Simultaneous estimation of N and O atom density in N_2 – O_2 discharges

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Titrating NO into N_2 afterglow containing nitrogen atoms, these reaction take part :

quick **$N + NO \rightarrow N_2 + O$** **[1]**

$k_1 = 1.6\ 10^{-10}\ cm^3s^{-1}$

A.N. Wright, C.A. Nelson : Active nitrogen Acad. Press, 1968

slow **$N + O$** $+ N_2 \rightarrow$ **NO^*** $+ N_2$ (NO beta system) **[2]**

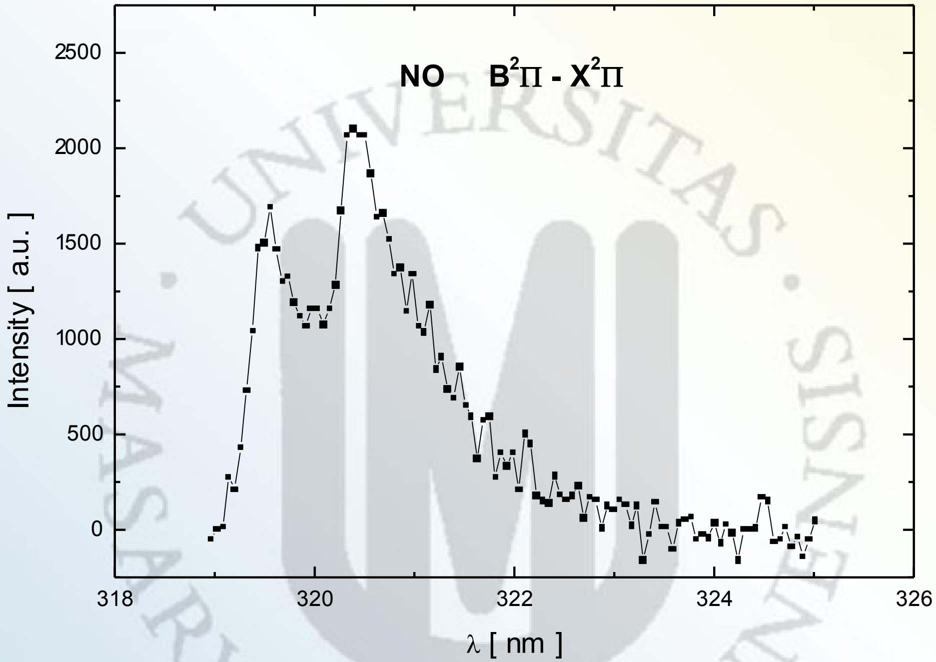
$k_2 = 9.1\ 10^{-33}\ cm^6s^{-1} \rightarrow 9.1\ 10^{-16}\ cm^3s^{-1}$ (400 Pa)

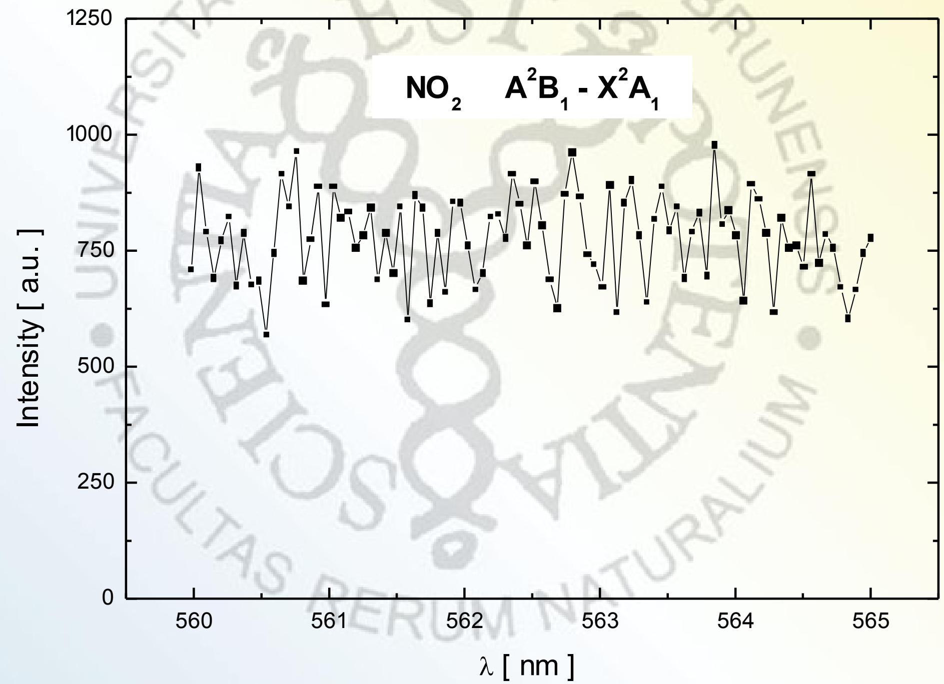
C.B. Kretschmer, H.L. Peterson : J. Chem. Phys., 1963

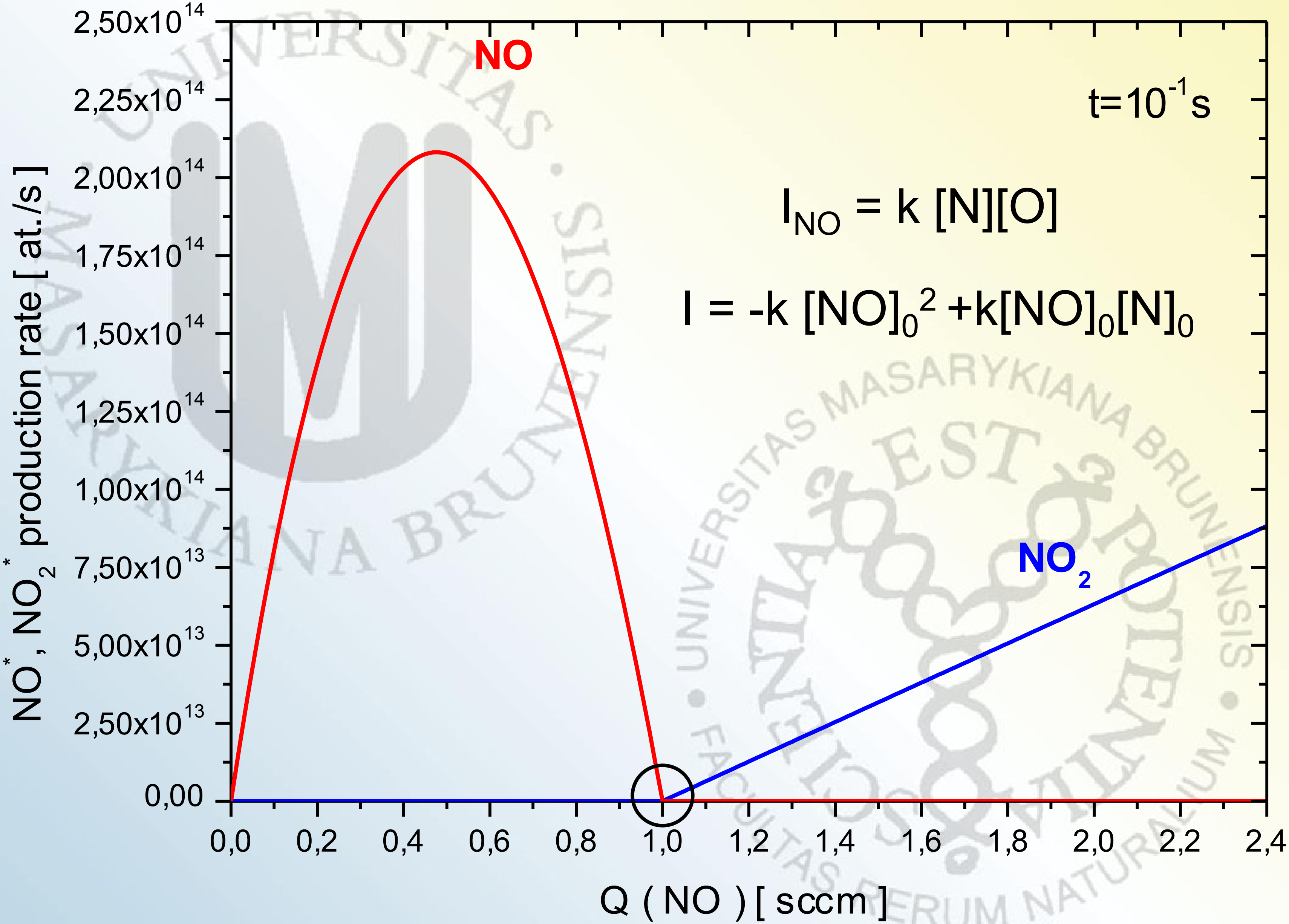
slow **$NO + O \rightarrow NO_2^*$** (green continuum) **[3]**

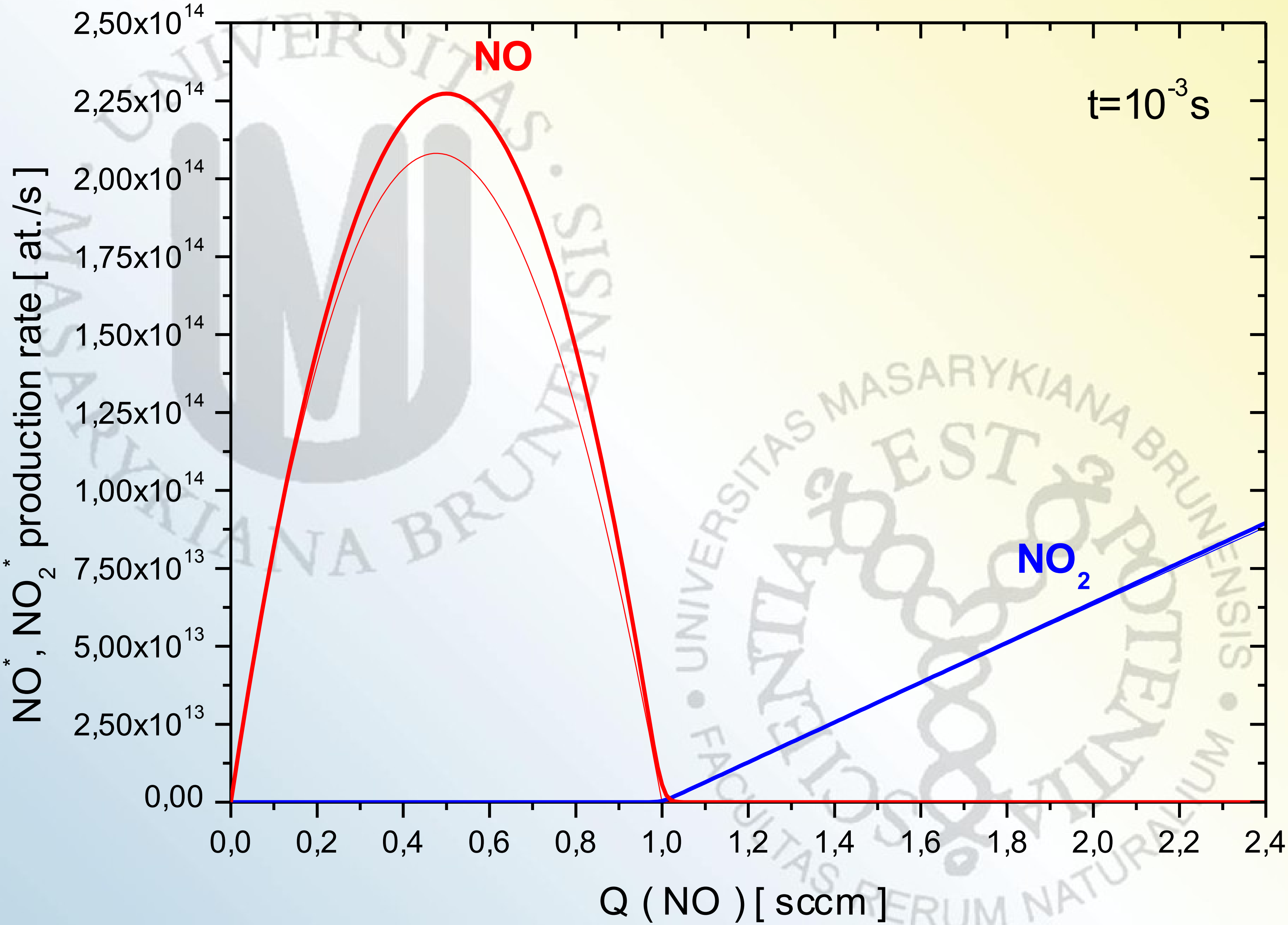
$k_3 = 6.4\ 10^{-17}\ cm^3s^{-1}$

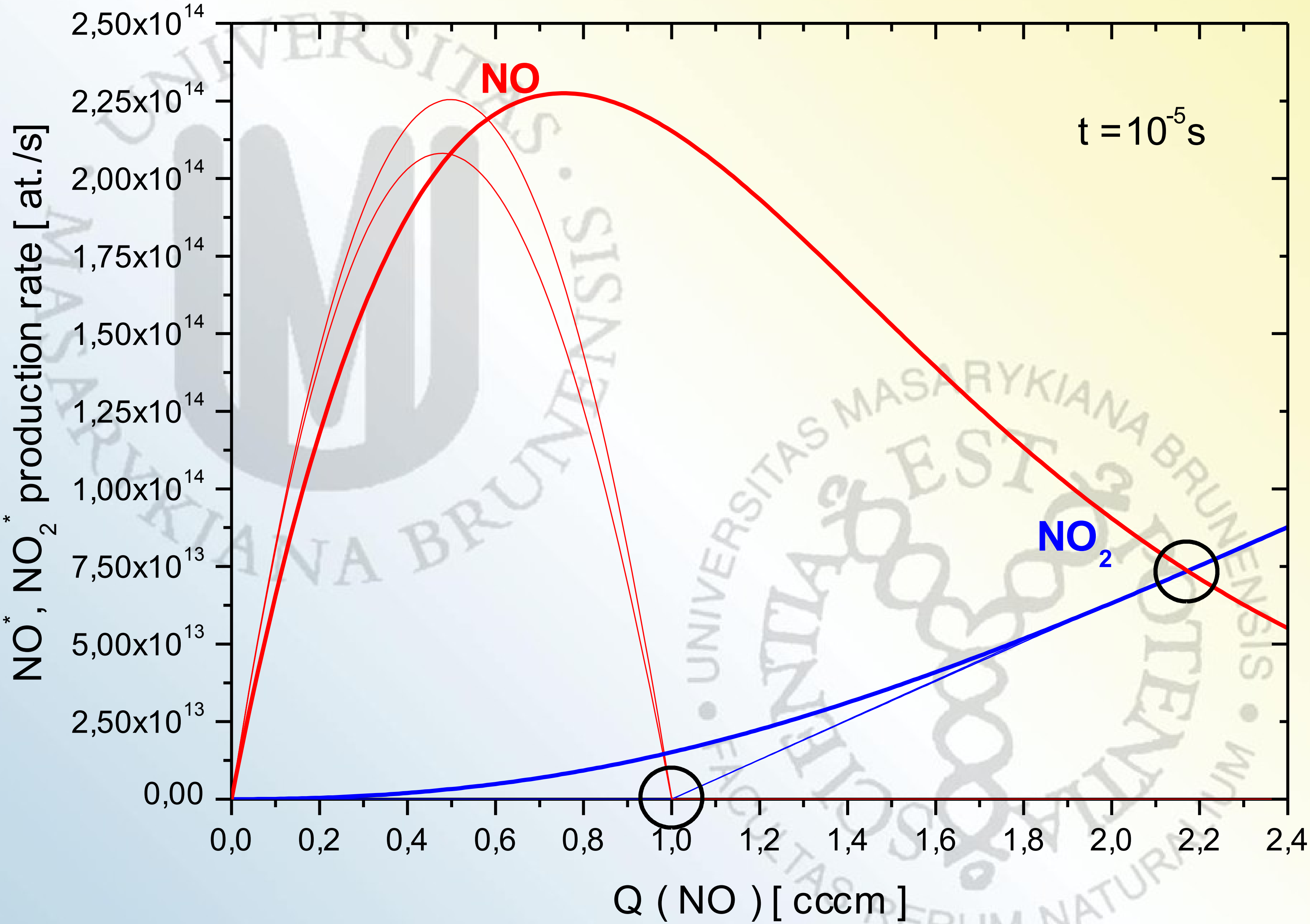
A. Fontijn, C.B. Meyer, H.I. Schiff : J. Chem. Phys., 1964


NO B²Π - X²Π
Intensity [a.u.]
λ [nm]
2500
2000
1500
1000
500
0
318
320
322
324
326


NO₂ A²B₁ - X²A₁
Intensity [a.u.]
λ [nm]
1250
1000
750
500
250
0
560
561
562
563
564
565


NO
$t=10^{-1}$s
$I_{NO} = k\ [N][O]$
$I = -k\ [NO]_0^2 + k[NO]_0[N]_0$
NO_2
NO^*, NO_2^* production rate [at./s]
$2{,}50 \times 10^{14}$
$2{,}25 \times 10^{14}$
$2{,}00 \times 10^{14}$
$1{,}75 \times 10^{14}$
$1{,}50 \times 10^{14}$
$1{,}25 \times 10^{14}$
$1{,}00 \times 10^{14}$
$7{,}50 \times 10^{13}$
$5{,}00 \times 10^{13}$
$2{,}50 \times 10^{13}$
0,00
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
1,8
2,0
2,2
2,4
Q (NO) [sccm]

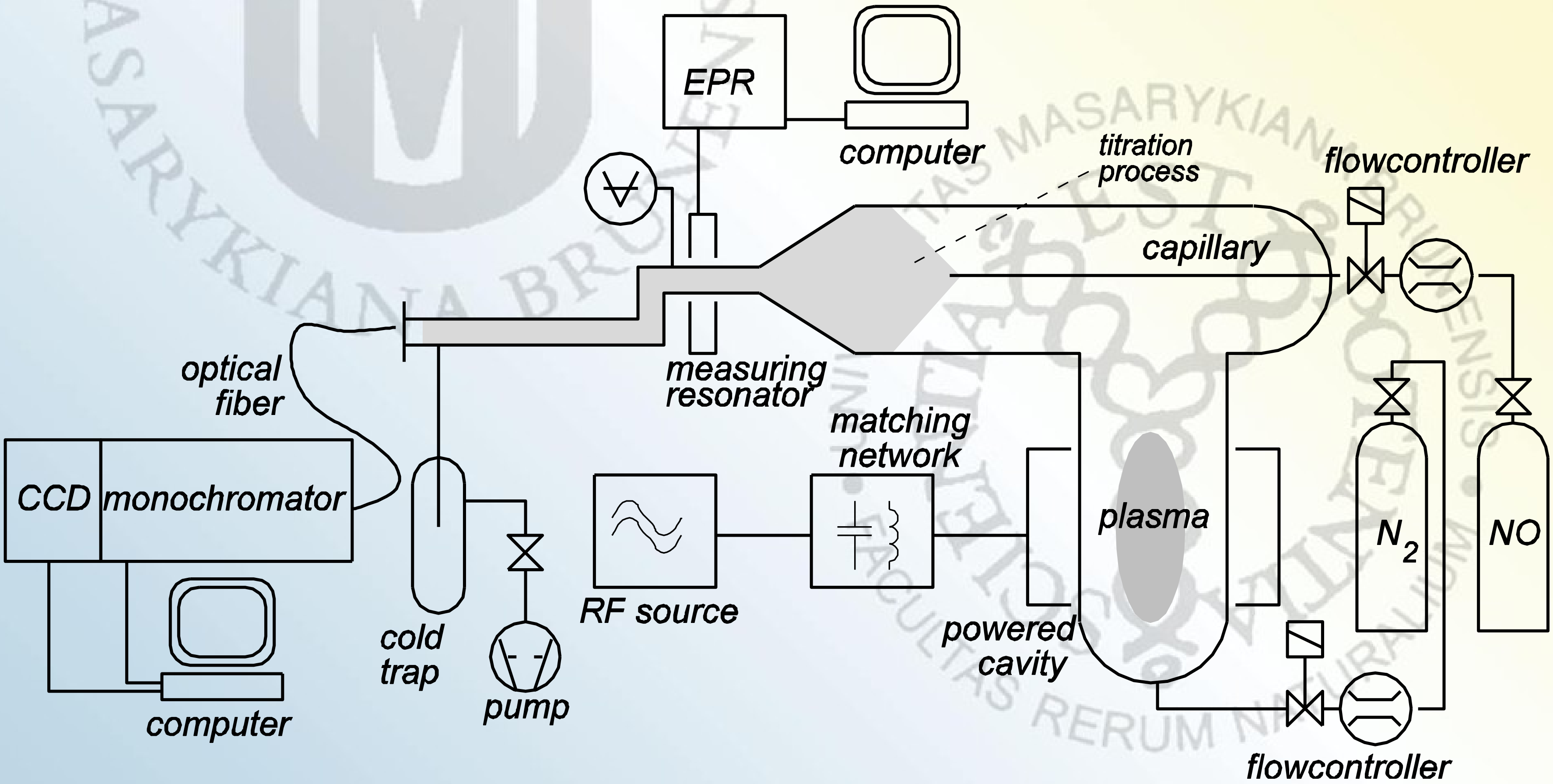

NO
t=10^-3 s
NO2
NO*, NO2* production rate [at./s]
Q (NO) [sccm]
2,50x10^14
2,25x10^14
2,00x10^14
1,75x10^14
1,50x10^14
1,25x10^14
1,00x10^14
7,50x10^13
5,00x10^13
2,50x10^13
0,00
0,0 0,2 0,4 0,6 0,8 1,0 1,2 1,4 1,6 1,8 2,0 2,2 2,4

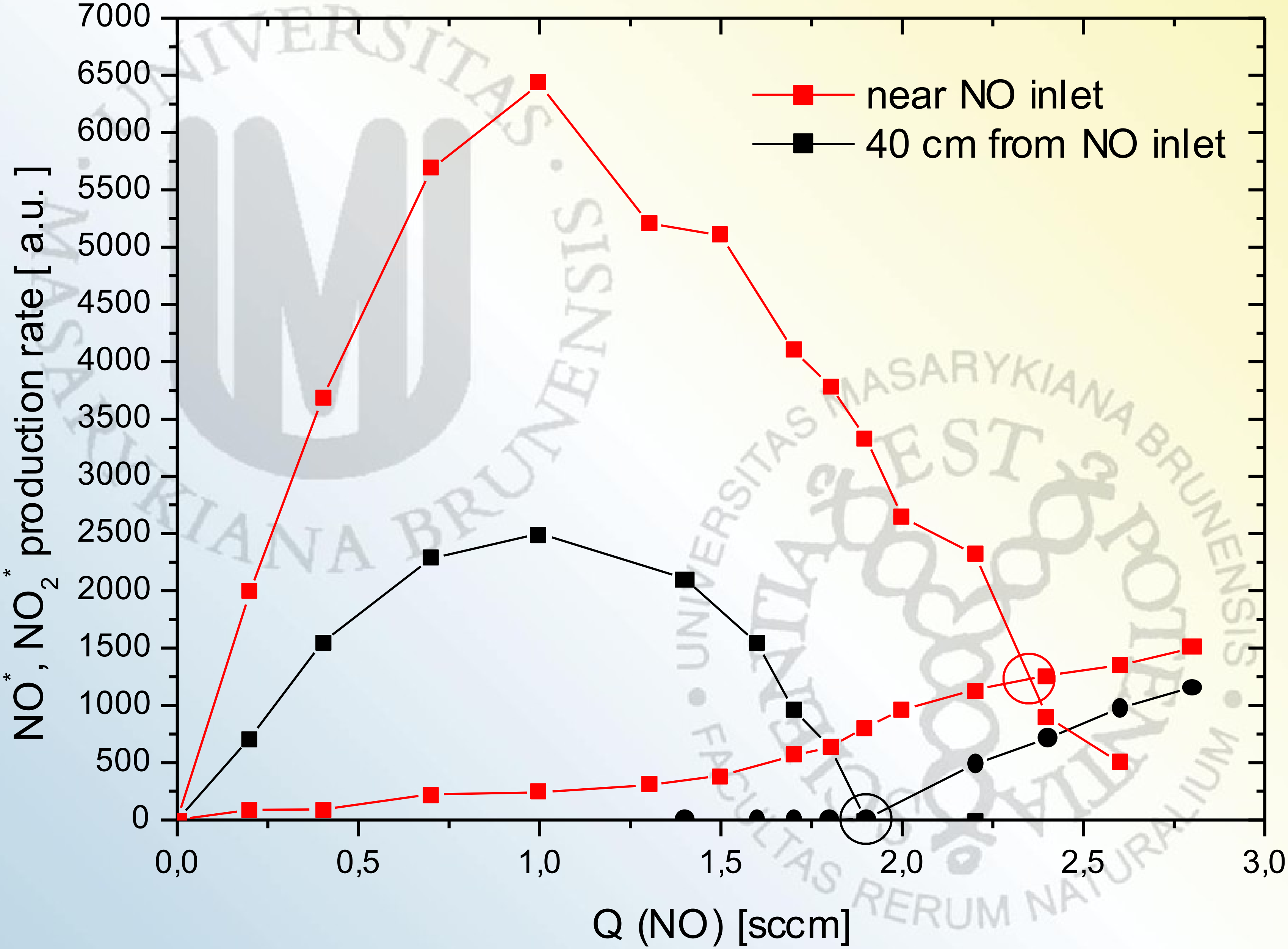


NO
NO2
t = 10-5 s
NO*, NO2* production rate [at./s]
Q (NO) [cccm]
2,50x10^14
2,25x10^14
2,00x10^14
1,75x10^14
1,50x10^14
1,25x10^14
1,00x10^14
7,50x10^13
5,00x10^13
2,50x10^13
0,00
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
1,8
2,0
2,2
2,4

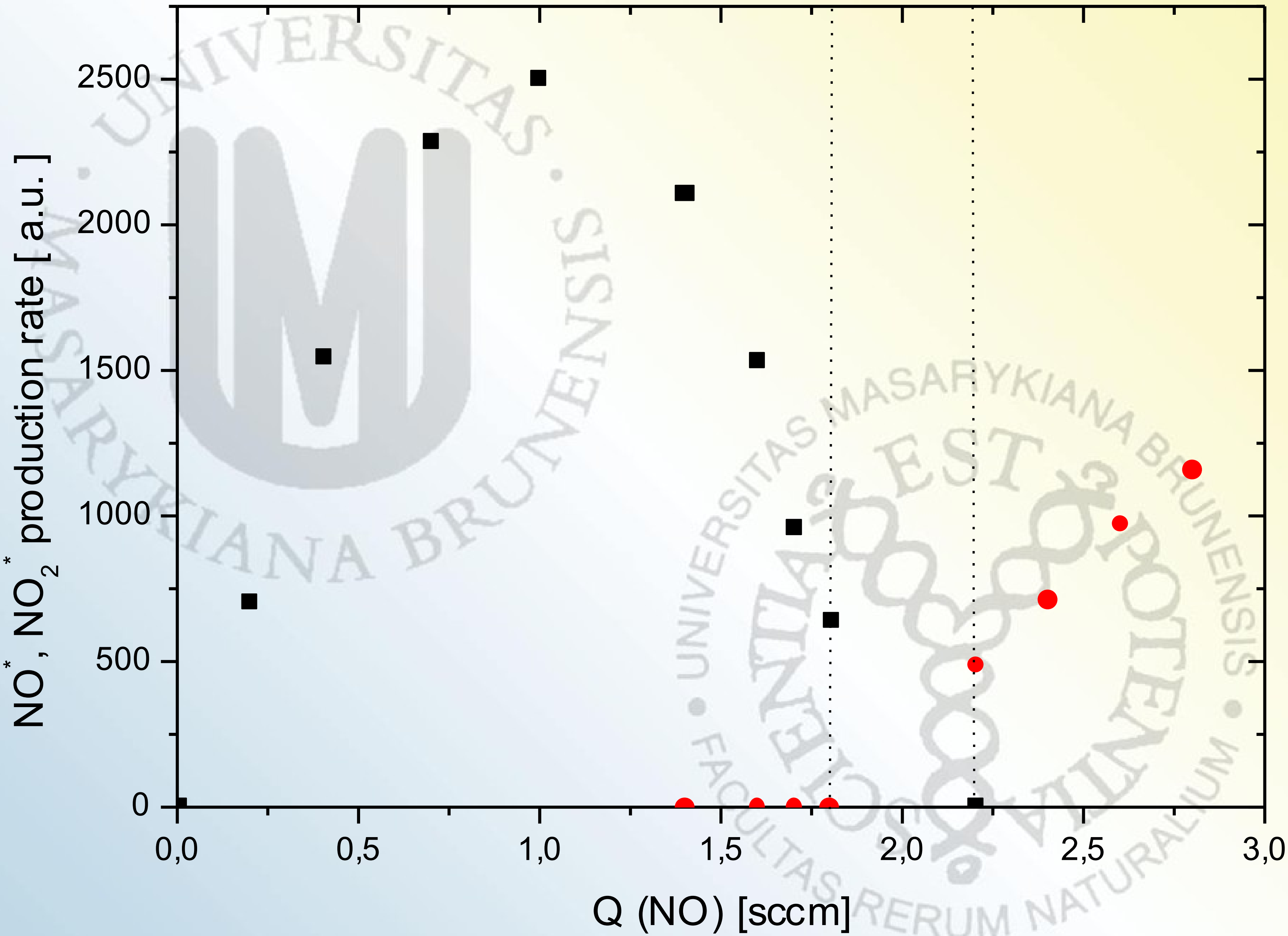
Experiment was done at following conditions :

N_2 flow = **200 sccm**
corresponding pressure = **400 Pa**
power output = **50 W**

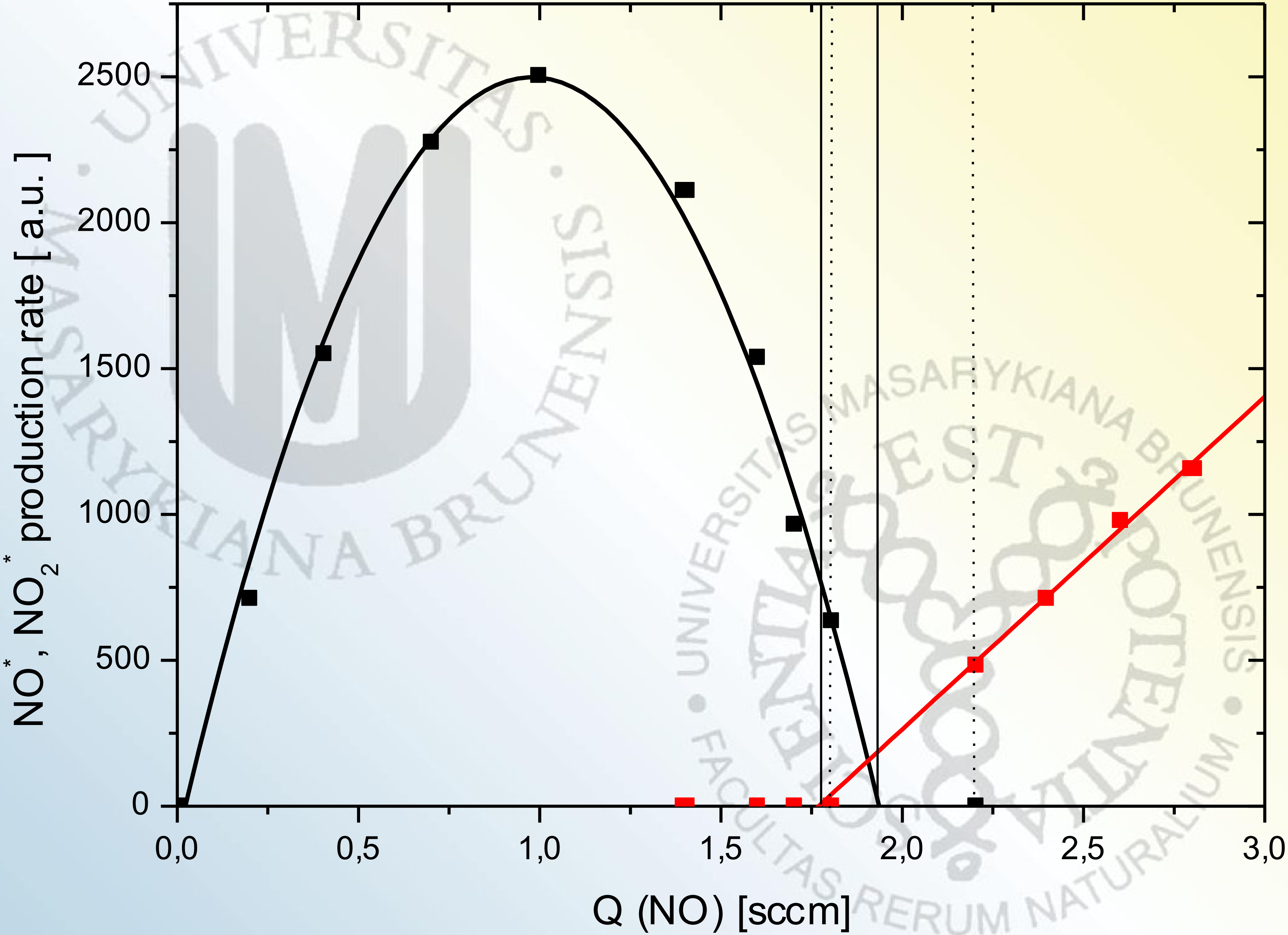




near NO inlet
40 cm from NO inlet
NO^*, NO_2^* production rate [a.u.]
Q (NO) [sccm]
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0,0
0,5
1,0
1,5
2,0
2,5
3,0



2500
2000
1500
1000
500
0
0,0
0,5
1,0
1,5
2,0
2,5
3,0
NO*, NO2* production rate [a.u.]
Q (NO) [sccm]



2500
2000
1500
1000
500
0
0,0
0,5
1,0
1,5
2,0
2,5
3,0
Q (NO) [sccm]
NO^*, NO_2^* production rate [a.u.]

Conclusion 1

N atom concentration is correctly estimated by NO titration if

-dark point corresponds to simultaneous zero intensity of NO^* and NO_2^*

or

-NO^* has parabolic shape

or

-NO_2^* is zero until a N extinction point and then increases linearly

Parabolic fit of NO^* enable us

-to determine dark point better than somewhere between the last positive value and the first zero value of NO^*

Linear fit of NO_2^* enable us

-to determine dark point better than somewhere between the last zero value and the first positive value of NO_2^*

Density of N and O atoms in N_2 and O_2 gas mixtures determined by NO titration

There are two ways how to determine density of N and O atoms in $N_2 – O_2$ discharges

- **from NO_2^***

A. Ricard, V. Monna, M. Mozetic : Production of O atoms in Ar-O_2 and N_2-O_2 microwave flowing post-discharges
Surface and Coating Technology, 174, (2003), 905-908

A. Ricard, V Monna : Reactive molecular plasmas
Plasma Sources Sci. Technol. 11, (2002), A150-A153

- **from NO^***

P. Vašina, V. Kudrle, A. Tálský, P. Botoš, M. Mrázková, M. Meško
Plasma Sources Sci. Technol. 13(4), (2004) 668-674

Determining of N and O atom density from NO_2^* - A. Ricard's method

1. Starting with a N_2 (or Ar – N_2) post-discharge, N atoms density **$[N]_1$** is determined from the extinction point between NO^* and NO_2^*.

2. After the extinction point, the NO_2^* intensity is linearly increasing with NO with a slope **r_1**

3. Then N_2 is replaced by N_2 – O_2 gas mixture, N atoms are transformed into O atoms by reaction [1]. N atoms density **$[N]_2$** is deduced from dark point. After the dark point, the NO_2^* intensity is linearly increasing with a slope **r_2**.

4. O atom density is given by the equation

$$[O] = [N]_1 \, r_2/r_1 - [N]_2$$

Determination of N and O atom density from NO* - our results

Assuming that reaction [1] is finished and taking into account that in afterglow there are not only oxygen atoms produced by discharge, but also oxygen atoms from reaction [1]

$$[O] = [O]_0 + [O]_{tr} = [O]_0 + [NO]_0$$

it is possible to write for NO* intensity

$$I = k \; [N] \; [O]$$

$$= k\,([N_0] - [NO]_0)\,([O]_0 + [NO]_0)$$

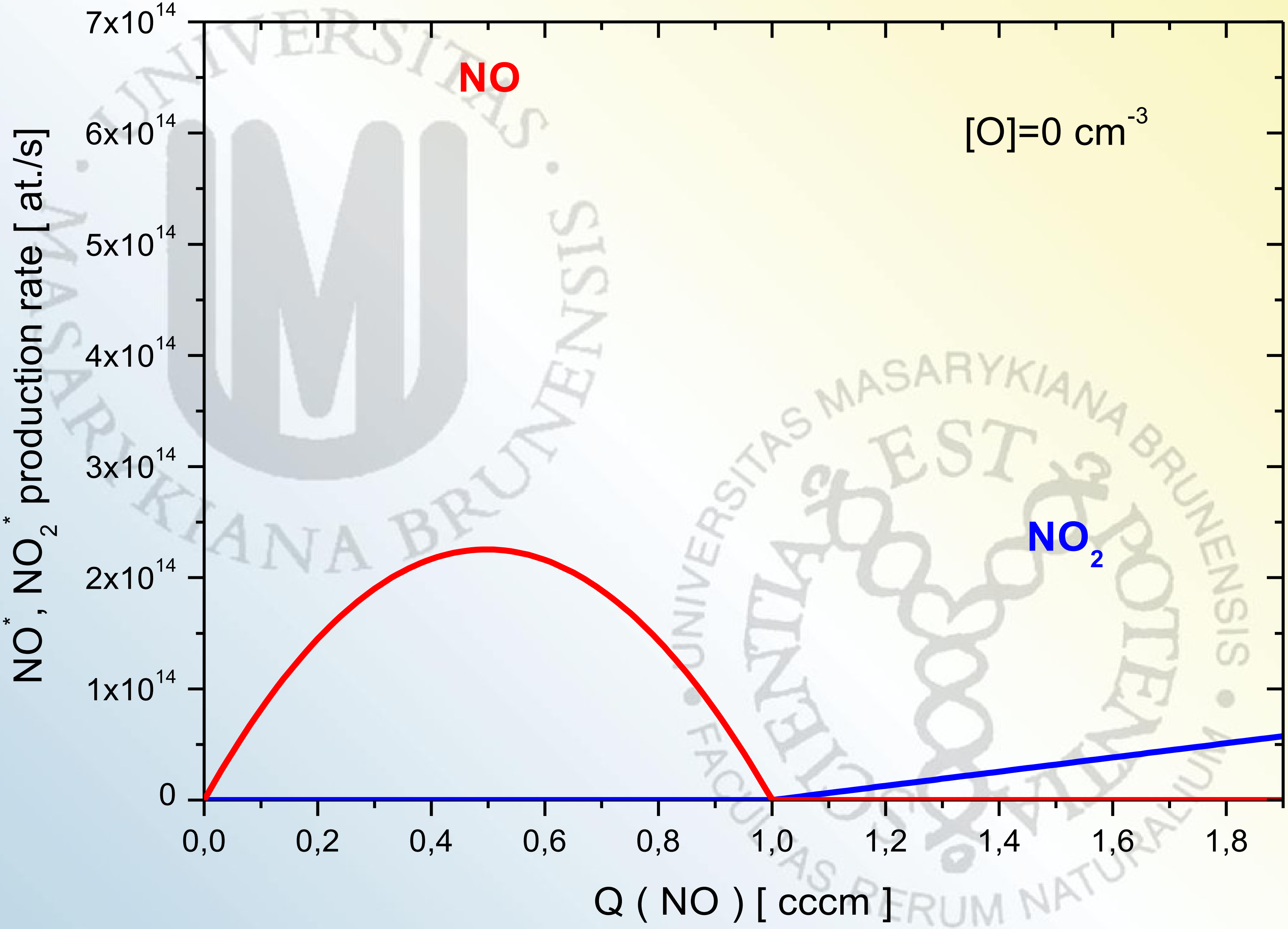
$$I = -k\,[NO]_0^2 + k\,([N]_0 - [O]_0)[NO]_0 + k\,[N]_0\,[O]_0$$

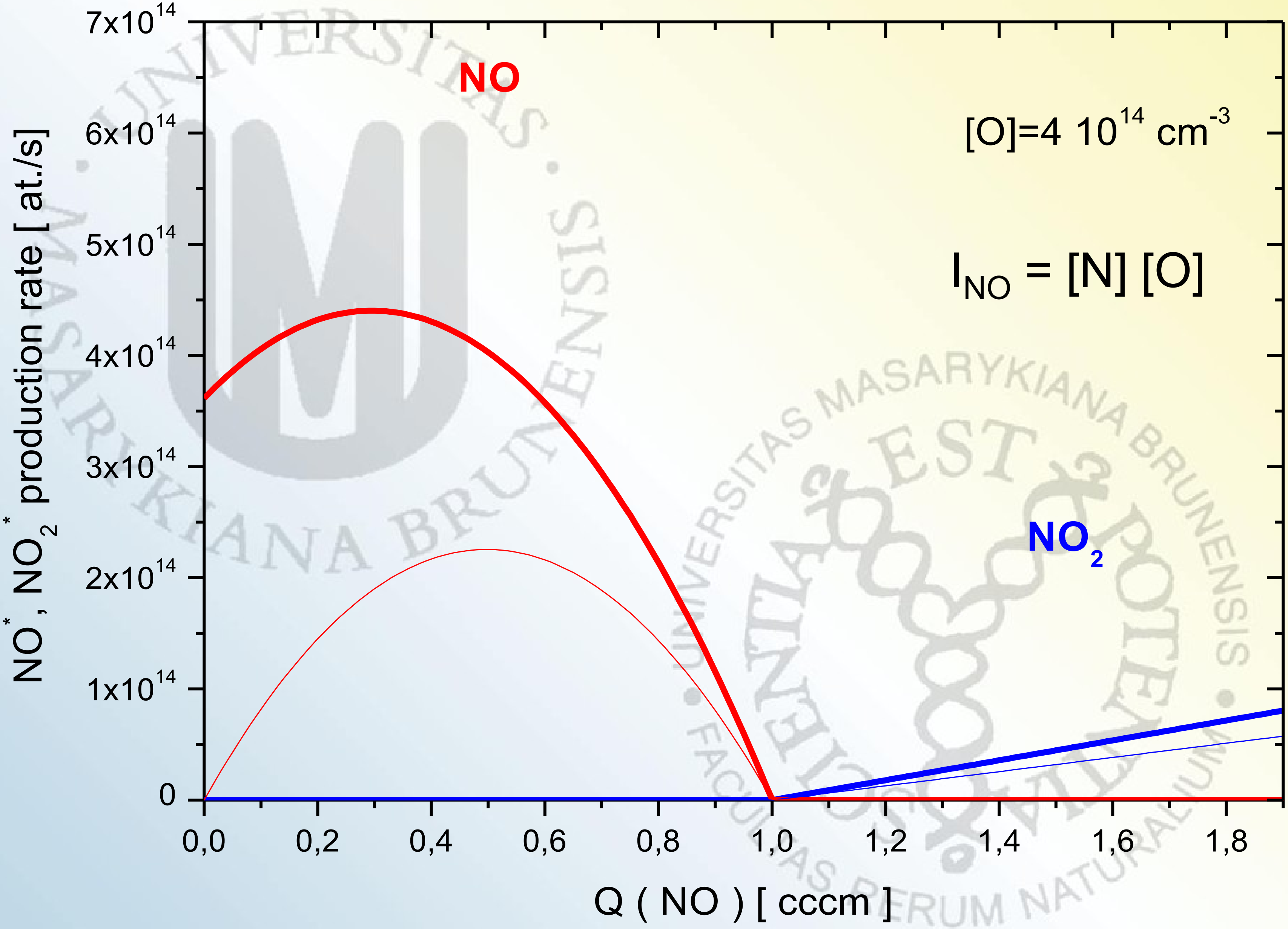
which is equation of parabola

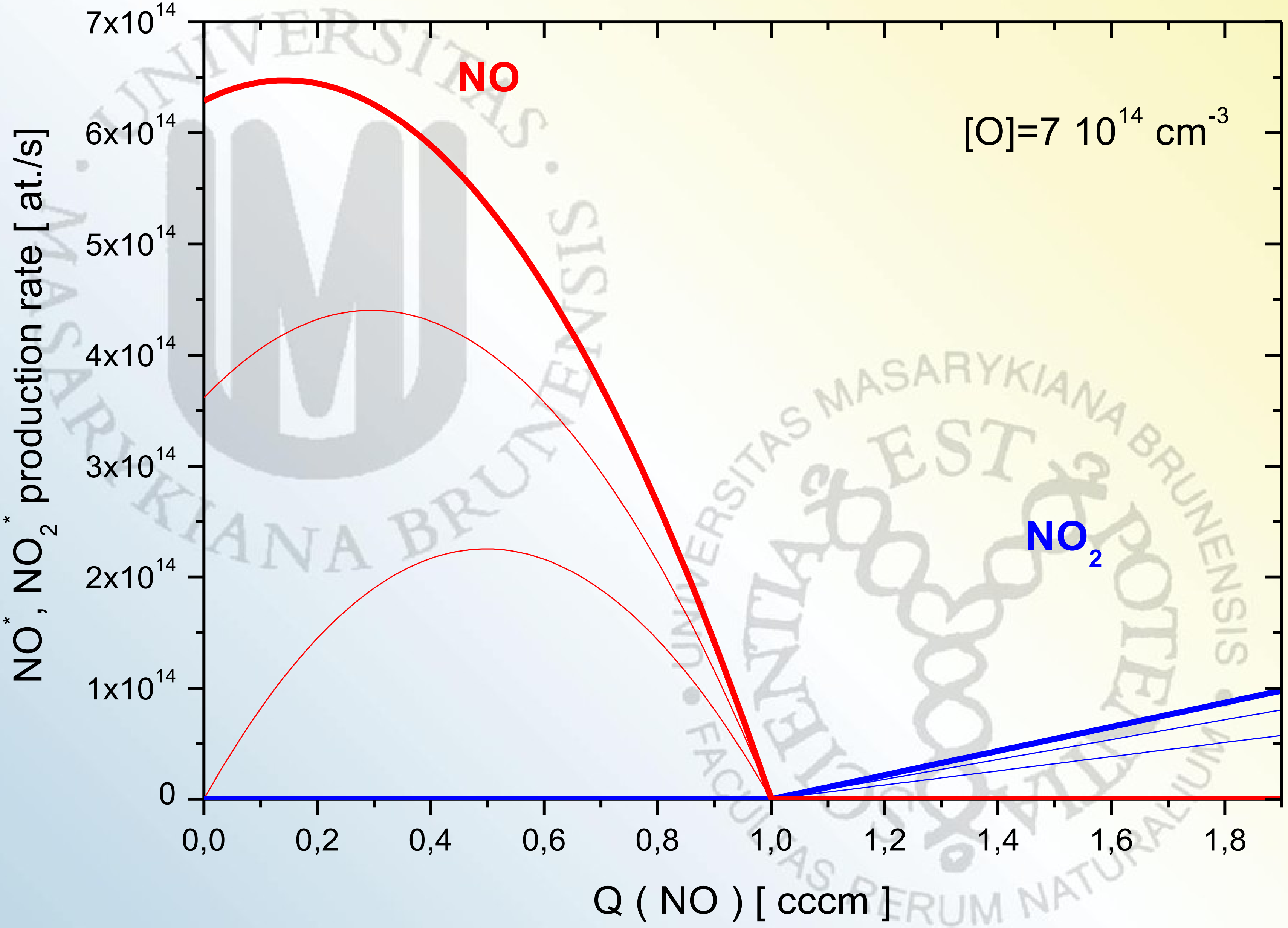
$a = -k$

$b = k\,([N]_0 - [O]_0)$

$c = k\,[N]_0\,[O]_0$


NO
[O]=0 cm-3
NO2
NO^*, NO_2^* production rate [at./s]
Q (NO) [cccm]
0
1x10^14
2x10^14
3x10^14
4x10^14
5x10^14
6x10^14
7x10^14
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
1,8


NO
[O]=4 10^14 cm^-3
I_NO = [N] [O]
NO_2
NO*, NO_2* production rate [at./s]
Q (NO) [cccm]
7x10^14
6x10^14
5x10^14
4x10^14
3x10^14
2x10^14
1x10^14
0
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
1,8



NO
NO_2
[O]=7 10^{14} cm^{-3}
NO^*, NO_2^* production rate [at./s]
Q (NO) [cccm]
$7x10^{14}$
$6x10^{14}$
$5x10^{14}$
$4x10^{14}$
$3x10^{14}$
$2x10^{14}$
$1x10^{14}$
0
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
1,8

How to determine N and O atom density from NO^* - our results

1. Perform a measurement, slowly increase concentration of NO added into $N_2 – O_2$ afterglow. Measure NO^* intensity.

2. Plot NO^* intensity as a function of NO concentration added into afterglow. Fit this dependence with a parabola to obtain parameters a, b and c and its errors da, db and dc.

3. Determine N atom density using equation

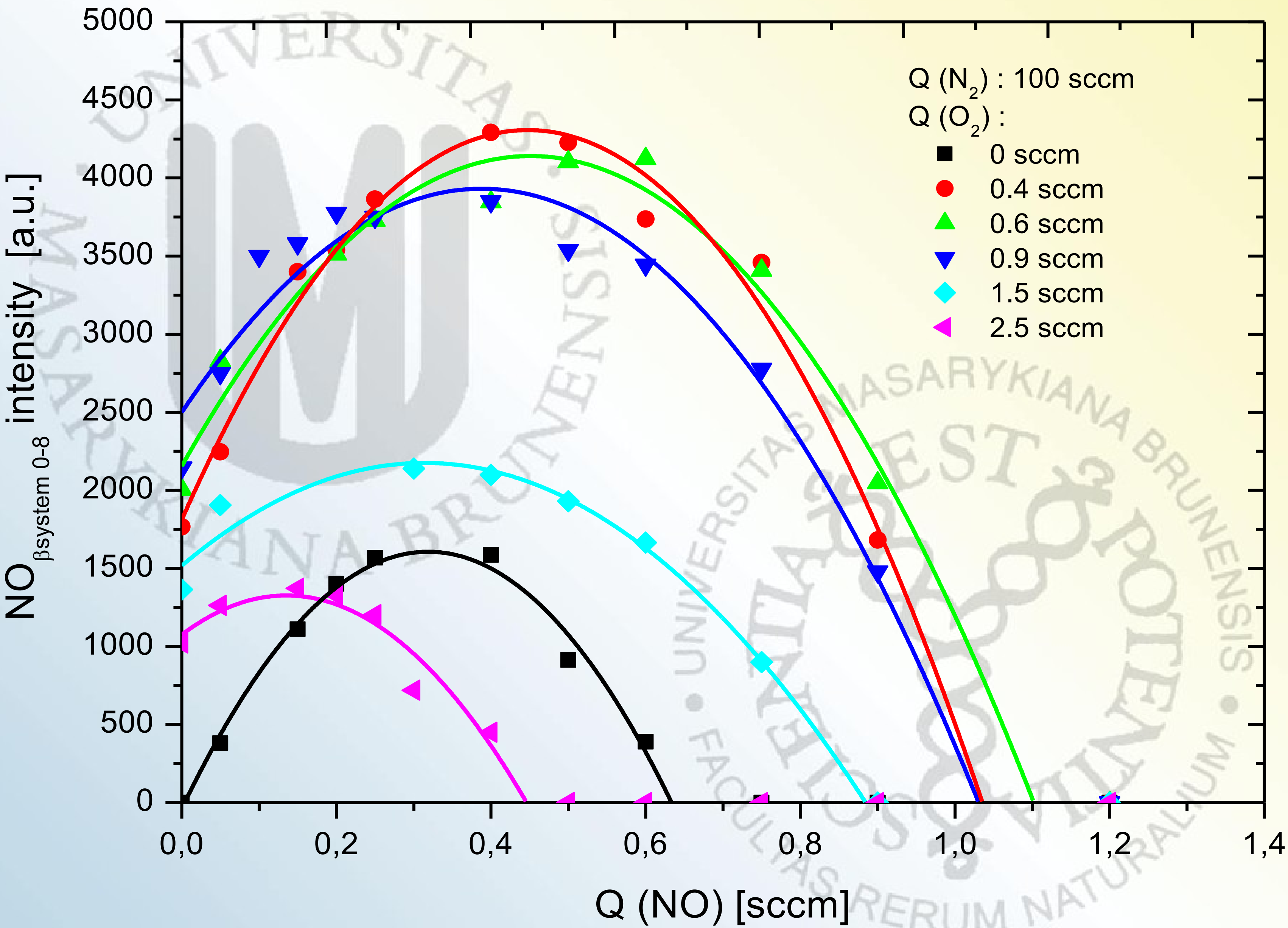
$$[N]_0 = (-b – (b^2 – 4ac)^{1/2}) / 2a$$

4. Determine O atom density using equation

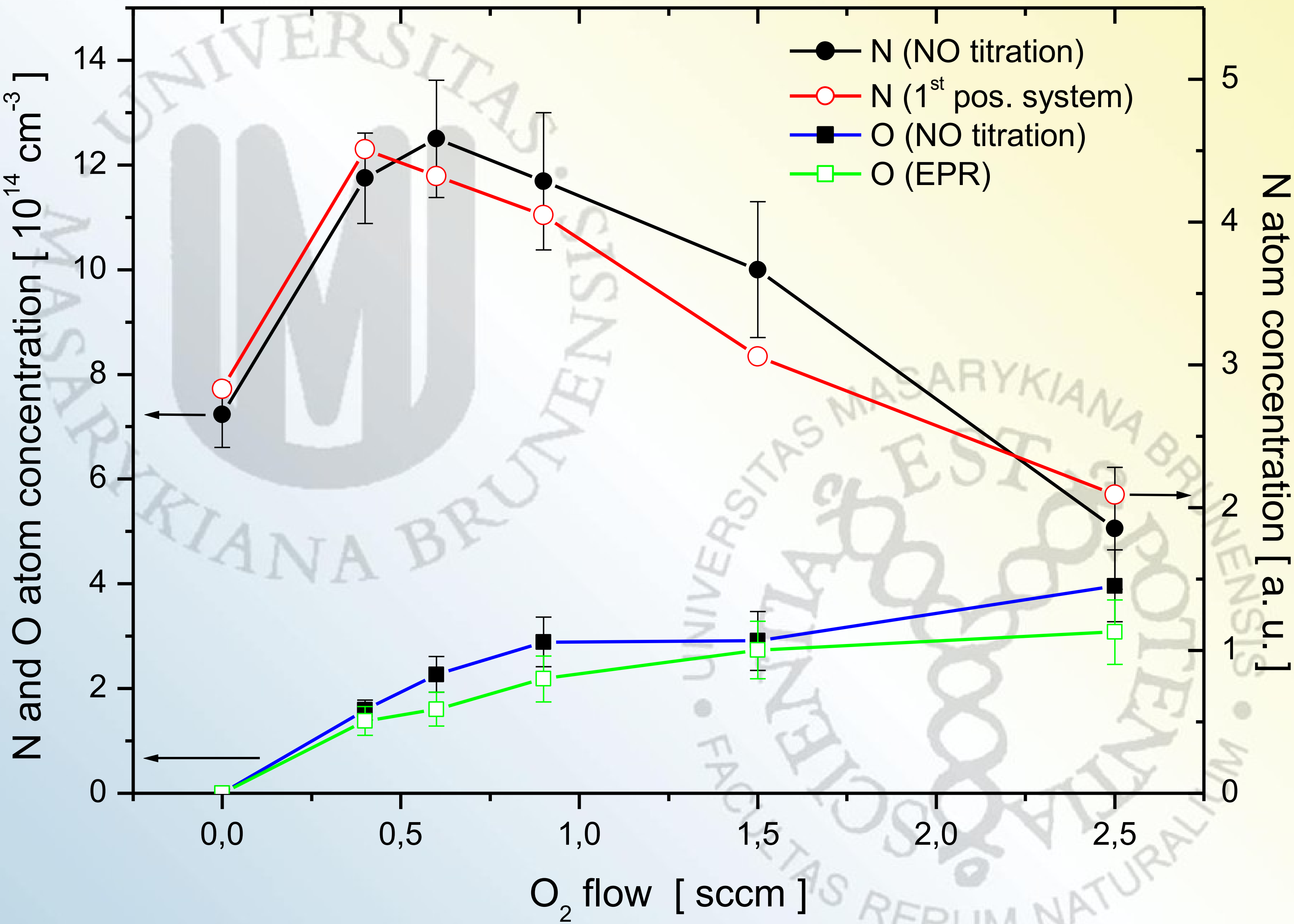
$$[O]_0 = -(-b + (b^2 – 4ac)^{1/2}) / 2a$$

Experiment was done at following conditions

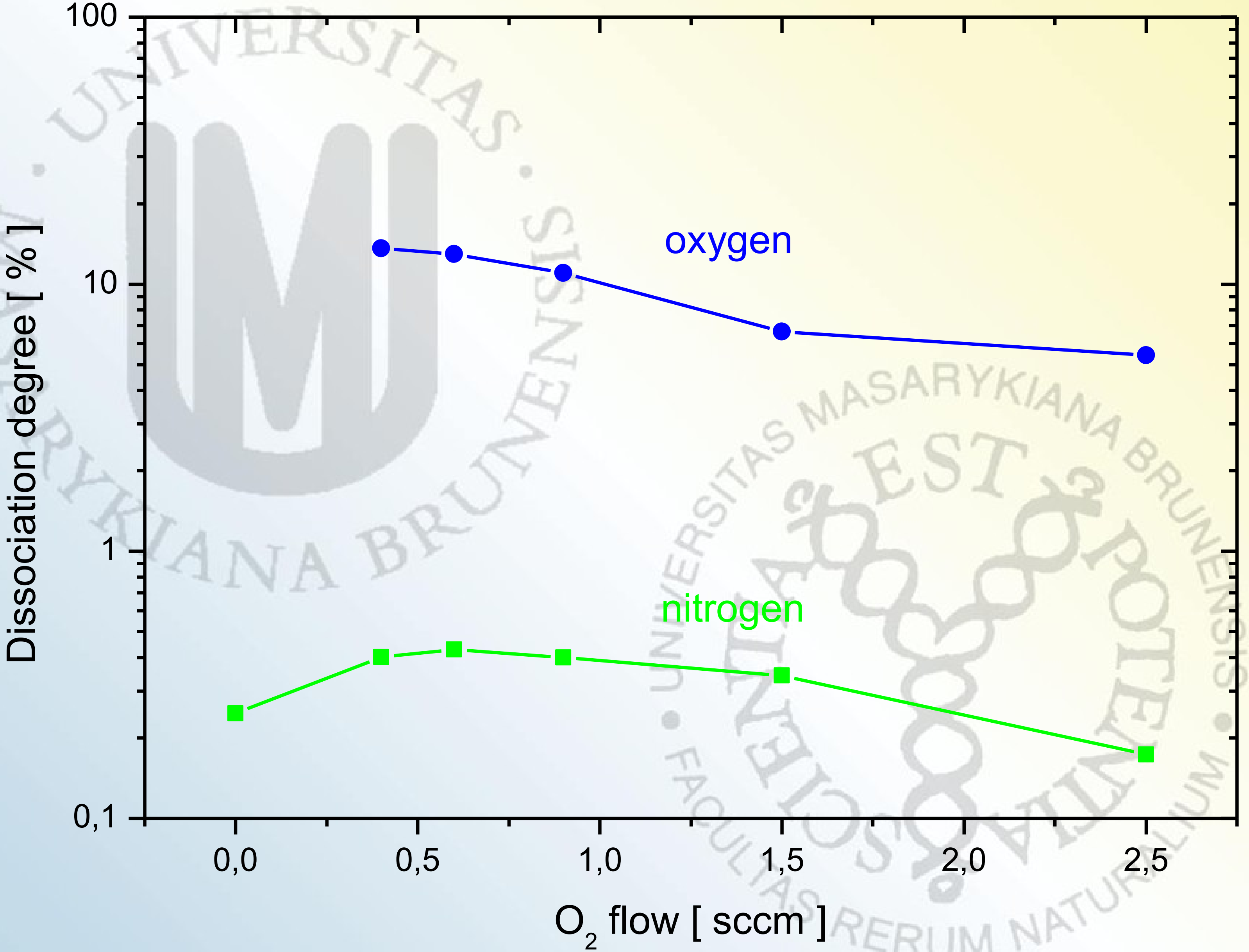
N_2 flow = **100 sccm**
O_2 flow = **0 - 2.5 sccm**
corresponding pressure = **460 Pa**
power output = **50 W**



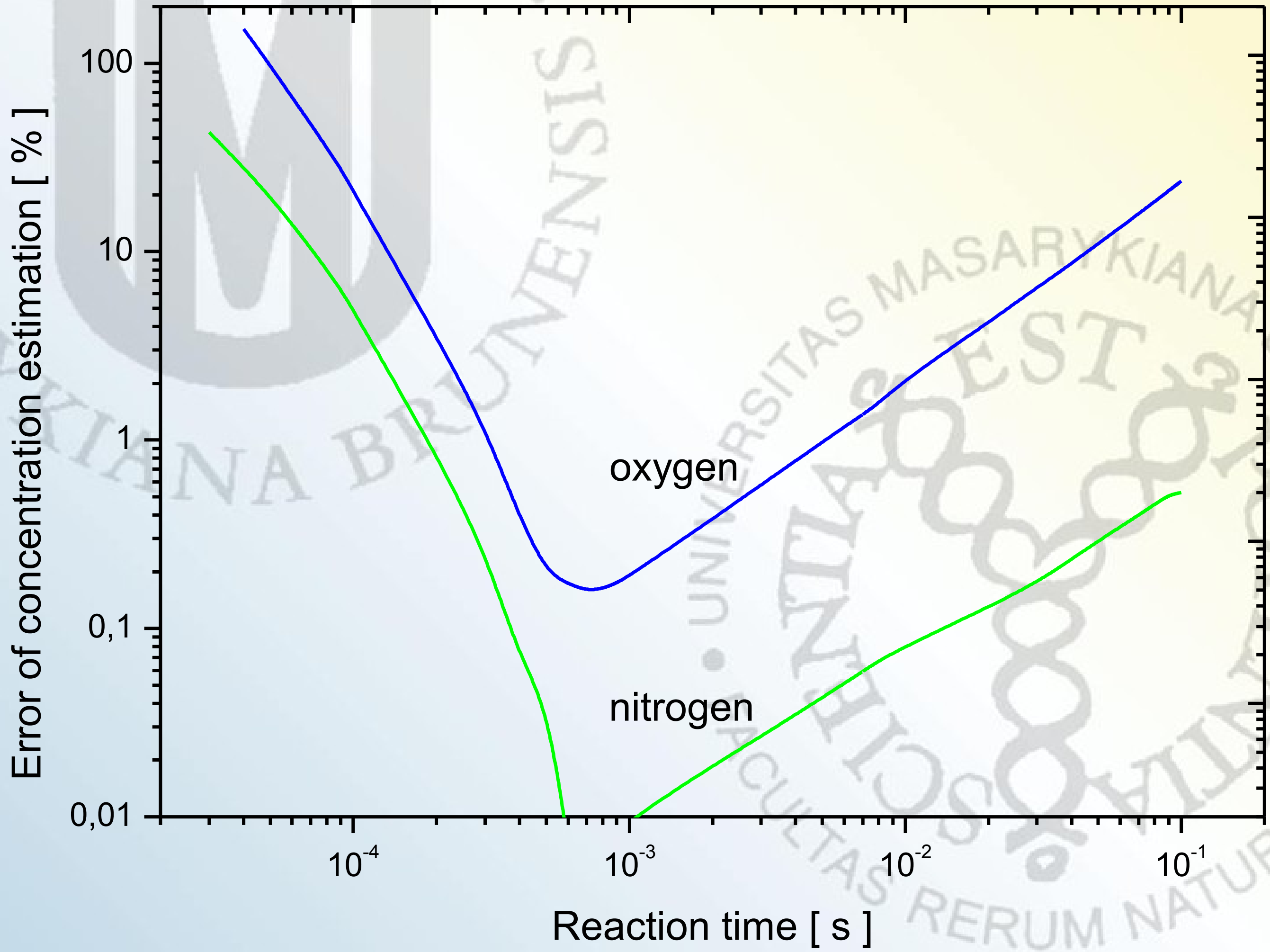
Q (N2) : 100 sccm
Q (O2) :
0 sccm
0.4 sccm
0.6 sccm
0.9 sccm
1.5 sccm
2.5 sccm
NO βsystem 0-8 intensity [a.u.]
Q (NO) [sccm]
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000

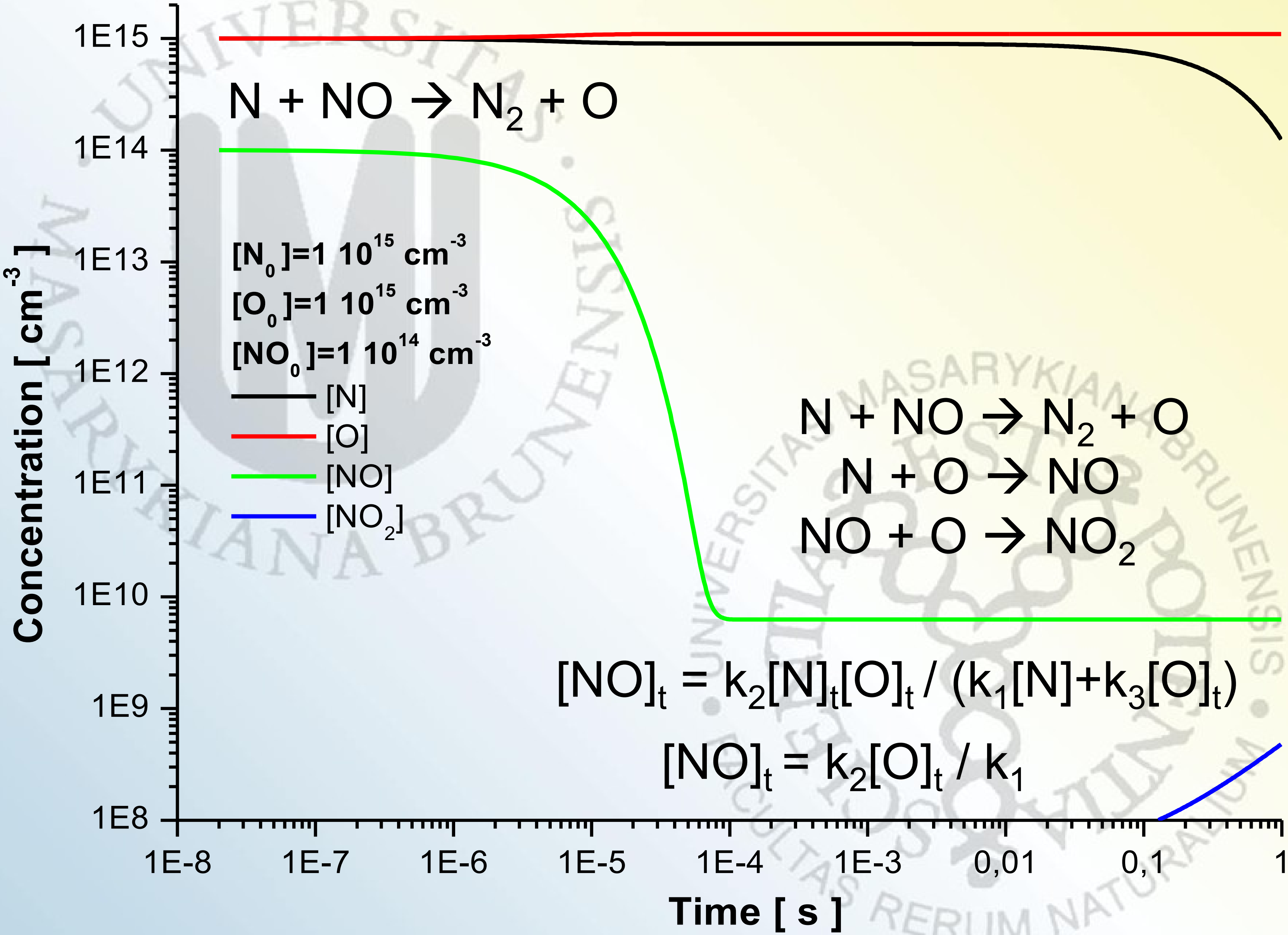


N (NO titration)
N (1st pos. system)
O (NO titration)
O (EPR)
N and O atom concentration [10^14 cm^-3]
N atom concentration [a. u.]
O2 flow [sccm]
0,0
0,5
1,0
1,5
2,0
2,5
0
2
4
6
8
10
12
14
1
3
5

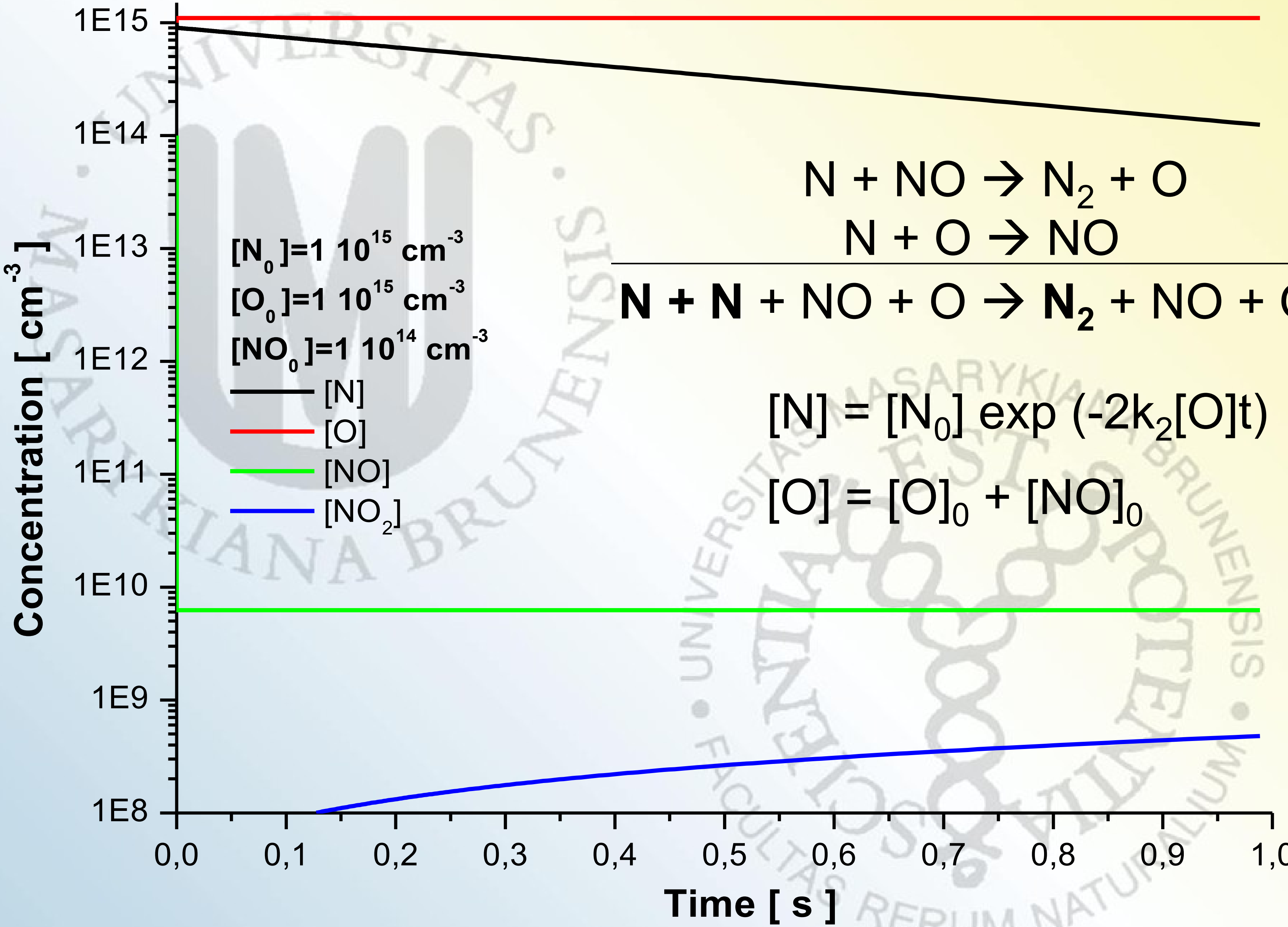

100
10
1
0,1
Dissociation degree [%]
oxygen
nitrogen
0,0
0,5
1,0
1,5
2,0
2,5
O2 flow [sccm]

How reaction time influences correctness of N and O atom density estimation?





N + NO → N2 + O
[N0]=1 10^15 cm^-3
[O0]=1 10^15 cm^-3
[NO0]=1 10^14 cm^-3
[N]
[O]
[NO]
[NO2]
N + NO → N2 + O
N + O → NO
NO + O → NO2
[NO]t = k2[N]t[O]t / (k1[N]+k3[O]t)
[NO]t = k2[O]t / k1
1E15
1E14
1E13
1E12
1E11
1E10
1E9
1E8
Concentration [cm^-3]
1E-8
1E-7
1E-6
1E-5
1E-4
1E-3
0,01
0,1
1
Time [s]



$$N + NO \rightarrow N_2 + O$$

$$N + O \rightarrow NO$$

$$\mathbf{N + N} + NO + O \rightarrow \mathbf{N_2} + NO + O$$

$$[N] = [N_0] \exp(-2k_2[O]t)$$

$$[O] = [O]_0 + [NO]_0$$

Conclusion 2

Calibration

- to estimate O atom density from NO_2^*, it is necessary to calibrate titration probe by pure N_2 before measurement. Estimation from NO^* does not need any calibration.

Sensitivity

- estimation of N and O atom density from NO^* is more sensitive for lower O atom densities (O < N). For high O atom densities, it is better to estimate O atom density from NO_2^*.

Accuracy

- to estimate correct value of O atom density from NO^*, it is necessary to measure at places corresponding to reaction times in range 10^{-1}-10^{-2} s.