in a text file named "deftemptime.txt" in the program folder. The temperature-time

function must be a MATLAB-interpretable function of time t. An example of the temperature-time function might be

$$\ldots + a * t^3 + b * t^2 + c * t + d + exp(t/e), \tag{3.1}$$

where a, b, c, d and e are constants. Swapping the x-axis between time and temperature can be done quickly by checking/unchecking the checkbox next to the temperature-time function text field.

Signal tab

The selection of mass/masses desorption rates to be plotted is done using the listbox on the left side of the main figure. Selection of multiple masses is possible by holding the left mouse button and moving the mouse up or down the list, holding the ⟨shift⟩ or ⟨control⟩ key while clicking on the mass adds it to the selection so any combination can be selected.

The two checkboxes in the upper-right corner allow the user to switch between the plotting of normalized and real data and to change the scaling of the y-axis to logarithmic.

It is possible to set an interval for further correlation calculation by typing the endpoints in the text fields in the upper-right corner. The calculation of the correlation matrix only from values around a significant desorption peak may be useful when the user is interested in the shape difference of peaks of several masses.

Correlation tab

The most apparent visual change after activating the Correlation tab is the replacement of the graph object with a table as seen in figure 3.3. Values in the table are correlation coefficients calculated for each combination of mass signals. Limiting the correlation calculation interval can be useful at times, in that case use the 'Time interval' text fields and the 'Limit to interval' checkbox in the upper-right corner.

To get a better overview of correlating desorption rates, the program offers a simple filter to show only correlations above a certain threshold. This function can be activated by checking the 'Enable filter' checkbox in the upper right corner; the threshold value can be changed in the 'Threshold value' text field. By enabling the filter, a new feature of the program becomes accessible: automatic selection of correlated masses in the Signal tab mass list.

High correlation coefficients may indicate that the source of the two signals is identical, e.g. multiple peaks in the spectrum created by molecule fragmentation. These values might be used to determine which molecules are present on the observed surface. The next step of the TDS spectrum evaluation is checking/unchecking the desired molecules in the left-side list. The list of molecules along with information on peak locations and intensities of each molecule is loaded as the program starts from the "peaks.csv" file.

Molecular intensity tab

The molecular intensity tab has two modes: plotting molecular intensity as a function of time/temperature (figure 3.4a) or showing molecule distribution for a single

TDS Data Evaluation tool : TDS.asc

Open ASCII file

Measure date: 10.12.2010
Measure time: 14:37:16
Converted cycles: 381

Background noise calibration time [s]: 30
Temperature-time function: ☑
7.37E-12*t.^4 - 8.17E-08*t.^3 + 2.7e-

Time interval [s]: 862 / 1027   Limit to interval ☐
Threshold: 0.9   Enable filter ☐

Close file   Quit

Signal | **Correlation** | Molecular intensity

Select potentially desorbed molecules

☑ H2   ☑ H2SO4
☑ CO   ☑ H20
☑ CO2   ☑ NH3
☑ C2H4 ☑ HCl
☑ C2H6 ☑ HF
☑ NO   ☑ N
☑ H3NO ☑ NO2
☑ H2S   ☑ O2
☑ C2HF ☑ SiH4

Ok

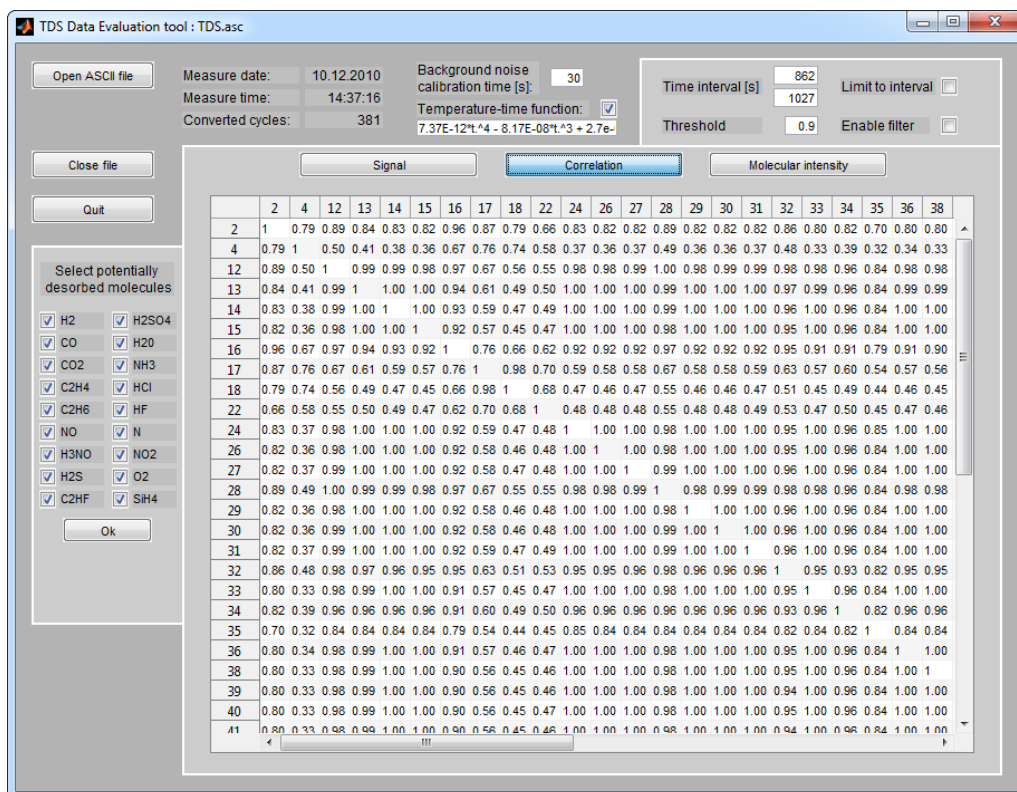|	2	4	12	13	14	15	16	17	18	22	24	26	27	28	29	30	31	32	33	34	35	36	38
2	1	0.79	0.89	0.84	0.83	0.82	0.96	0.87	0.79	0.66	0.83	0.82	0.82	0.89	0.82	0.82	0.82	0.86	0.80	0.82	0.70	0.80	0.80
4	0.79	1	0.50	0.41	0.38	0.36	0.67	0.76	0.74	0.58	0.37	0.36	0.37	0.49	0.36	0.36	0.37	0.48	0.33	0.39	0.32	0.34	0.33
12	0.89	0.50	1		0.99	0.99	0.98	0.97	0.67	0.56	0.55	0.98	0.98	0.99	1.00	0.98	0.99	0.99	0.98	0.98	0.96	0.84	0.98
13	0.84	0.41	0.99	1		1.00	1.00	0.94	0.61	0.49	0.50	1.00	1.00	1.00	0.99	1.00	1.00	1.00	0.97	0.99	0.96	0.84	0.99
14	0.83	0.38	0.99	1.00	1		1.00	0.93	0.59	0.47	0.49	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.96	1.00	0.96	0.84	1.00
15	0.82	0.36	0.98	1.00	1.00	1		0.92	0.57	0.45	0.47	1.00	1.00	1.00	0.98	1.00	1.00	1.00	0.95	1.00	0.96	0.84	1.00
16	0.96	0.67	0.97	0.94	0.93	0.92	1		0.76	0.66	0.62	0.92	0.92	0.92	0.97	0.92	0.92	0.92	0.95	0.91	0.91	0.79	0.91
17	0.87	0.76	0.67	0.61	0.59	0.57	0.76	1		0.98	0.70	0.59	0.58	0.58	0.67	0.58	0.58	0.59	0.63	0.57	0.60	0.54	0.57
18	0.79	0.74	0.56	0.49	0.47	0.45	0.66	0.98	1		0.68	0.47	0.46	0.47	0.55	0.46	0.46	0.47	0.51	0.45	0.49	0.44	0.46
22	0.66	0.58	0.55	0.50	0.49	0.47	0.62	0.70	0.68	1		0.48	0.48	0.48	0.55	0.48	0.48	0.49	0.53	0.47	0.50	0.45	0.47
24	0.83	0.37	0.98	1.00	1.00	1.00	0.92	0.59	0.47	0.48	1		1.00	1.00	0.98	1.00	1.00	1.00	0.95	1.00	0.96	0.85	1.00
26	0.82	0.36	0.98	1.00	1.00	1.00	0.92	0.58	0.46	0.48	1.00	1		1.00	0.98	1.00	1.00	1.00	0.95	1.00	0.96	0.84	1.00
27	0.82	0.37	0.99	1.00	1.00	1.00	0.92	0.58	0.47	0.48	1.00	1.00	1		0.99	1.00	1.00	1.00	0.96	1.00	0.96	0.84	1.00
28	0.89	0.49	1.00	0.99	0.99	0.98	0.97	0.67	0.55	0.55	0.98	0.98	0.99	1		0.98	0.99	0.99	0.98	0.98	0.96	0.84	0.98
29	0.82	0.36	0.98	1.00	1.00	1.00	0.92	0.58	0.46	0.48	1.00	1.00	1.00	0.98	1		1.00	1.00	0.96	1.00	0.96	0.84	1.00
30	0.82	0.36	0.99	1.00	1.00	1.00	0.92	0.58	0.46	0.48	1.00	1.00	1.00	0.99	1.00	1		1.00	0.96	1.00	0.96	0.84	1.00
31	0.82	0.37	0.99	1.00	1.00	1.00	0.92	0.59	0.47	0.49	1.00	1.00	1.00	0.99	1.00	1.00	1		0.96	1.00	0.96	0.84	1.00
32	0.86	0.48	0.98	0.97	0.96	0.95	0.95	0.63	0.51	0.53	0.95	0.95	0.96	0.98	0.96	0.96	0.96	1		0.95	0.93	0.82	0.95
33	0.80	0.33	0.98	0.99	1.00	1.00	0.91	0.57	0.45	0.47	1.00	1.00	1.00	0.98	1.00	1.00	1.00	0.95	1		0.96	0.84	1.00
34	0.82	0.39	0.96	0.96	0.96	0.96	0.91	0.60	0.49	0.50	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.93	0.96	1		0.82	0.96
35	0.70	0.32	0.84	0.84	0.84	0.84	0.79	0.54	0.44	0.45	0.85	0.84	0.84	0.84	0.84	0.84	0.84	0.82	0.84	0.82	1		0.84
36	0.80	0.34	0.98	0.99	1.00	1.00	0.91	0.57	0.46	0.47	1.00	1.00	1.00	0.98	1.00	1.00	1.00	0.95	1.00	0.96	0.84	1	
38	0.80	0.33	0.98	0.99	1.00	1.00	0.90	0.56	0.45	0.46	1.00	1.00	1.00	0.98	1.00	1.00	1.00	0.95	1.00	0.96	0.84	1.00	1
39	0.80	0.33	0.98	0.99	1.00	1.00	0.90	0.56	0.45	0.46	1.00	1.00	1.00	0.98	1.00	1.00	1.00	0.94	1.00	0.96	0.84	1.00	1.00
40	0.80	0.33	0.98	0.99	1.00	1.00	0.90	0.56	0.45	0.47	1.00	1.00	1.00	0.98	1.00	1.00	1.00	0.95	1.00	0.96	0.84	1.00	1.00
41	0.80	0.33	0.98	0.99	1.00	1.00	0.90	0.56	0.45	0.46	1.00	1.00	1.00	0.98	1.00	1.00	1.00	0.94	1.00	0.96	0.84	1.00	1.00

Figure 3.3: Screenshot of TDS data evaluation tool Correlation tab. Values in the table are correlation coefficients calculated for each combinations of mass signals.
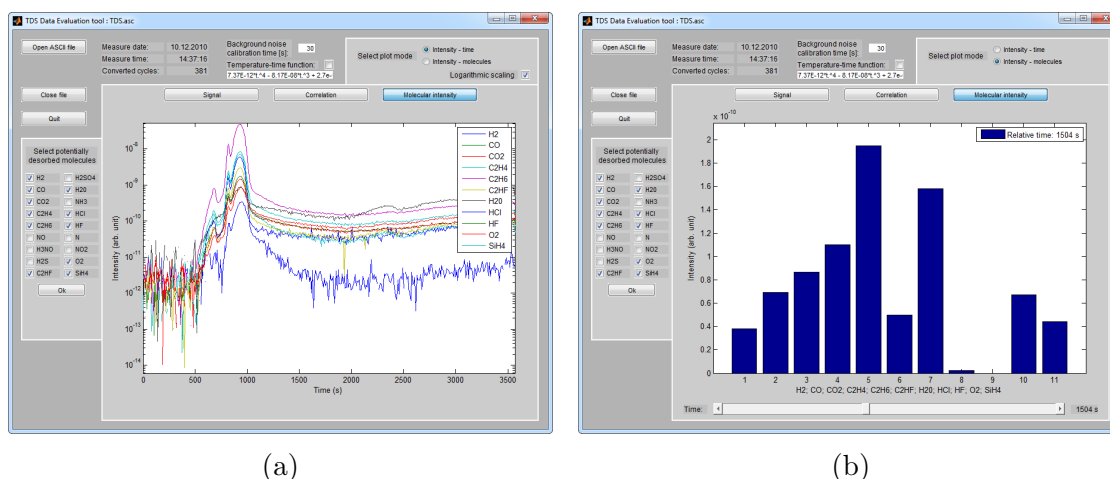
(a)   (b)

Figure 3.4: Screenshot of both modes of TDS data evaluation tool Molecular intensity tab. Molecular intensities are calculated according to equation (2.6).

time/temperature (figure 3.4b). Molecular intensities are calculated according to equation (2.6) using peak information $S(m, g)$ loaded from the "peaks.csv" file in the program folder. Editing of the potentially present molecules (checkboxes on the left side) is allowed on this tab, too. The user might find it useful to change the y-axis scaling to logarithmic in the upper-right corner.

In the latter mode, i.e. plotting molecule distribution histograms for a single time, the time can be set using the slider.

Export of computed matrices (either to a file or the MATLAB workspace) is possible in all tabs by clicking the appropriate item of the right-click context menu. Graphs can be saved as images.

The TDS data evaluation window can be resized arbitrarily; all labels and GUI controls will resize proportionally (especially useful on high-resolution monitors).

3.3   Analysis of previously measured spectra

TDS data evaluation tool was tested on formerly measured TDS spectra provided by Ing. M. Potoček, Ph.D. A detailed analysis of a specific experiment [4] is given in the following.

The experiment

Silicon samples were treated with a 2 nm thick native oxide layer, etched by 2% and 40% solution of hydrofluoric acid for 1 minute and rinsed with demineralized water for 1 minute. The prepared samples were then placed in the UHV chamber Žeryk (figure 2.3) with a base pressure of 4×10^{-8} Pa. Signal of the desorbed molecules was measured with a QMS 200M spectrometer attached to the main chamber as described in section 2.2.2. Boron-doped silicon was used for the experiment with resistivity $\rho = 0.001\,\Omega{\cdot}$cm. The sample was heated with a rate of 5℃/s. TDS measurement with QMS is limited to the measurement only of pre-selected masses. It turned out to be optimal to measure 30–40 signals in pseudo-parallel mode.

Results

After the whole oxide layer is removed, a silicon surface terminated with H and F in a certain ratio is formed. With increasing concentration of the HF solution this ratio decreases (more bonds are terminated with F).

In the spectrum of the 2% HF etched sample, peaks on masses 31 and 81 appeared with very similar desorption characteristics. These peaks are probably caused by molecules CF and C_2F_3.

Molecules C_xF_y are most likely the products of reactions involving C_xH_y as the C−F bond is energetically more beneficial. Therefore, desorption of selected C_xF_y molecules was measured in repeated experiments and their potential presence was observed on samples etched by 2% and 40% HF solutions. Desorption spectra in figure 3.5 confirm the possibility of C−F bond formation. Comparing corresponding peaks in figures 3.5a and 3.5b, it can be stated that C_xF_y molecules desorb at
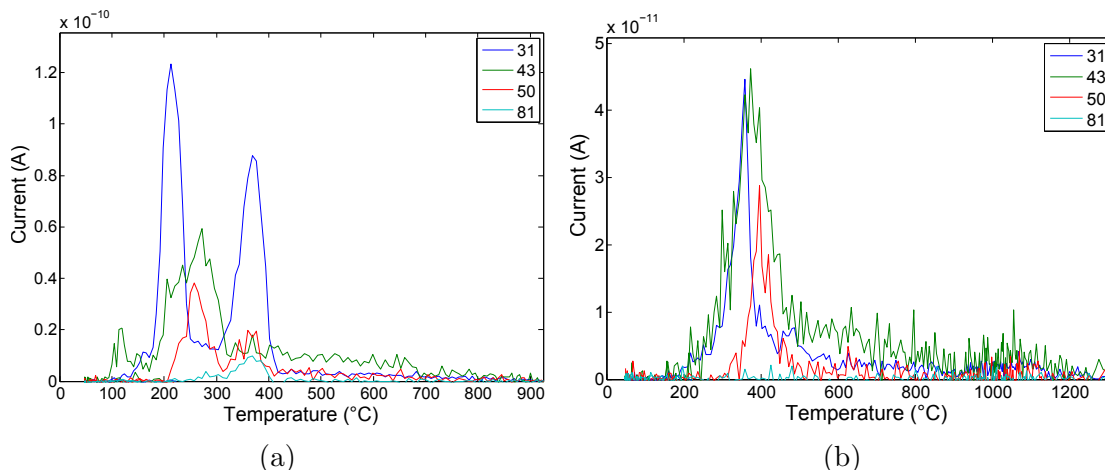
Figure 3.5: Desorption spectra of selected C_xF_y molecules: CF (mass 31 AMU), C_2F (43), CF_2 (50) and C_2F_3 (81). Silicon sample etched by 2% (a) and 40% (b) solutions of HF.

higher temperatures from the surface etched by 40% HF. This indicates stronger bonds between the C_xF_y molecules and the F terminated silicon surface and, consequently, higher desorption energies. CF_2 molecules may further react and start a polymerization process $(CF_2 + P_n \longrightarrow P_{n+1})$.

Calculation of desorption parameters

Desorption parameters of some of the measured spectra of 2% HF treated surface[2] were determined. A curve fitting program created by Ing. M. Potoček, Ph.D. and Ing. J. Zlámal, Ph.D. in MATLAB environment implementing the Levenberg–Marquardt algorithm was used. Table 3.1 contains fitted desorption energies E_d and preexponential factors ν for possible orders of desorption $l = 1, 2$. The desorption order is hard to determine when only a single set of data is available. Figure 3.6 shows a typical example of the curve fitting. The fitted values are merely approximative as only a few desorption values are available in the peak temperature range and the fitted curves show significant deviation from measured data in some cases. Also, the uniqueness of the experiment results in no available references for comparison.

Conclusion

The TDS measurements of HF etched silicon surfaces revealed the presence of molecules formed during chemical synthesis of C and F. The presence of C_xF_y in the spectrum suggests that beside etching, fluoridation of C atoms and partial polymerization take place as well. All calculated desorption energies are in the 0.36–0.52 eV interval, these are typical for physisorptive bonds.

---

[2]The signal-to-noise ratio of the 40% HF treated surface desorption was too low to get a reasonable fit.

Mass (AMU)	Molecule	$l = 1$ E_d (eV)	$l = 1$ ν 10^6 (s^{-1})	$l = 2$ E_d (eV)	$l = 2$ ν 10^6 (s$^{-1}\cdot$ML^{-1})
12	C	-	-	0.36	252.0
28	CO	-	-	0.36	311.0
31	CF	0.31	13.2	0.52	86.9
50	CF$_2$	0.57	59.5	0.38	24.6

Table 3.1: Calculated desorption energies and preexponential factors of several molecules.
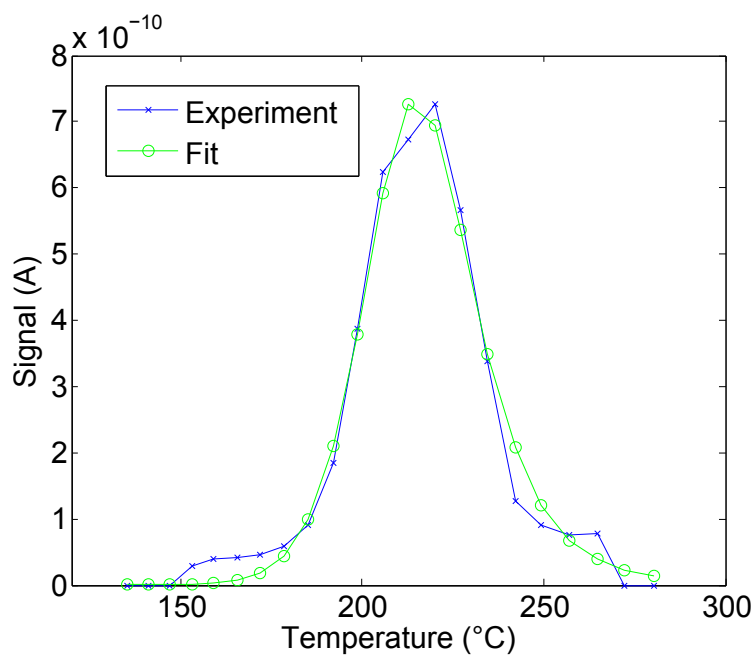

Figure 3.6: Example of curve fitting result for C desorption.

4   CONCLUSION

This work is focused on the automatization of thermal desorption spectroscopy (TDS) data evaluation. The main task was to calculate a matrix of correlation coefficients of each combination of measured mass-to-charge ratio.

As an introduction to the problem, chapter 2 discusses the main physical principles related to TDS, i.e. adsorption and desorption. It also gives a detailed description of the instruments used in TDS measurements, particularly the quadrupole mass spectrometer (QMS), as well as of the quantitative analysis of the quadrupole mass spectrometer signal.

The main aim of this work was to create a computer software for the automatization of TDS data evaluation; the program was named *TDS data evaluation tool*. It was created in the MATLAB environment (version R2011a; also tested on versions from R2007). The program is presented in chapter 3 where a detailed description is given. As a part of this work, a user guide for the created software was written.

TDS data evaluation tool automatically subtracts background signal from the measured data. However, the consideration of mass dependence of QMS transmission ratio and ionization probabilities of different particles are not implemented in the current version. The program calculates the correlation coefficients and is able to estimate the relative quantity of desorbed molecules (molecular intensities) as described in the user guide. The calculations of partial pressures and number of desorbed particles are not yet implemented. This is planned in a future release. TDS data evaluation tool plots results in a simple and user-friendly way but also provides exportation of the calculated matrices either to a file or directly to the MATLAB workspace to allow further analysis in third-party software.

As an example, a profound analysis of previously measured TDS spectra was performed. Silicon samples were etched with variously concentrated solutions of hydrofluoric acid and the adsorbed molecules on their surface were measured. Detailed description of the experiment can be found in section 3.3. The experiment led to a conclusion that formation of $C-F$ bonds as well as partial polymerization take place on the surface. By fitting the measured data with a curve, desorption energies of several adsorbed particles could be determined. Values of desorption energies were in every case around $0.4\,\mathrm{eV}$ which is typical for physisorptive bonds.

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CONTENTS OF THE ENCLOSED CD

Thesis.pdf An electronic version of this thesis in portable document format.

TDS data evaluation tool

> **TDS.m** Source code of the program.
>
> **peaks.csv** The file contains desorption peak information of several molecules. Needed for the calculation of molecular intensities.
>
> **measure.asc** A sample measurement file (poly(methyl methacrylate) (PMMA) desorption; measurement by Ing. M. Potoček, Ph.D.).
>
> **deftemptime.txt** An example of a default temperature-time function file.