Resist round robin outgassing

@ ELETTRA

Trieste - Italy

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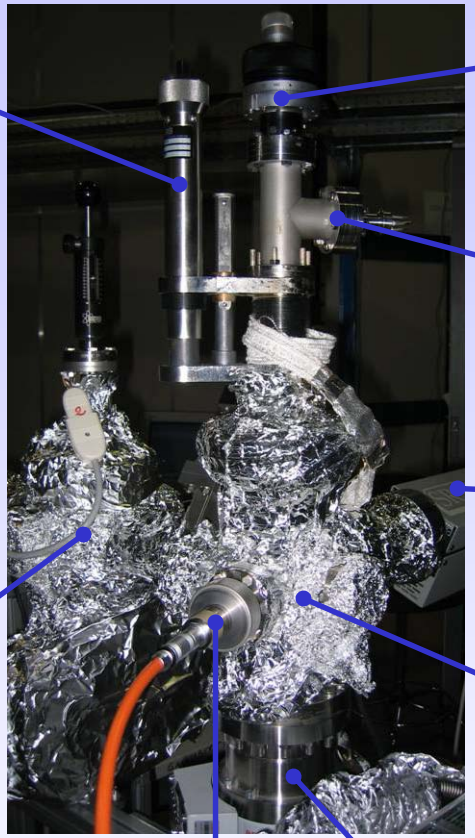
Experimental setup (1)

Double side sample holder

Sample size: 12mm x 100mm

100 mm linear translator

Beam direction

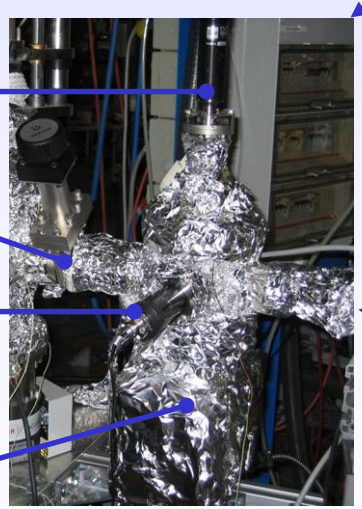


Sample manipulator

Sample holder thermocouple feedthrough

Residual Gas Analyser (RGA) by Stanford Reseach Systems (SRS), model RGA200

Main chamber



Mask manipulator

Vacuum valve

Photodiode manipulator

Varian StarCell 75 l/s ion pump

Pfeiffer inverted magnetron pressure gauge

Beam direction

200 l/s Pfeiffer turbomolecular drag pump + Alcatel pumping station

Experimental setup (2)

Remarks:

1) During the residual gas analyser (RGA) calibration with toluene, the sample manipulator was replaced by a leak valve. The main chamber was baked-out at a temperature T=180 C

2) Before starting the outgassing test, the main chamber was first baked at a temperature of 180 C. The base pressure after the 8h bake-out and the 6h cooling down to room temperature was ~ 2·10-9 mbar, with the RGA filament on. The chamber was vented to allow the sample installation. After ~48h of pumping without the bake-out, the base pressure was one order of magnitude higher.

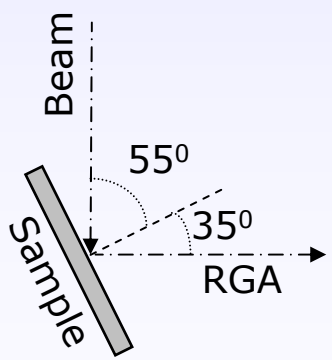
3) The experiment was carried out at the Gas Phase 6.2 beamline of ELETTRA. The photon energy was 95.0 eV (λ = 13 nm) and the flux could be varied adjusting the gap of the storage ring undulator and the beamline exit slits. The photon beam size on the sample was defined by a rectangular mask.

4) The measurement of the photon flux was provided by an IRD photodiode behind the mask.

5) The total pressure was measured by an inverted magnetron gauge (IMG).

6) The RGA main operational parameters are listed in the table below. We always used the macro multi-channel continuous dynode electron multiplier detector.

7) The measurement geometry is shown in the picture to the right. The distance of the sample from the RGA is about 30 mm.



Scan rate	200 msec/a.m.u.
Filament current	2 mA
Electron energy	70 eV
Ion energy	12 eV

Simulation (1)

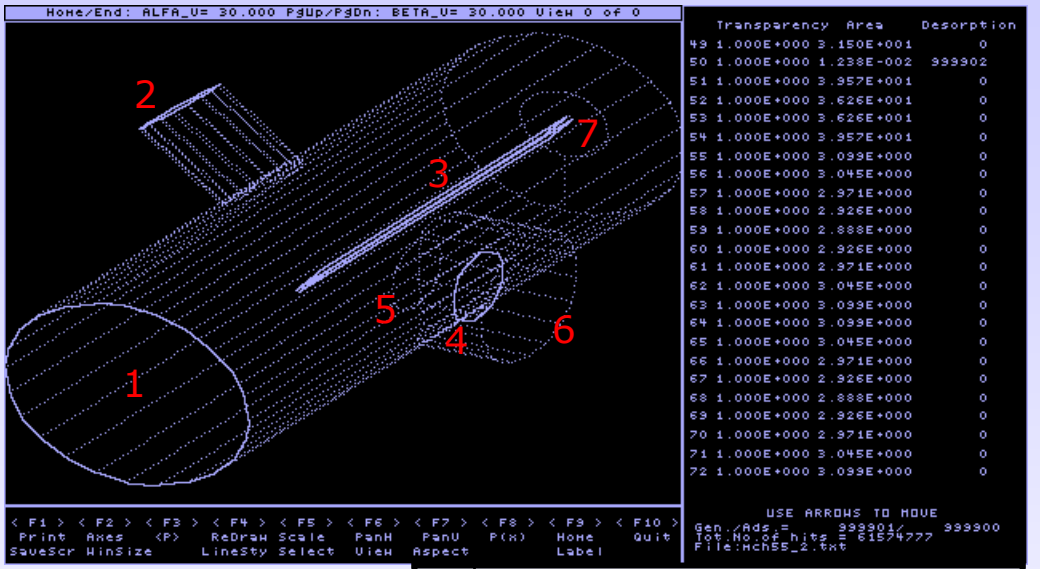
Motivation

In order to obtain a relationship between the pressure at the RGA head and the specific outgassing of the sample, we performed 2 Monte Carlo simulations, one for the mass spectrometer calibration and one for the outgassing measurements.

The code MOLFLOW [1] was used.

Model description

The system was described by means of a three-zone model. Tubes flanged CF40 and CF63 are defined with 18 facets, tubes flanged CF100 with 24 facets; bellows are considered like tubes. Moreover the turbomolecular pump was replaced with a "pumping" facet with an equivalent sticking coefficient σ. A snapshot of the simulation is represented here: the main chamber (simplified) and the most important facets are shown.



MOLFLOW generates particles considering the mean molecular speed <v> of the Maxwell-Boltzmann distribution at temperature T, for a certain mass M. The average pressure P_j on the facet j can be calculated:

Mass [a.m.u.]	92
Temperature [C]	22
Stick. Coeff. σ	0.35

$$P_j = \frac{4\,Q\,N_j}{\langle v \rangle\, A_j\, N} = \alpha_j\, Q$$

$$\langle v \rangle \sim (T/M)^{1/2}$$

where Q is the gas load, N_j is the number of hits on that facet, N the number of the total traced molecules, A_j is the area of the facet

1	Pumping surface
2	Total pressure gauge
3	Sample holder
4	Average position of RGA head
5	Top position of RGA head
6	Link to the RGA zone
7	Link to the manipulator zone

[1] R. Kersevan, MolFlow User's Guide, ST/M-91/17, Sincrotrone Trieste, 1991

Simulation (2)

Results:

In the simulation, the molecules were generated from a surface corresponding to the area illuminated by the photon beam. Because we are interested in the average molecules per second generated during the exposure, we can consider this value as the steady state condition of our system.

For our purposes, we use the RGA sensitivity S and the spot area A_s obtained experimentally and the α_4 factor obtained from the simulation to find the relationship between the specific outgassing rate q of the resist and the ion current I measured by the RGA.

In general, for a pressure variation ΔP we have: $\Delta P = \frac{\Delta I}{S} = \alpha\, Q$ and $Q = q\, A_s$

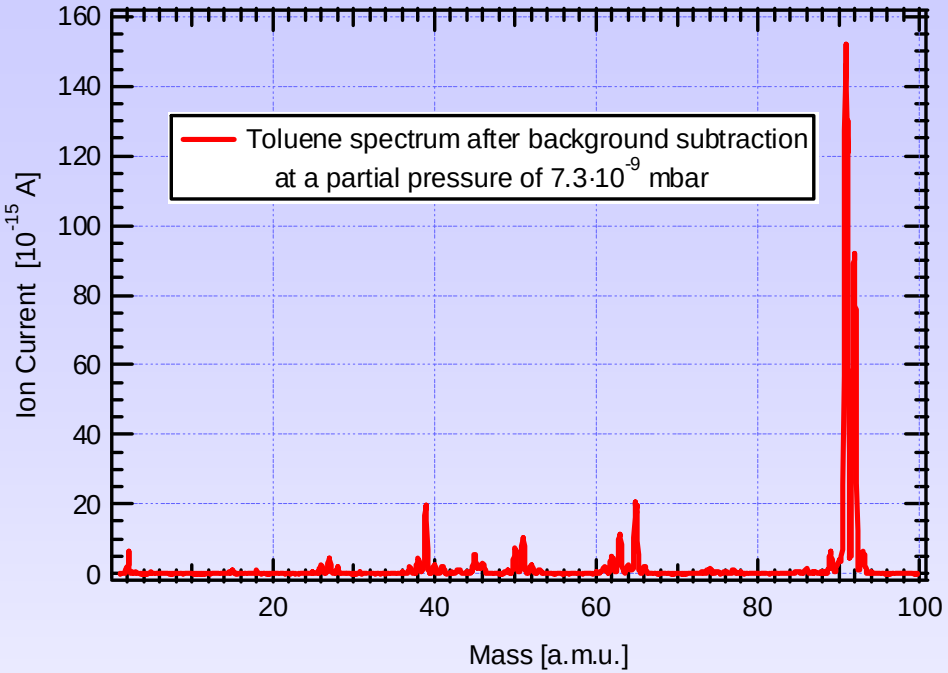
S	$2.1 \cdot 10^{-5}$ A/mbar
α_4	$8.653 \cdot 10^{-3}$ s/l
A_s	1.2375 cm^2

Using the parameters reported in the table, we find the specific outgassing:

$$q = \frac{\Delta I}{\alpha_4\, S\, A_s} = 4.447 \cdot 10^{-8} \cdot \Delta I[A]\ \text{mbar}\cdot\text{l/s/cm}^2$$

$$= 1.0913 \cdot 10^{28} \cdot \Delta I[A]\ \text{molec/s/cm}^2 \quad @T = 22\ C$$

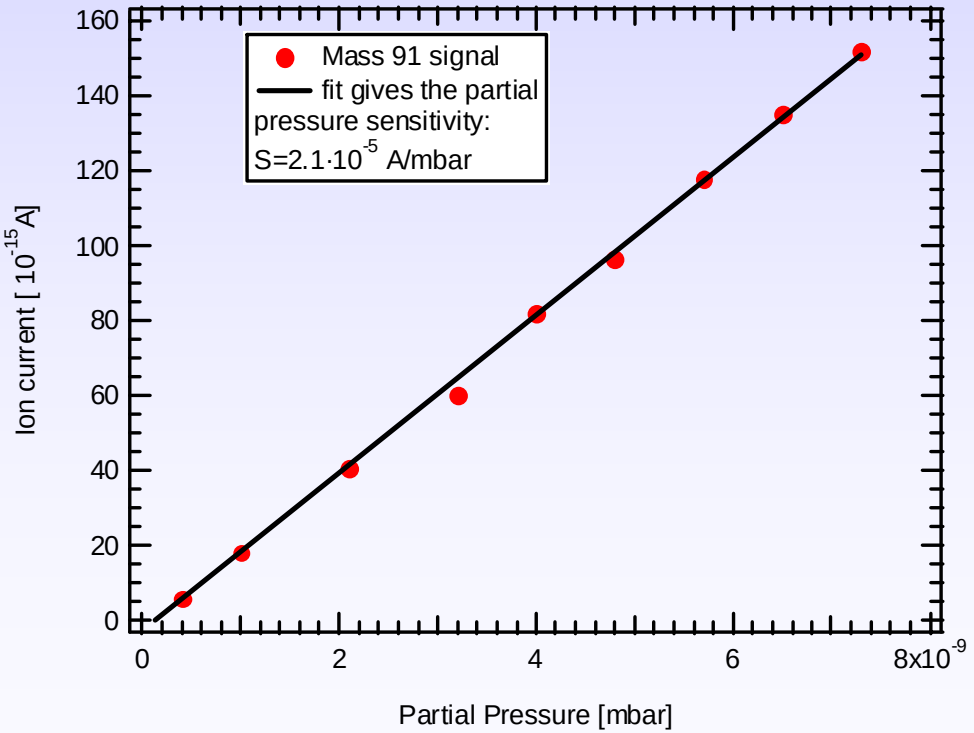
RGA calibration



The toluene (purity: 99.7%) was gasified in a very small vacuum chamber where the vacuum is obtained by means of an independent pumping station.
It is introduced in the main vacuum chamber using a leak valve. The base pressure of the main chamber is $2.2 \cdot 10^{-9}$ mbar.

The calculated sensitivity for toluene is $2.1 \cdot 10^{-5}$ A/mbar.

The mass position calibration has also been performed.



E_0 determination

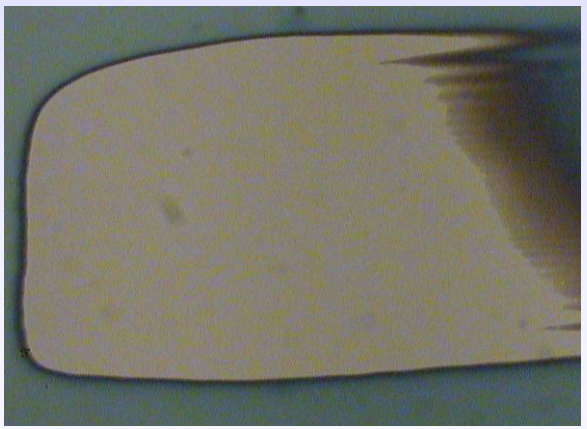
We performed several exposures of the sample, varying the time and the power density so as to cover the largest interval of energy density around the given estimated E_0=5.6 mJ/cm^2.

In one case the sample was deliberately overexposed.

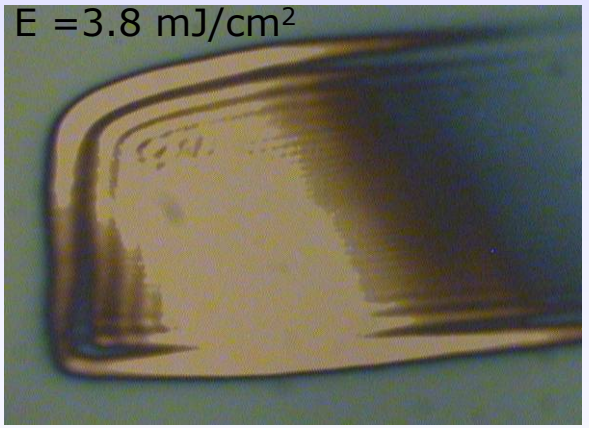
We measured the spot area after developing the resist. The calculated area of the spot at E_0 is 0.7 mm^2. During the gas desorption experiment, the spot area was about 1.24 mm^2 and the energy dose was 7.2 mJ/cm^2 (10s exposure), i.e. ~1.3 E_0.

E =50.7 mJ/cm^2

E_0 =5.6 mJ/cm^2

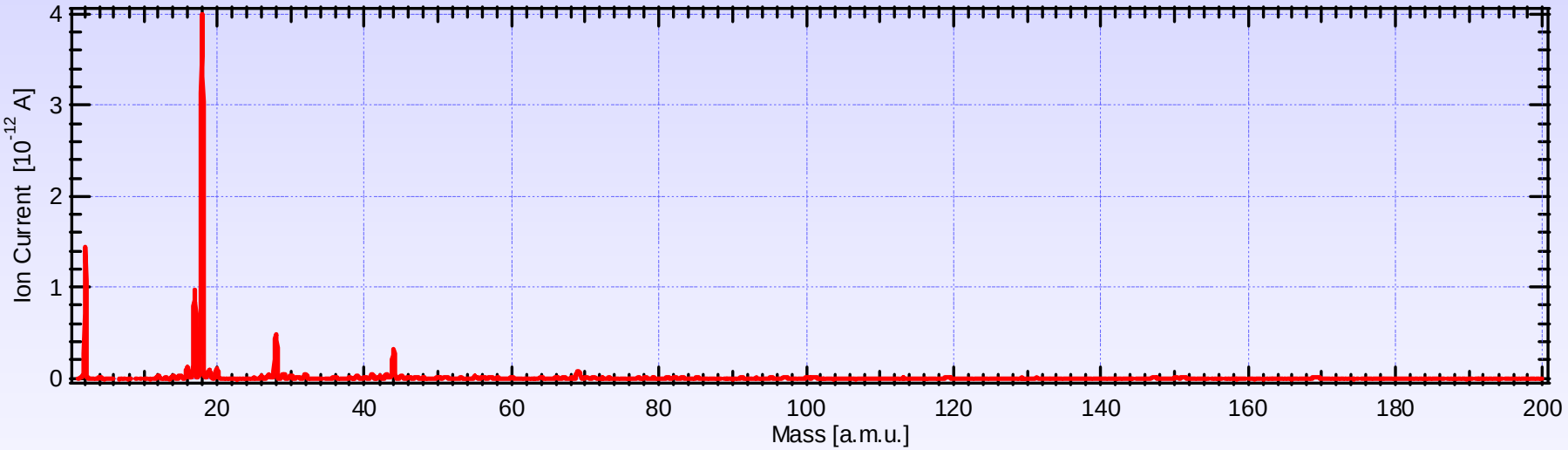


E =3.8 mJ/cm^2



Outgassing (1)

The sample was prepared according to the indicated procedure. This gave an average photoresist thickness of 140nm instead of 125nm, as expected. It was put inside the vacuum chamber which has been pumped for ~48 hours in order to reach a good vacuum level without baking.
The base pressure was $2 \cdot 10^{-8}$ mbar. During the experiment the pressure did not change significantly.
The background mass spectrum before starting the outgassing experiment is shown here.



Since the mass spectrometer calibration had been performed only up to mass 92a.m.u., outgassing data acquisition was stopped at mass 100a.m.u. The measurements can be performed up to mass 200a.m.u. once higher mass references are used for calibration of the instrument.

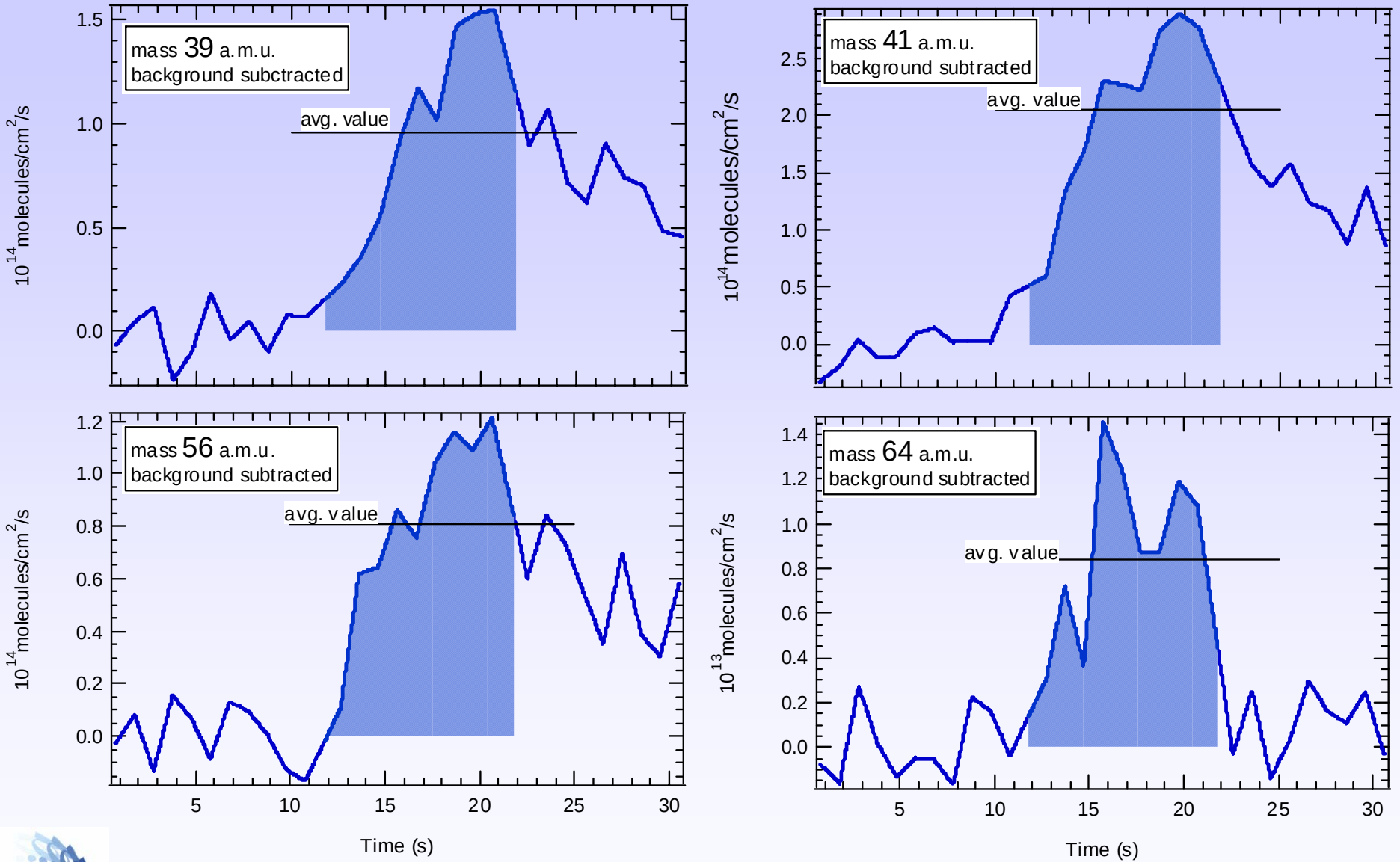
Outgassing (2)

The data acquisition protocol was the following:
i) The mass spectrometer was set to measure the time evolution of masses 1 to 3 a.m.u. The time needed to acquire one reading for all 3 masses was set to 1 s. After 10 seconds of acquisition, the photon beam shutter was opened to start the exposure, which was interrupted after 10 seconds (once the 7.2 mJ/cm^2 energy dose was reached). After 10 more seconds the acquisition stopped.
ii) Afterwards, the sample was moved to a new region and the same measurement was performed for masses 4 to 6 a.m.u.
iii) The same procedure was repeated until the whole range 1÷100 a.m.u. was covered.

Data have been processed as follows:
1) Background signal has been determined for each mass using the first 10 seconds data (before exposing the resist).
2) For each mass the background signal has been subtracted.
3) The integral average of the signal during the exposure time has been calculated and plotted.

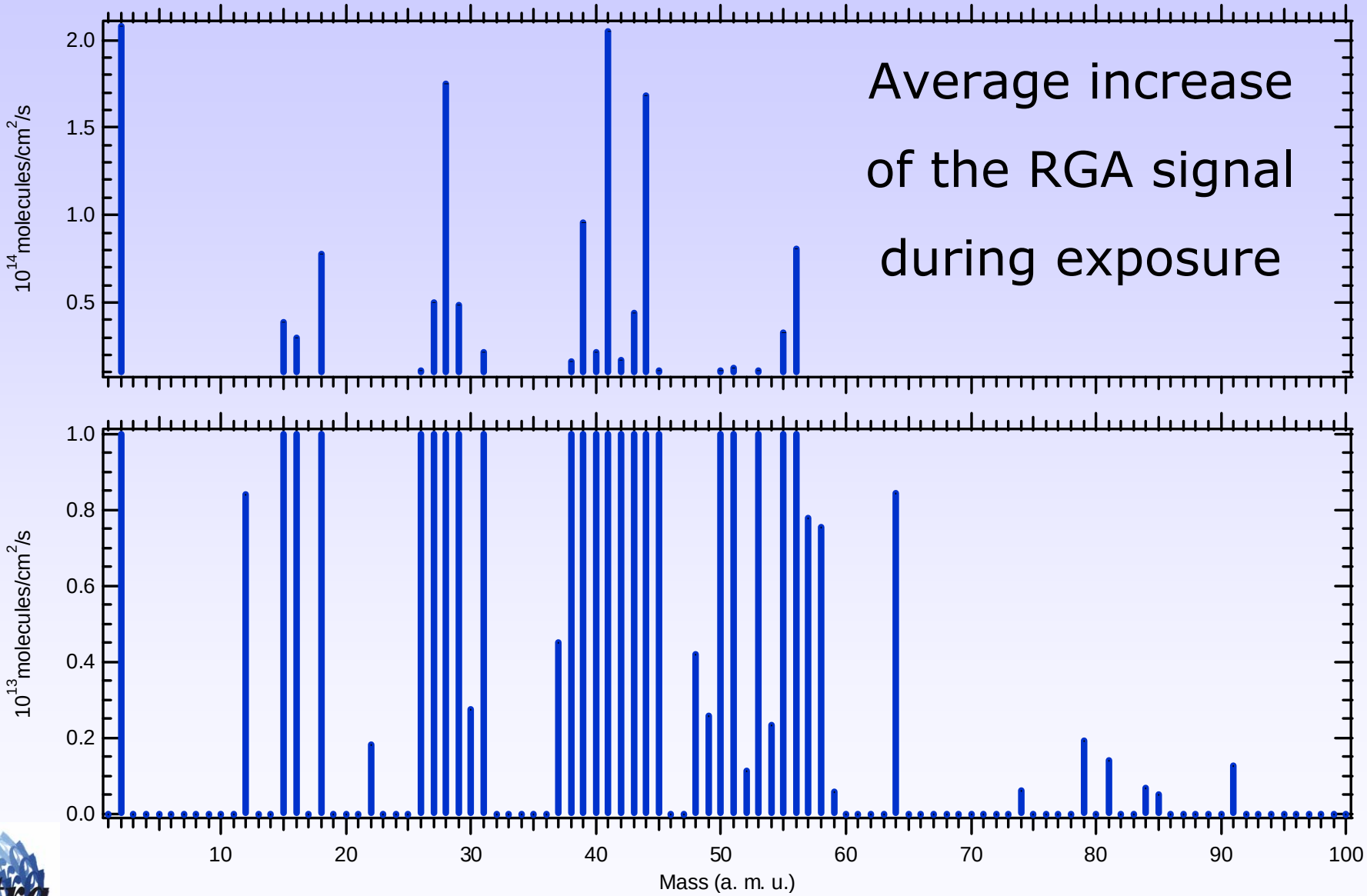
In the next two slides examples of mass trends and data processing are presented, together with the complete spectrum showing the average number of molecules desorbed from the resist during beam exposition.

Outgassing(3)



Examples of mass trends

Outgassing (3)



Final remarks

The observed mass peaks indicates the presence of 2-methyl-1-propene and probably isobutane. The main peak of benzene does not appear.

Outlook:

The main improvement we are thinking of is setting up a fast entry lock in order to allow the insertion of the sample into the experimental chamber without breaking the vacuum. In this way we could reduce the time in vacuum of the resist before measurement and we could work at a pressure level that would be in the 10^{-9} mbar range or better, improving the signal-to-noise ratio.

Acknowledgements:

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