Baku Branch, M.V. Lomonosov Moscow State university

PRACTICAL EXAMINATION July 23, 2015

RESULTS OVERVIEW

Science committee

Skills

	Skills
Task 1	Advanced procedures in organic synthesis and product isolation
Task 2	General laboratory skills Analysis of experimental results
Task 3	Kinetic studies using a photometer Analysis of experimental data using computer software

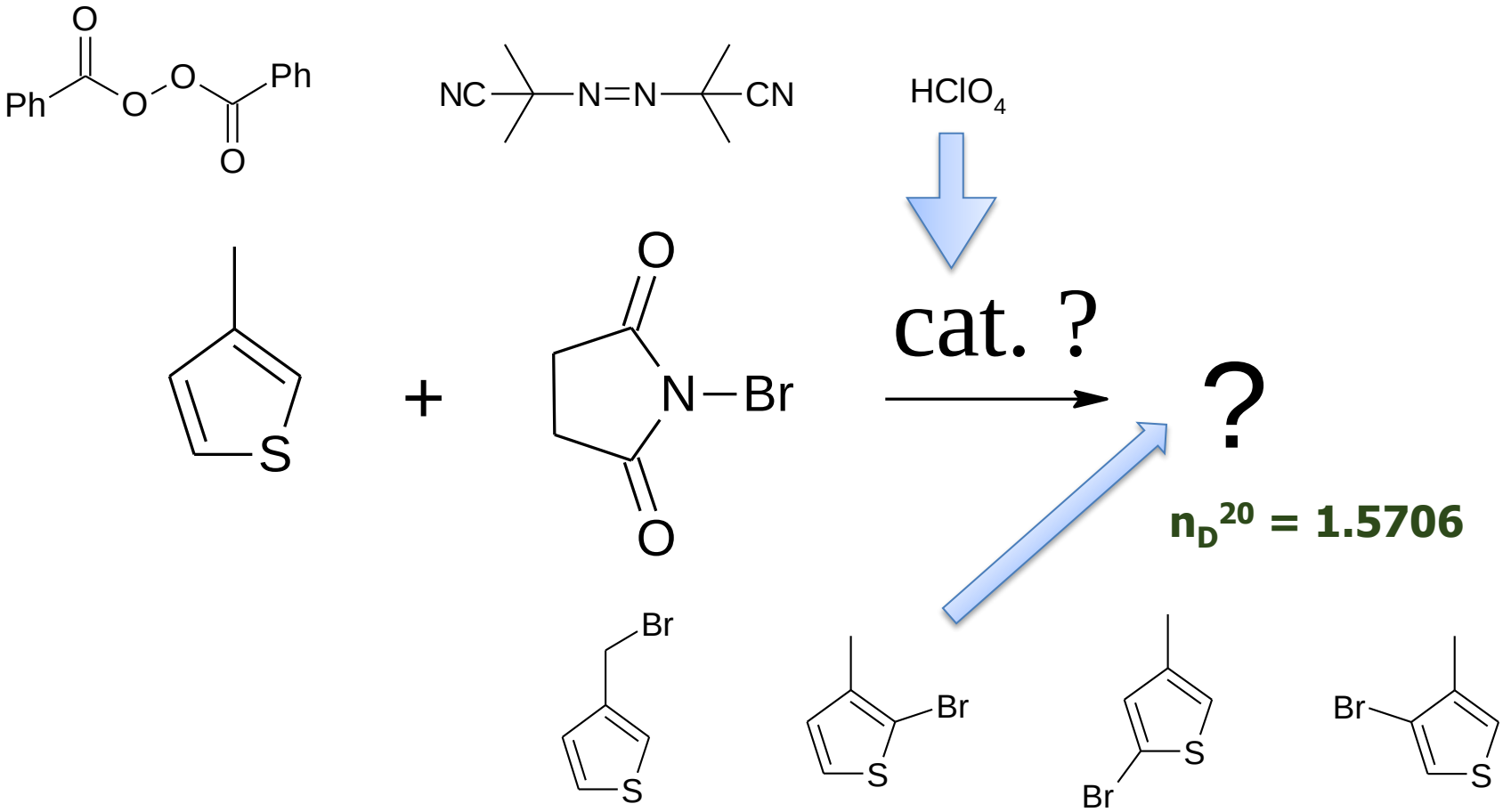
T1. General idea

Tuning bromination selectivity by catalysis

In this task, student will:

- **Synthesize a monobrominated thiophene derivative using one of the catalysts from the list;**
- **Measure the product refractive index (n_D);**
- **Compare the results obtained with literature data and decide on the product structure and the catalysts given.**

T1. General idea



n_D^{20}	1.5961	1.5706	1.5786	1.5795

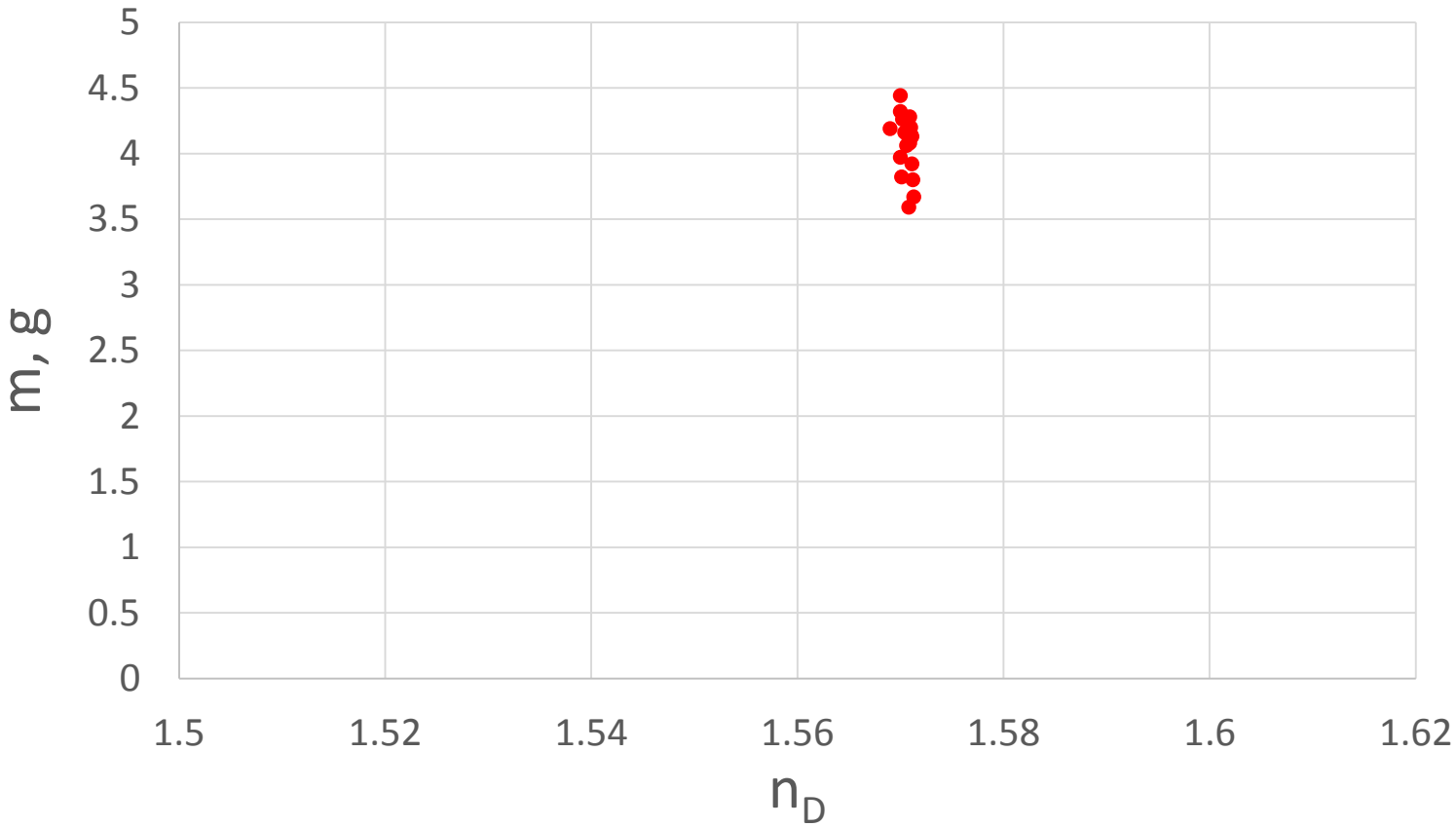
T1. Set-up needed

Apparatus for the synthesis

Apparatus for filtration and vacuum distillation

T1. Statistical results

Highly qualified team – 20 experiments
Test team – 72 experiments, 2 failed
Model experiments – 12



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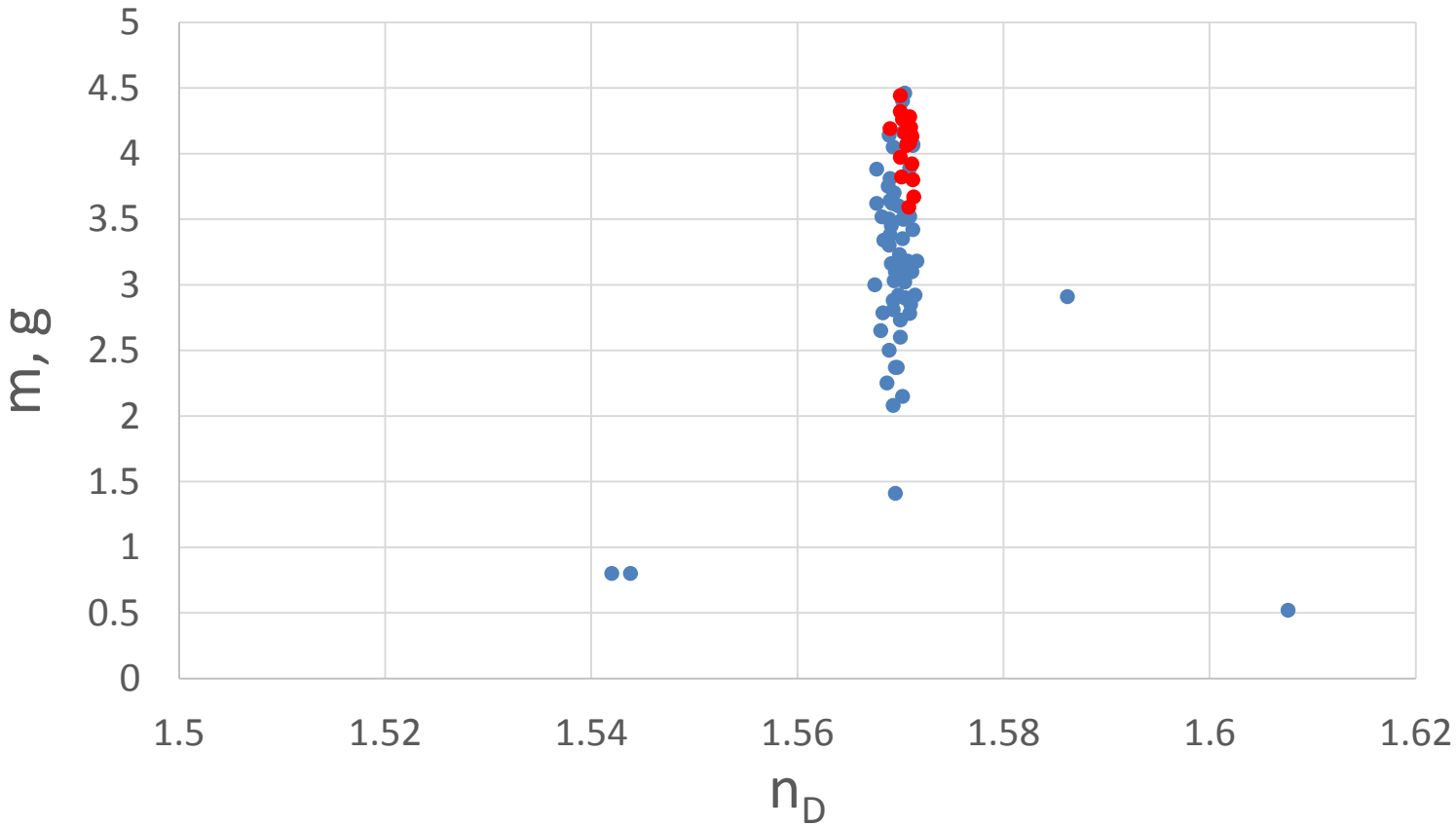

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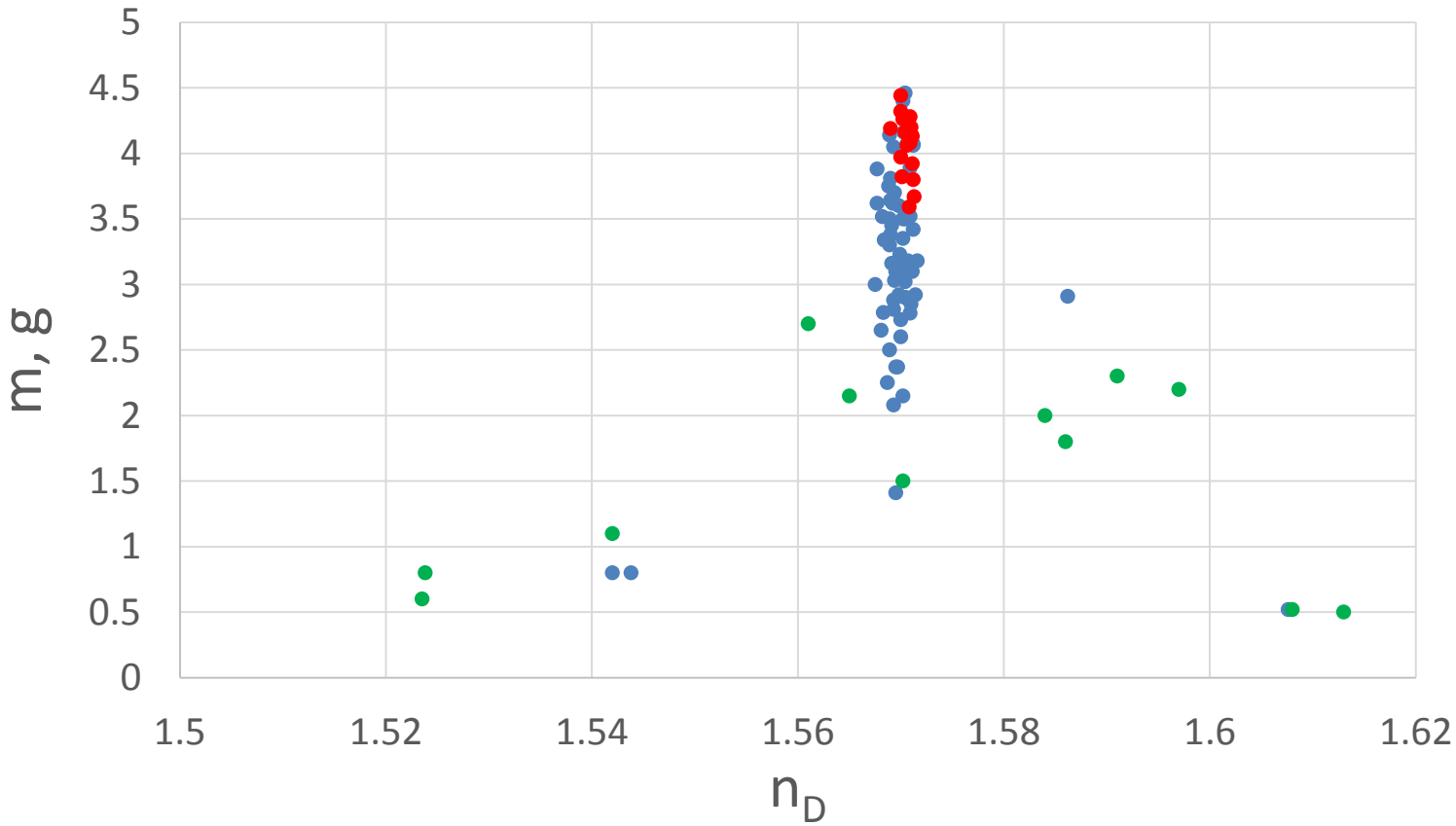

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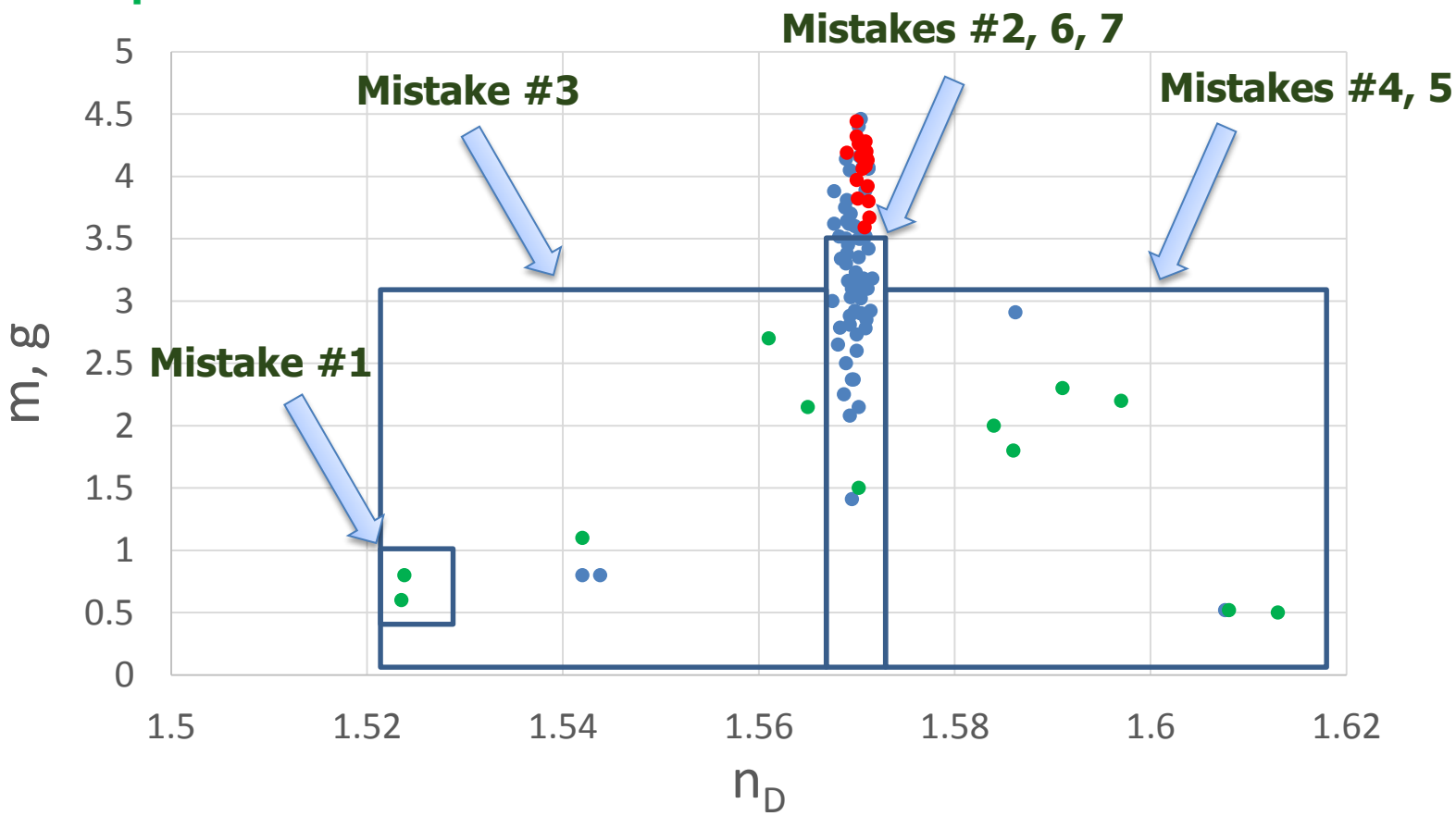


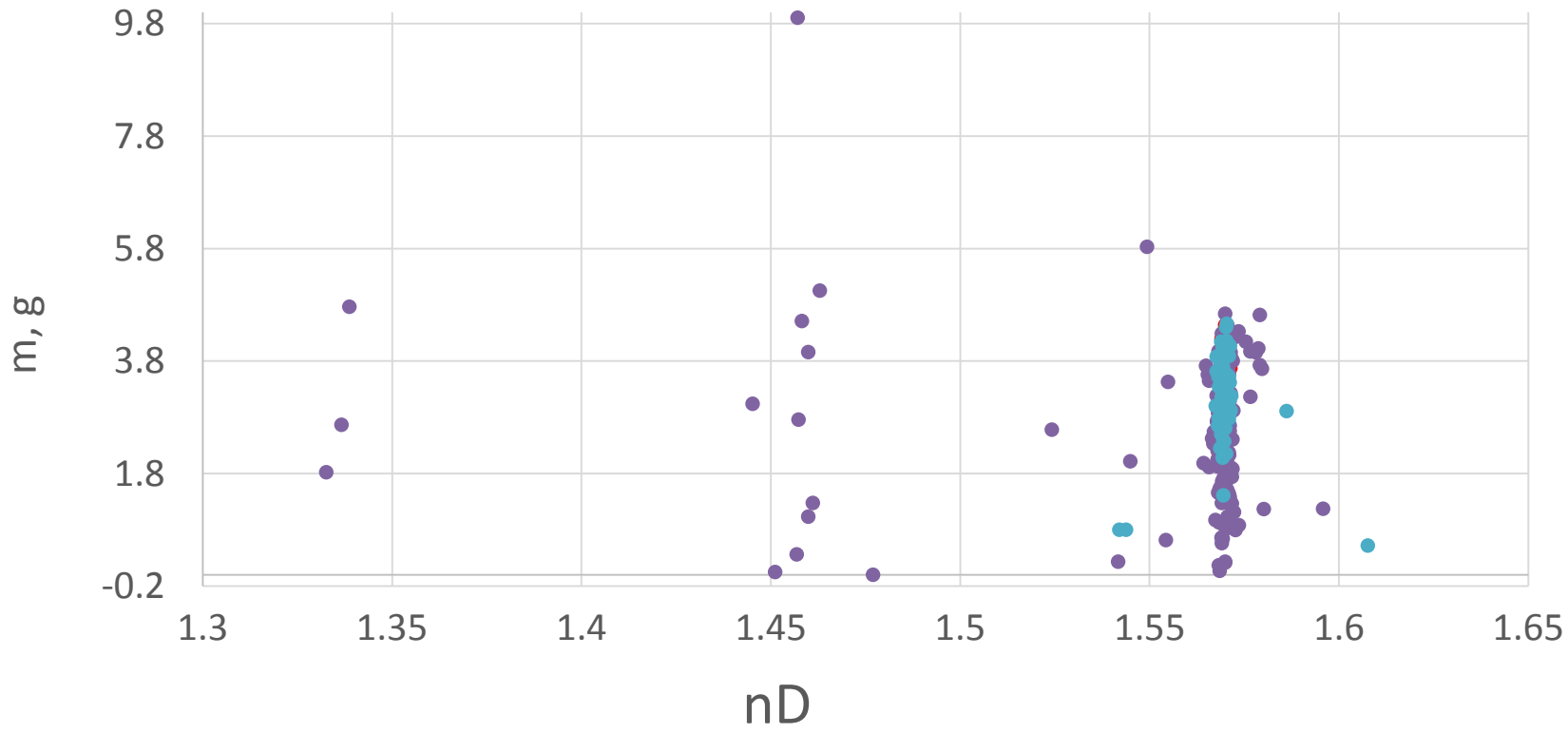
T1. Typical mistakes

#	Mistakes	Results
1	Adding of catalyst was missed	No reaction, after distillation the starting material was recovered in small yield
2	The transfer of starting materials was made incomplete, but distillation was made carefully with fractioning	Pure product in small yield
3	The transfer of NBS was made incomplete with followed distillation without fractioning	Mixture of product with starting 3-methylthiophene
4	The transfer of 3-methylthiophene was made incomplete with followed distillation without fractioning	Mixture of product with by-product 2,5-dibromo-3-methythiophene
5	Adding of the starting materials without cooling with followed distillation without fractioning	Mixture of product with by-product 2,5-dibromo-3-methythiophene
6	Adding of the starting material without cooling, but distillation was made carefully with fractioning	Pure product in small yield
7	Traces of water in the reaction mixture	Lowering of yield

All mistakes came true

T1. Statistical results

Highly qualified team; Test team; Model experiments
Students: 217 products was delivered to lab assistant



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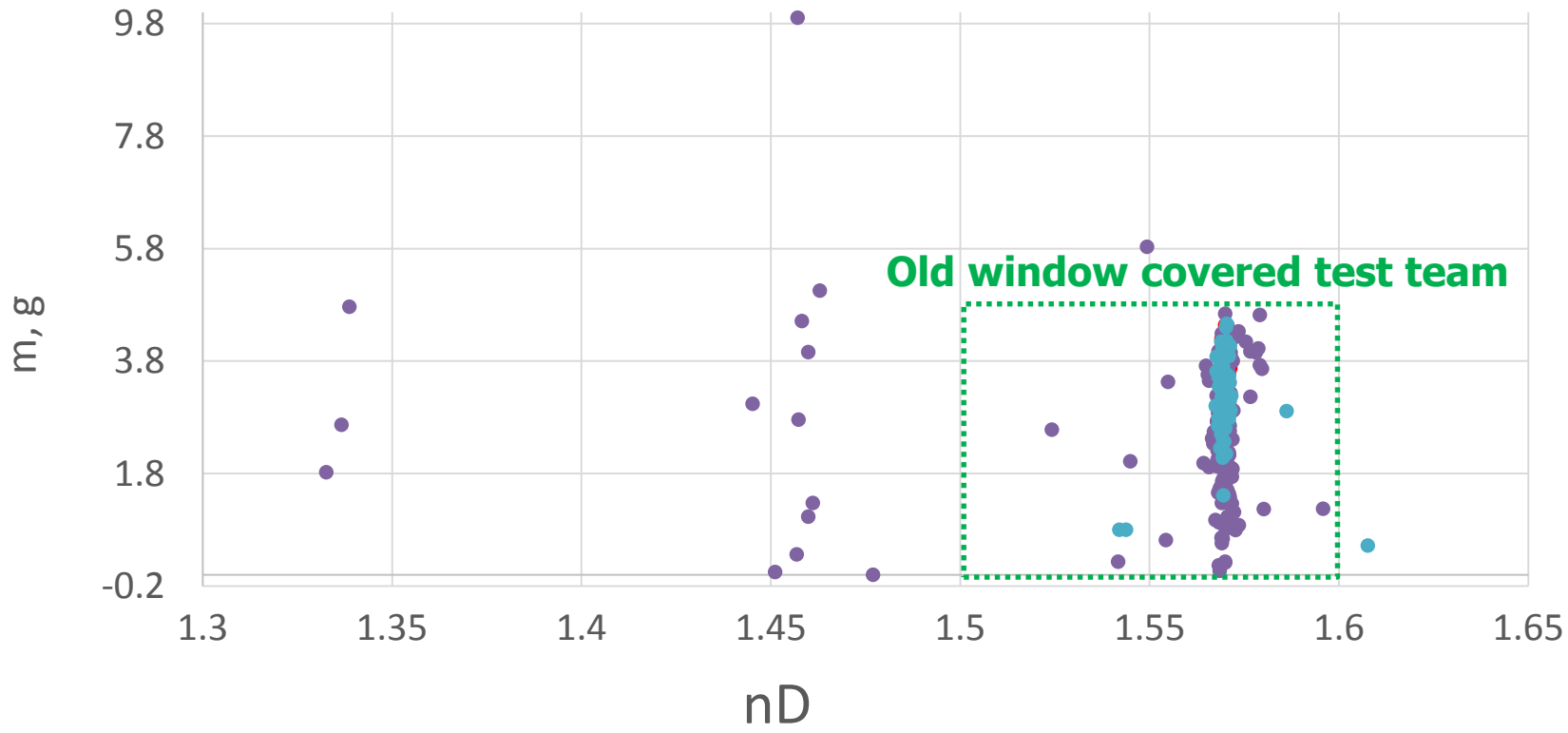

T1. Statistical results

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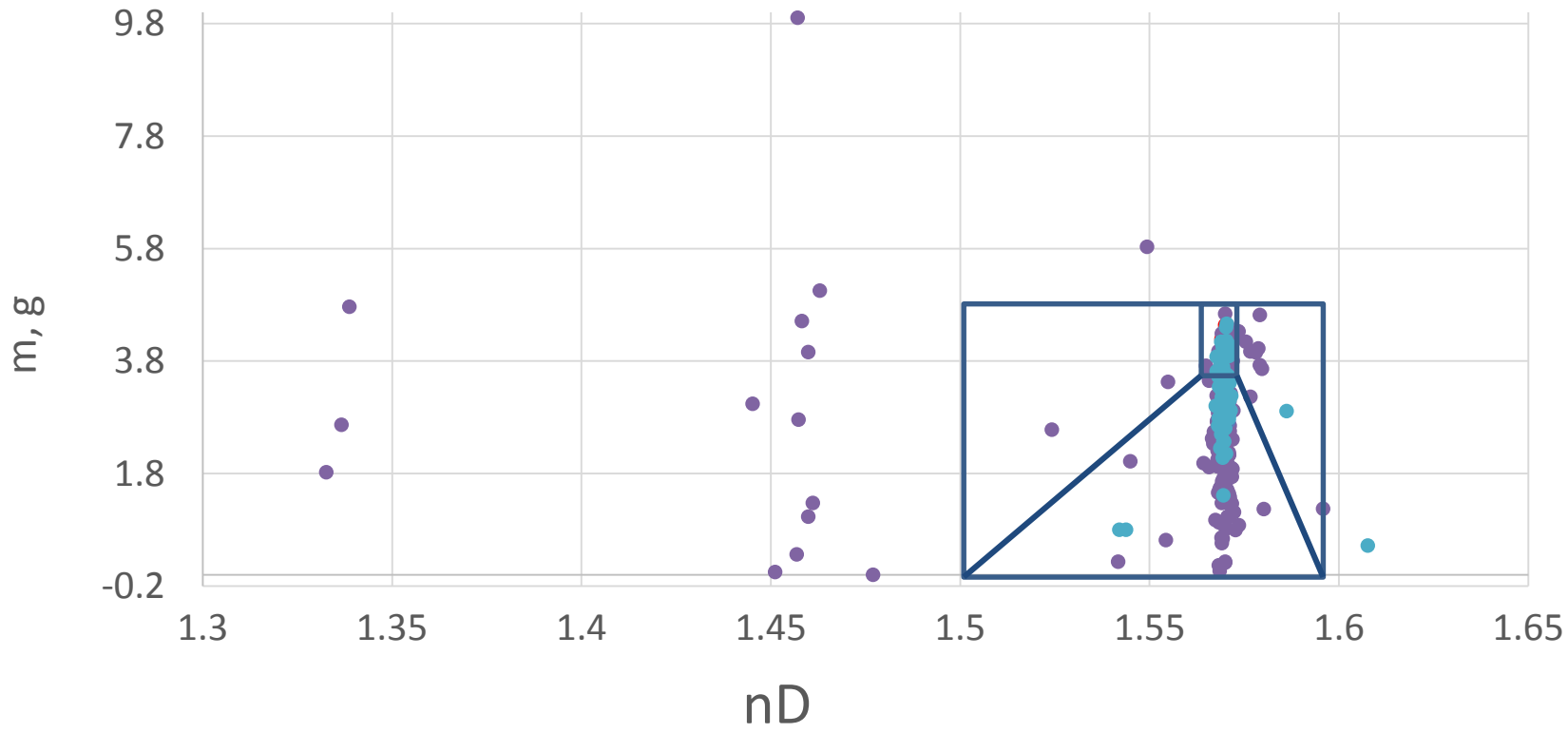
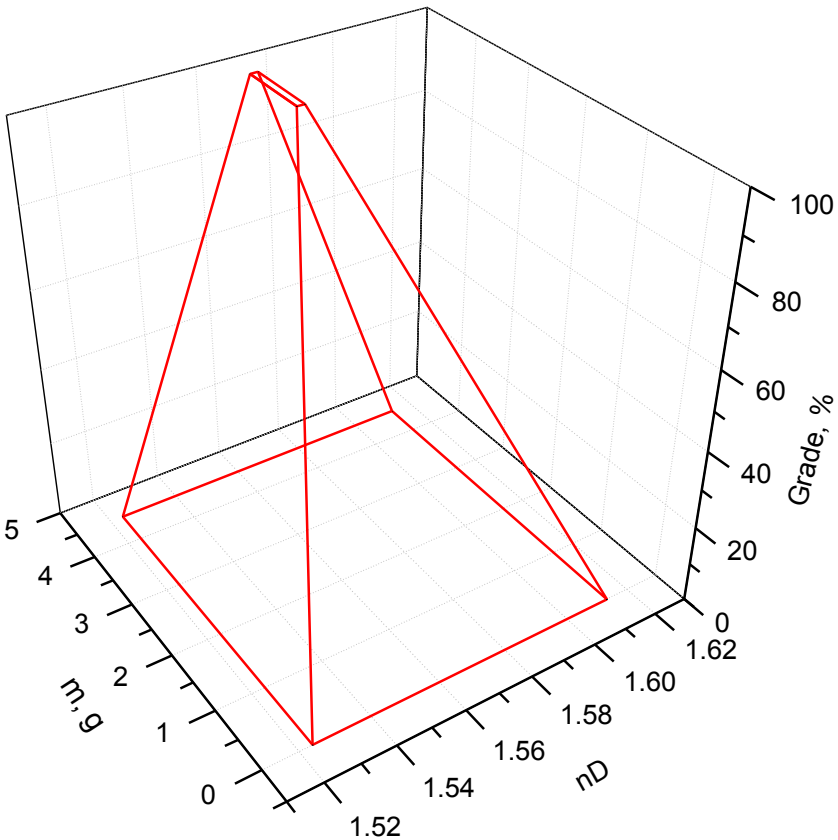
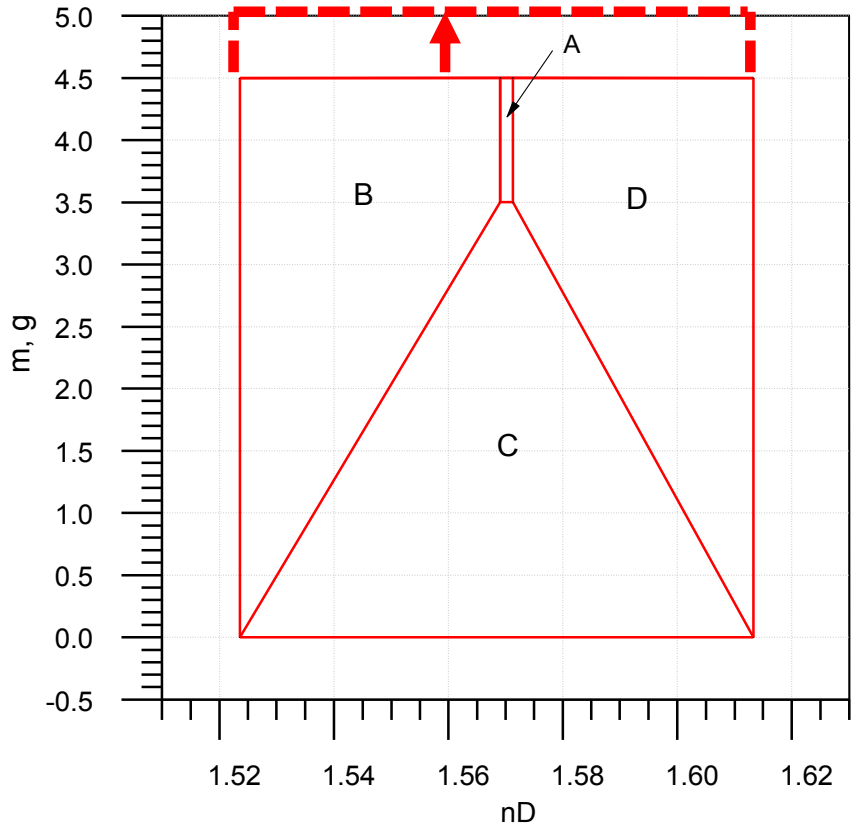


T1. Grading pyramide 1.0

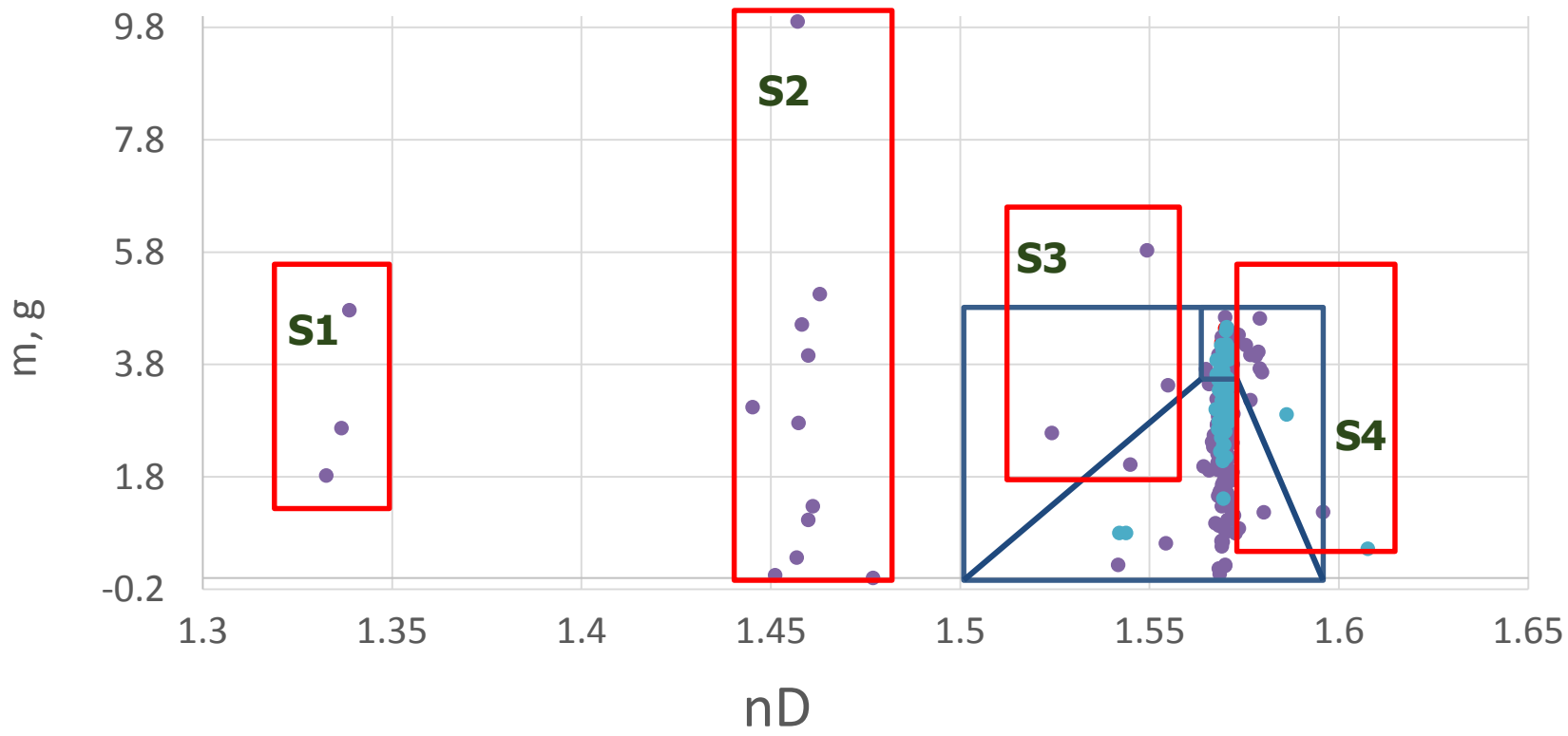




Grading pyramide final parameters							
m1	m2	m3_best	m4_best	nD1	nD2	nD3_best	nD4_best
0	**5**	**3.5**	**5**	**1.5236**	**1.6133**	**1.569**	**1.5713**

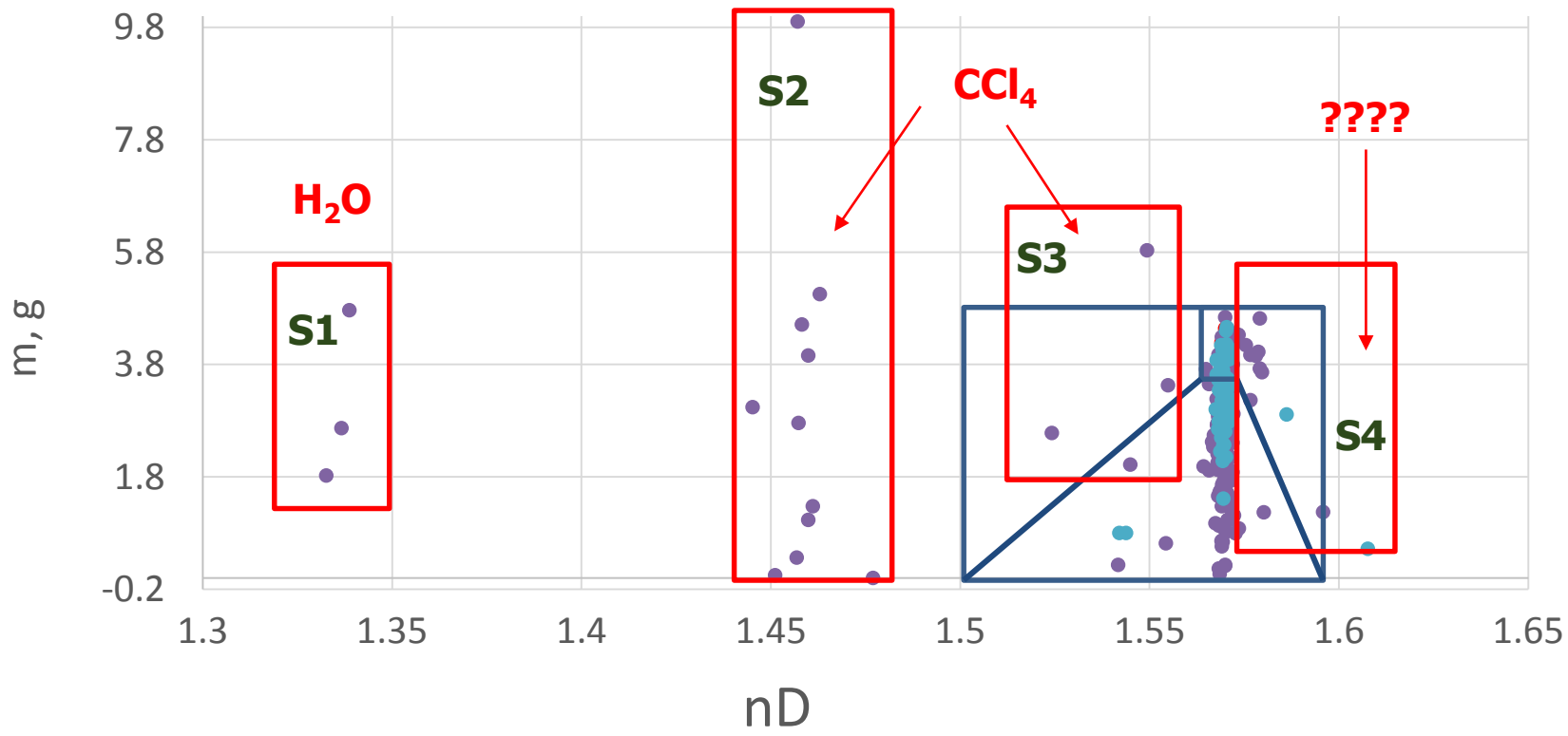
T1. Statistical results – more speculations

Highly qualified team; Test team; Model experiments
Students: 217 products was delivered to lab assistant

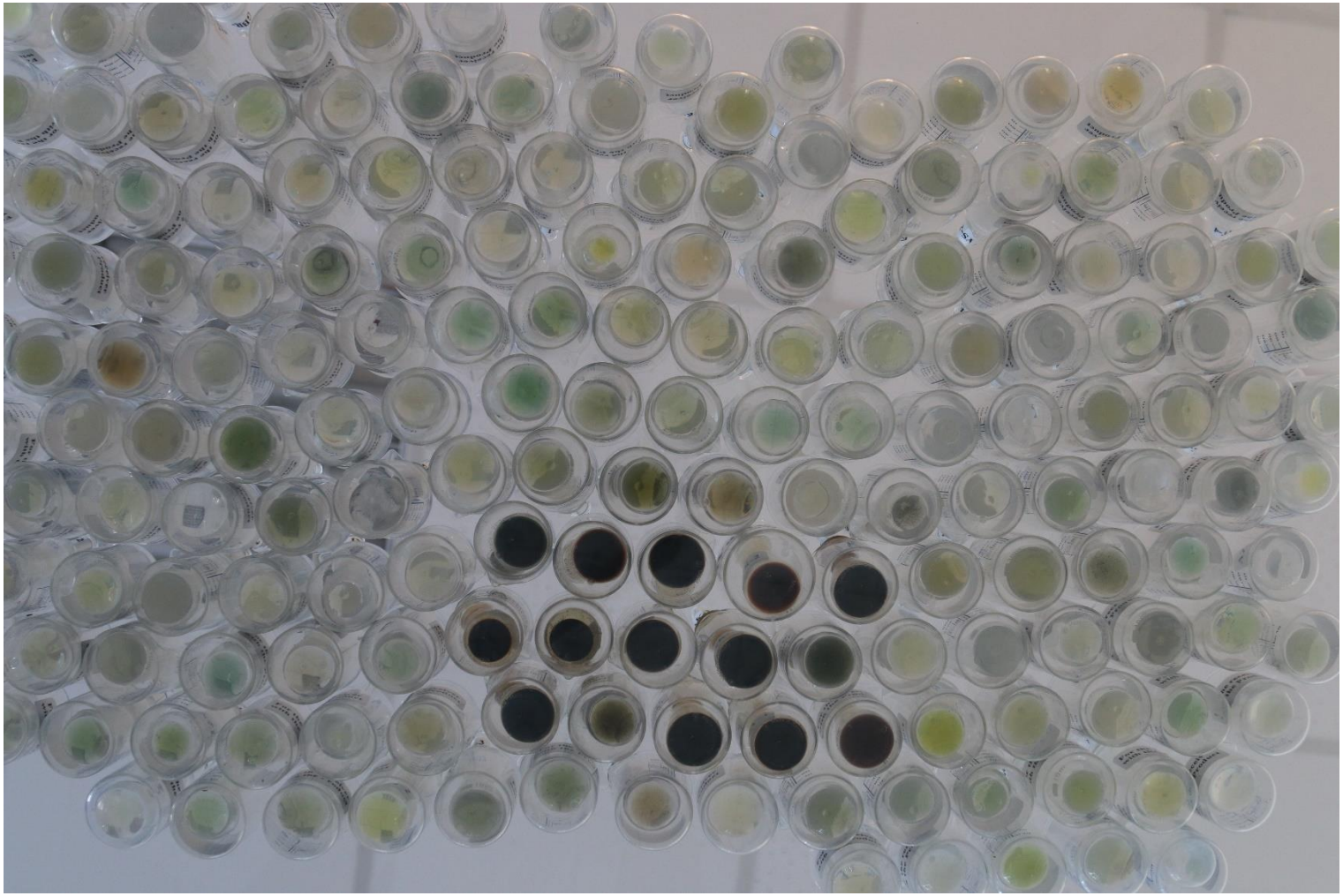


T1. Statistical results – more speculations

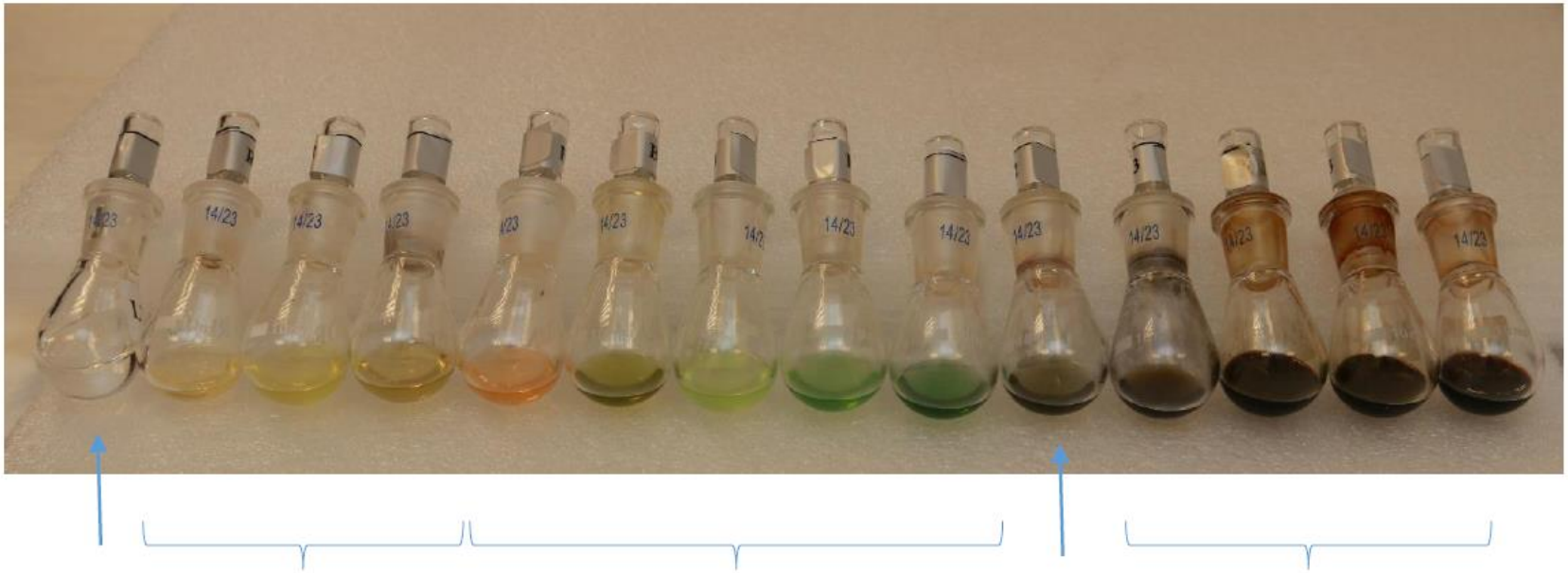
Highly qualified team; Test team; Model experiments
Students: 217 products was delivered to lab assistant



T1. Speculation zone #4

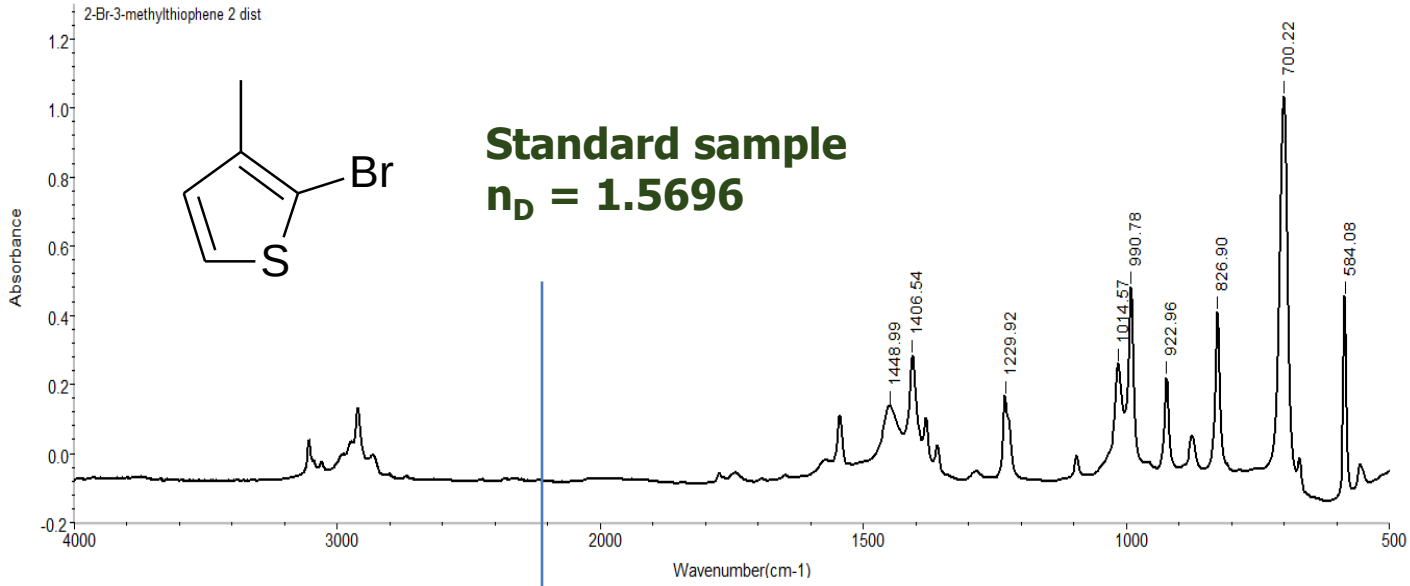


T1. Speculation zone #4

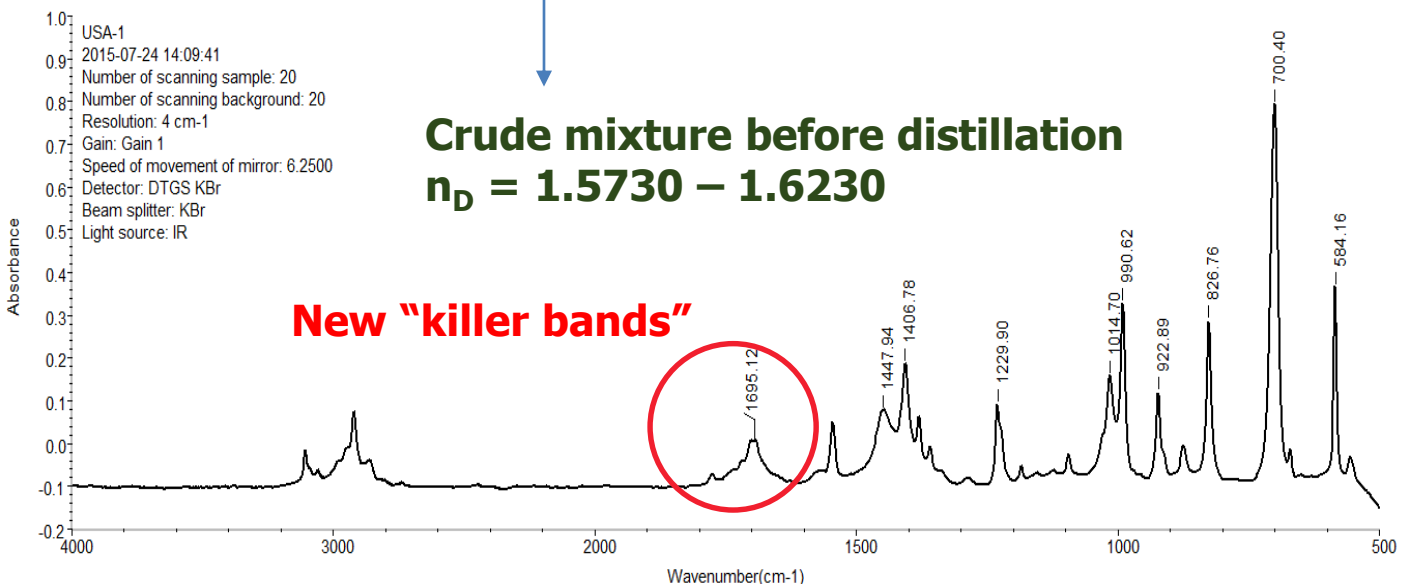


A B C D E

A – CCl_4; **B** – "master" color; **C** – slightly oxidized; D - significantly oxidized; **E** – the reaction mixture was not distilled



Standard sample
n_D = 1.5696



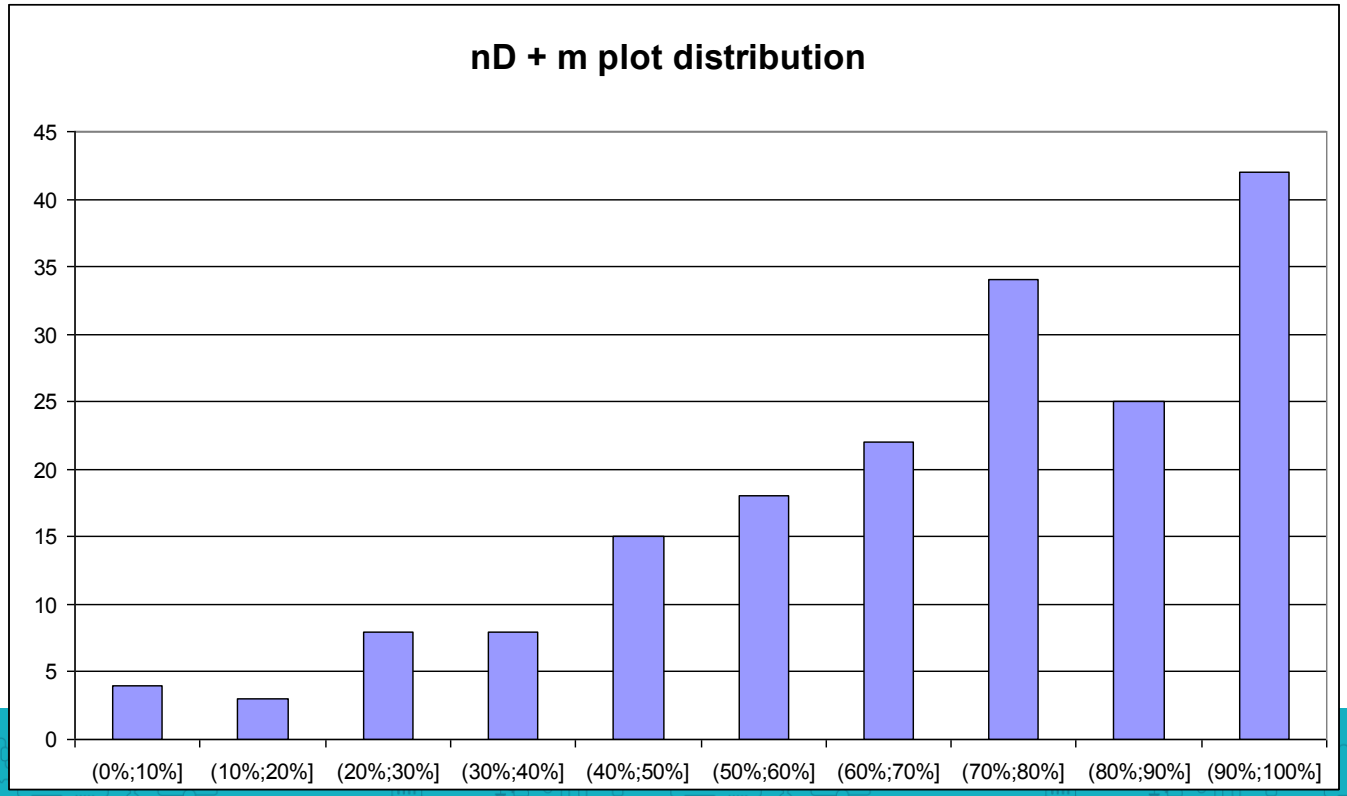
Crude mixture before distillation
n_D = 1.5730 – 1.6230

New "killer bands"

T1. Statistical results

Statistics for problem #1 by room

Room #	8	36	42	26	41	3	37	43	25	49	27	2	7	35	30	47	52	Total	count
Total count	22	18	13	18	8	10	16	9	18	32	22	10	22	18	18	14	22	290	
Product delivered, %	68,2	100,0	53,8	72,2	87,5	90,0	68,8	100,0	66,7	84,4	72,7	70,0	81,8	55,6	83,3	78,6	77,3	76,6	**222**
W. skills, %	63,6	82,4	66,7	94,4	85,7	80,0	76,9	100,0	88,2	92,6	95,5	87,5	86,4	88,2	88,2	71,4	95,2	80,3	
nD skills, %	66,7	100,0	71,4	83,3	100,0	80,0	100,0	100,0	76,9	96,0	86,7	85,7	94,4	80,0	86,7	81,8	72,2	86,1	
nD+m plot, zeroes (%)	22,7	50,0	15,4	5,6	0,0	0,0	0,0	0,0	5,6	9,4	27,3	20,0	4,5	22,2	11,1	14,3	22,7	14,8	**43**
nD+m plot, average	13,9	9,2	11,1	14,0	20,3	21,1	20,9	21,1	19,3	19,4	15,9	15,8	21,4	15,3	17,4	13,8	15,7	16,8	
nD+m plot, max	29,6	28,6	26,7	29,5	30,0	30,0	25,6	30,0	30,0	30,0	30,0	28,7	29,5	30,0	28,5	26,1	30,0	30,0	



Task 2

Analysis of a chromium – vanadium solution

T2. Antiferromagnetic materials

Test solution imitates the product of digestion of vanadium – chromium alloy sample

T2. Experimental plan

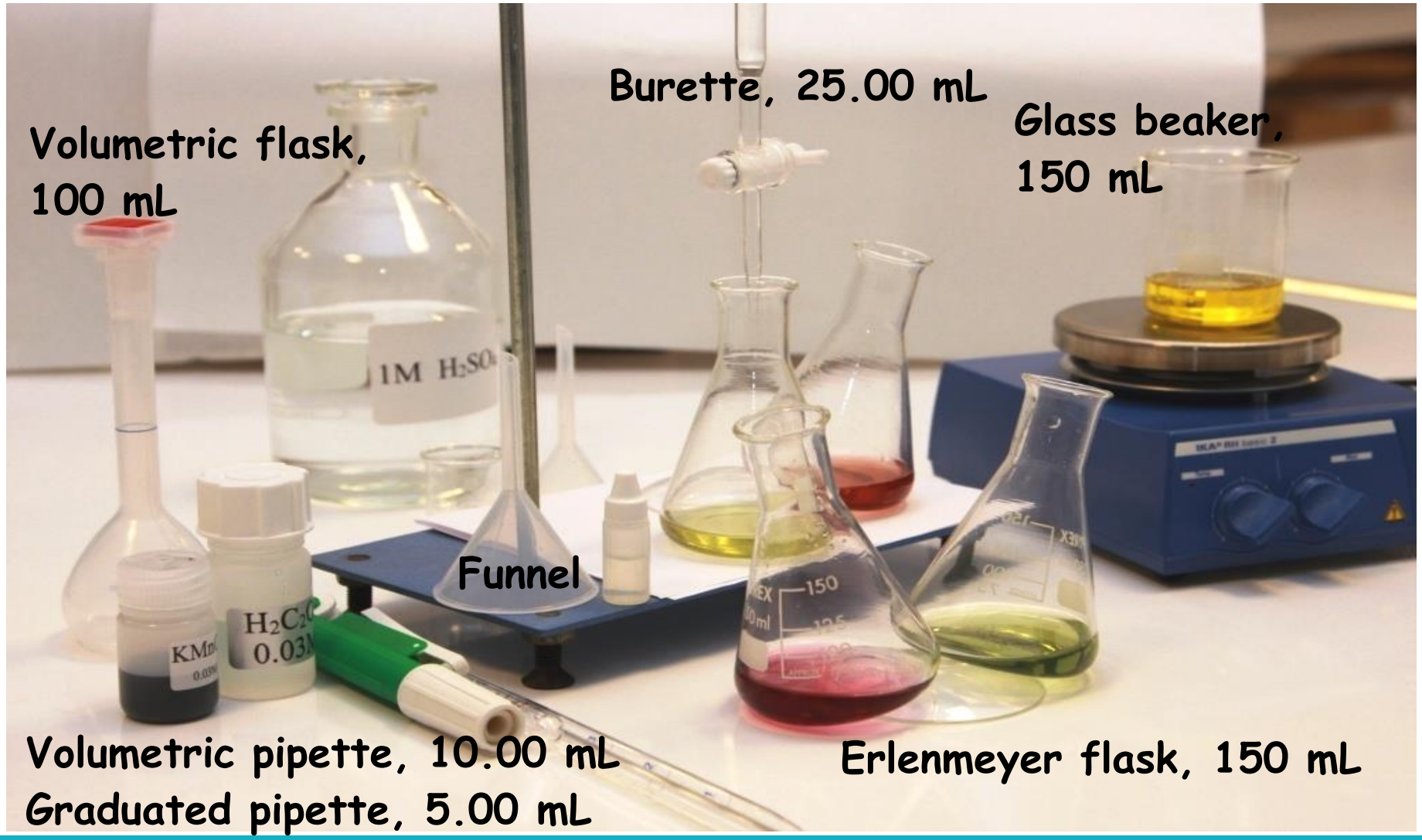
PART A.
Oxidation of an aliquot of the test solution with ammonium persulfate

PART B.
Titrimetric determination of standalone vanadium in test solution with prior conversion of vanadyl to vanadate
V^{4+}

PART C.
Titrimetric determination of the total content of vanadium and chromium in the oxidized test solution
$\Sigma\ (Cr^{3+}+V^{4+})$

Chromium and vanadium to be calculated in mg per 100 mL of the test solution.

T2. Equipment



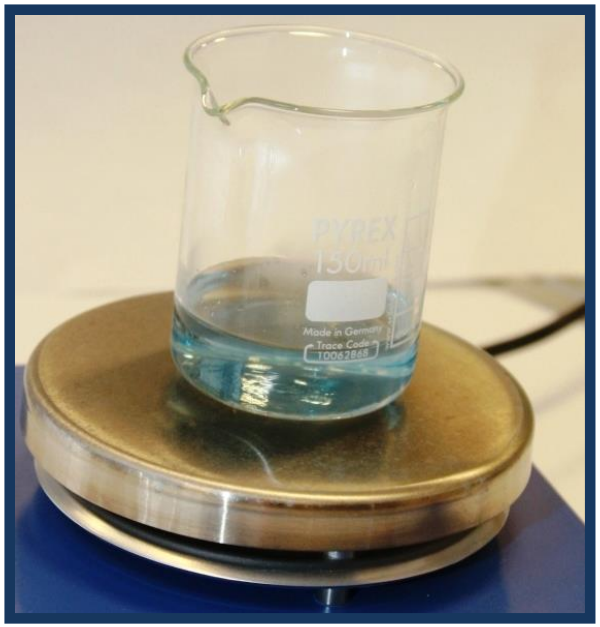
T2. Preparation section

(Part A)

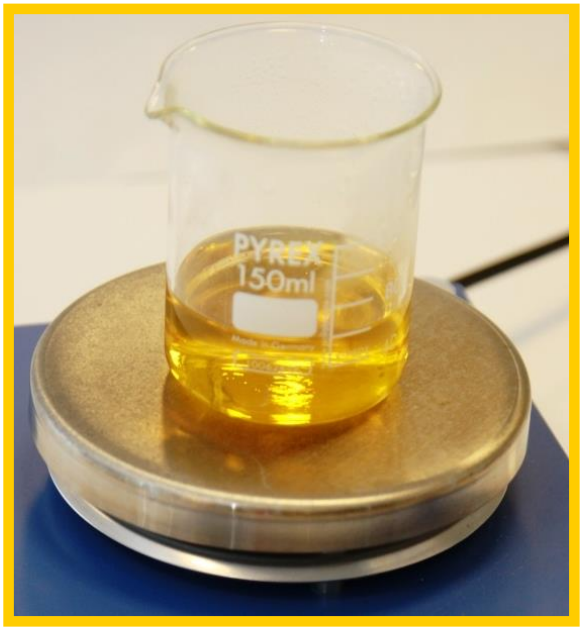
Oxidation of the test solution (catalyst: 0.3% $AgNO_3$ solution)

$$2Cr^{3+} \xrightarrow{(NH_4)_2S_2O_8,\ t^\circ C} Cr_2O_7^{2-}$$

$$VO^{2+} \xrightarrow{(NH_4)_2S_2O_8,\ t^\circ C} VO_3^{-}$$



$$\xrightarrow{(NH_4)_2S_2O_8,\ t^\circ C}$$



T2. Titration section

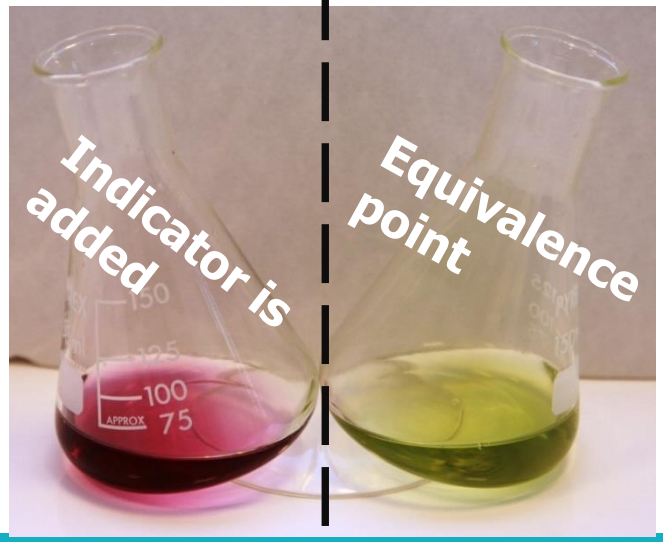
Starting solution:

$$VO^{2+} \xrightarrow{KMnO_4} VO_3^-$$

PART B.

$$VO_3^- \xrightarrow{Fe^{2+},\ H^+} VO^{2+}$$

Titrant : Mohr's salt solution ($(NH_4)_2Fe(SO_4)_2$)

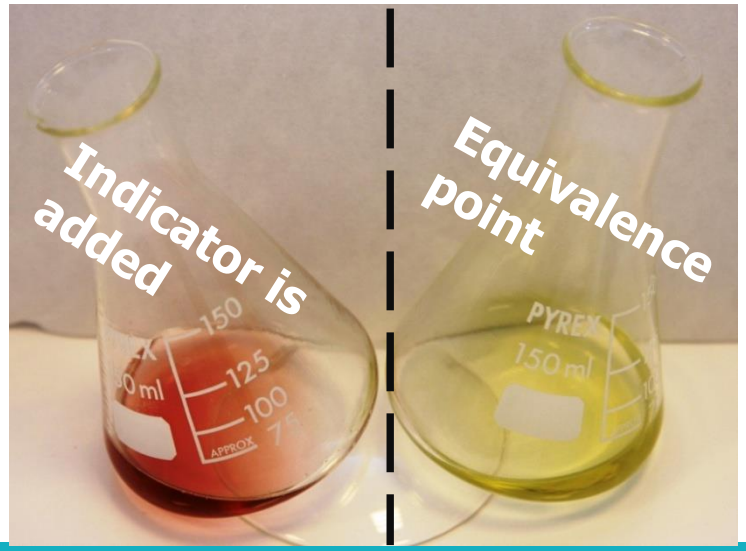


PART C.

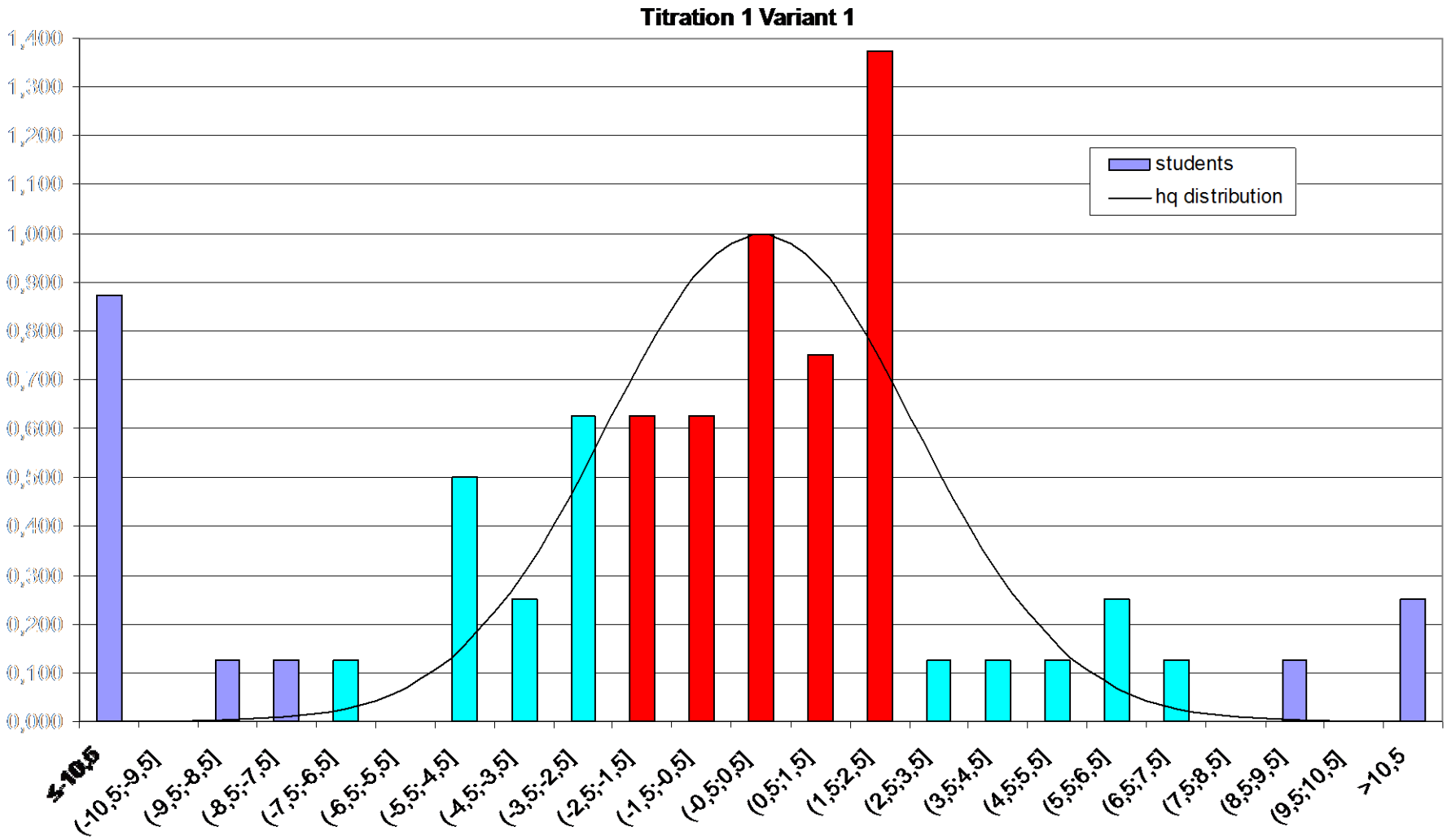
Oxidized solution (with ammonium persulfate in PART A):

$$VO_3^- \xrightarrow{Fe^{2+},\ H^+} VO^{2+}$$

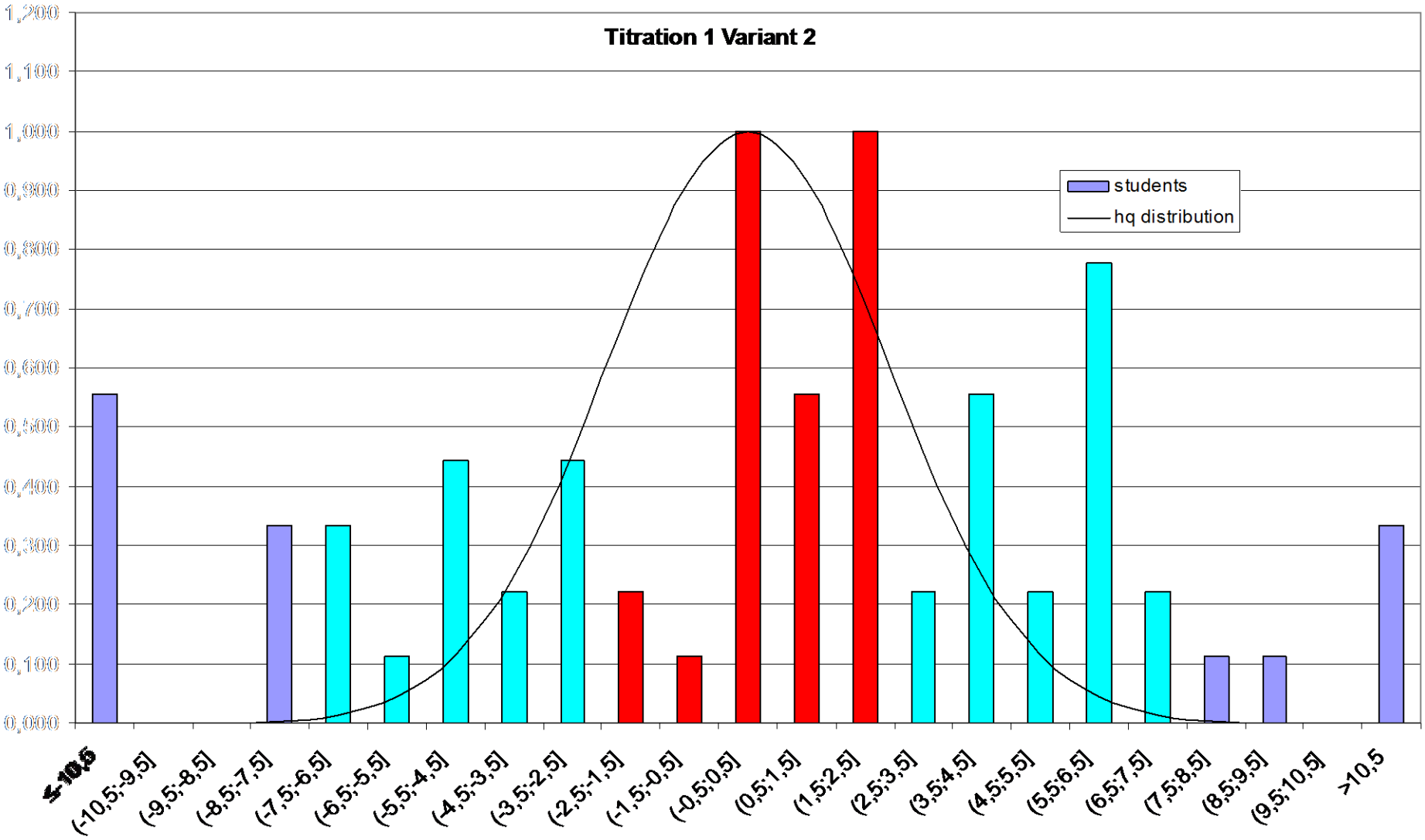
$$Cr_2O_7^{2-} \xrightarrow{Fe^{2+},\ H^+} 2Cr^{3+}$$



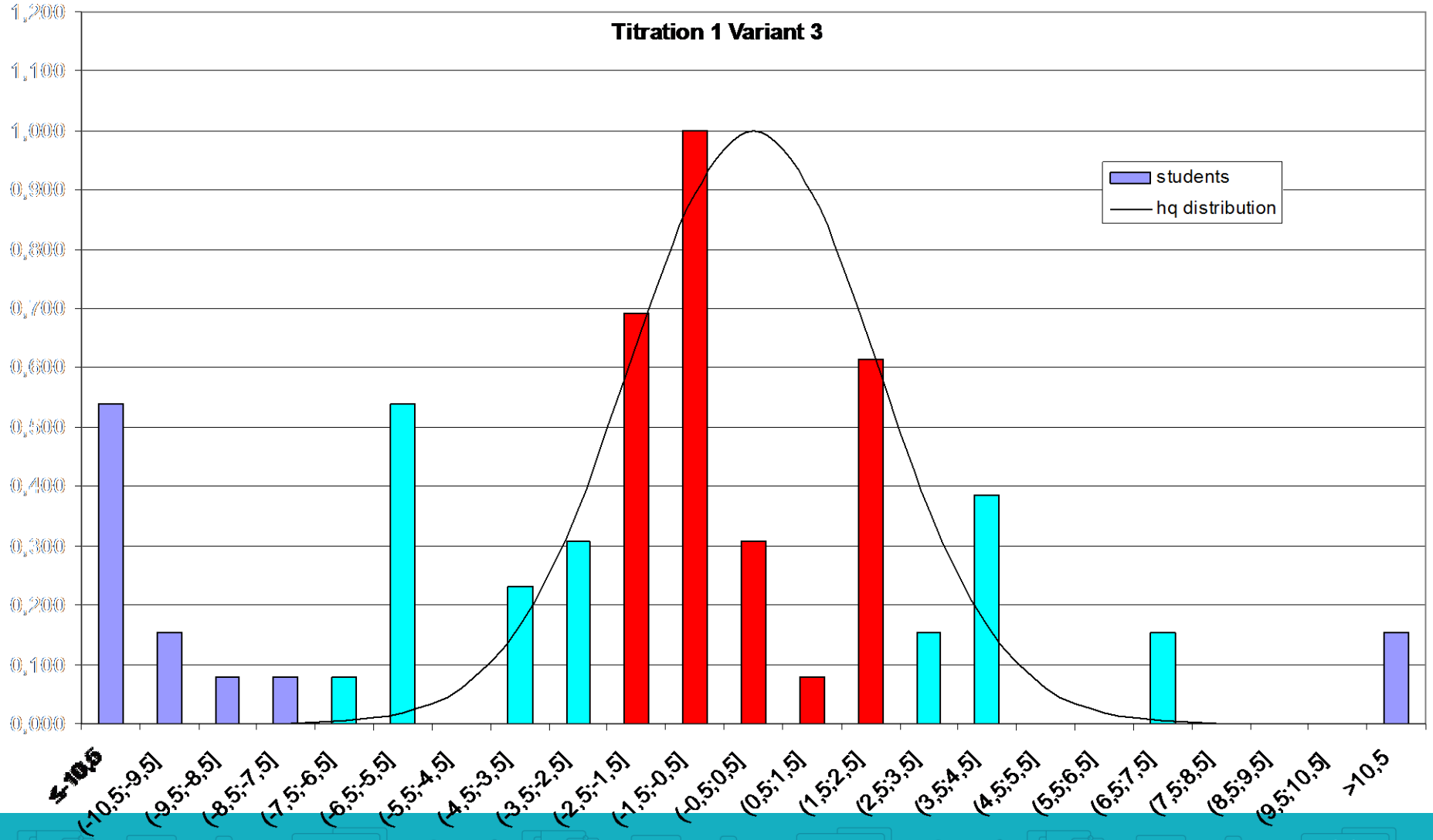
T2. Statistical results
Titration 1 Variant 1



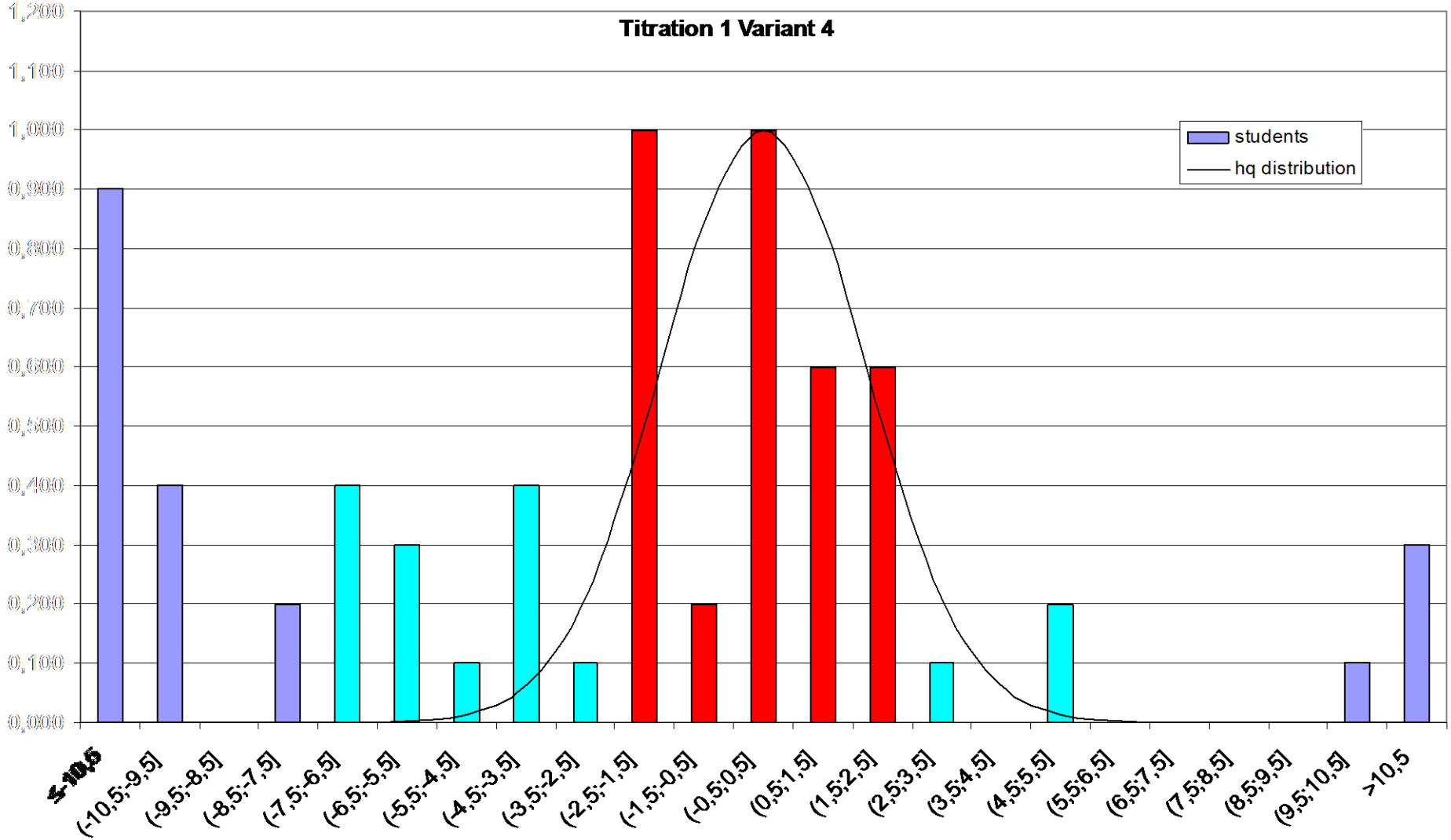
T2. Statistical results
Titration 1 Variant 2



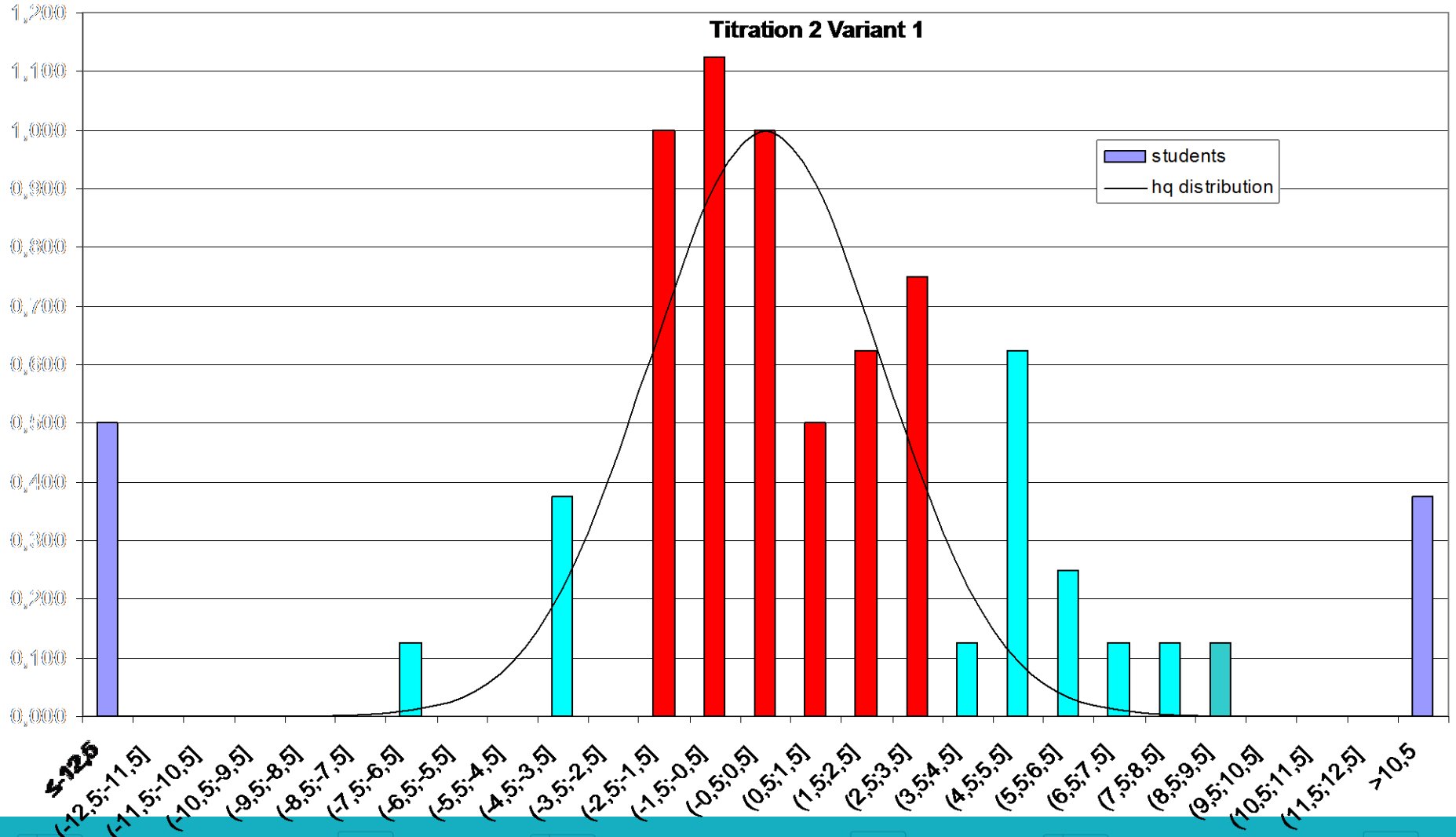
T2. Statistical results
Titration 1 Variant 3



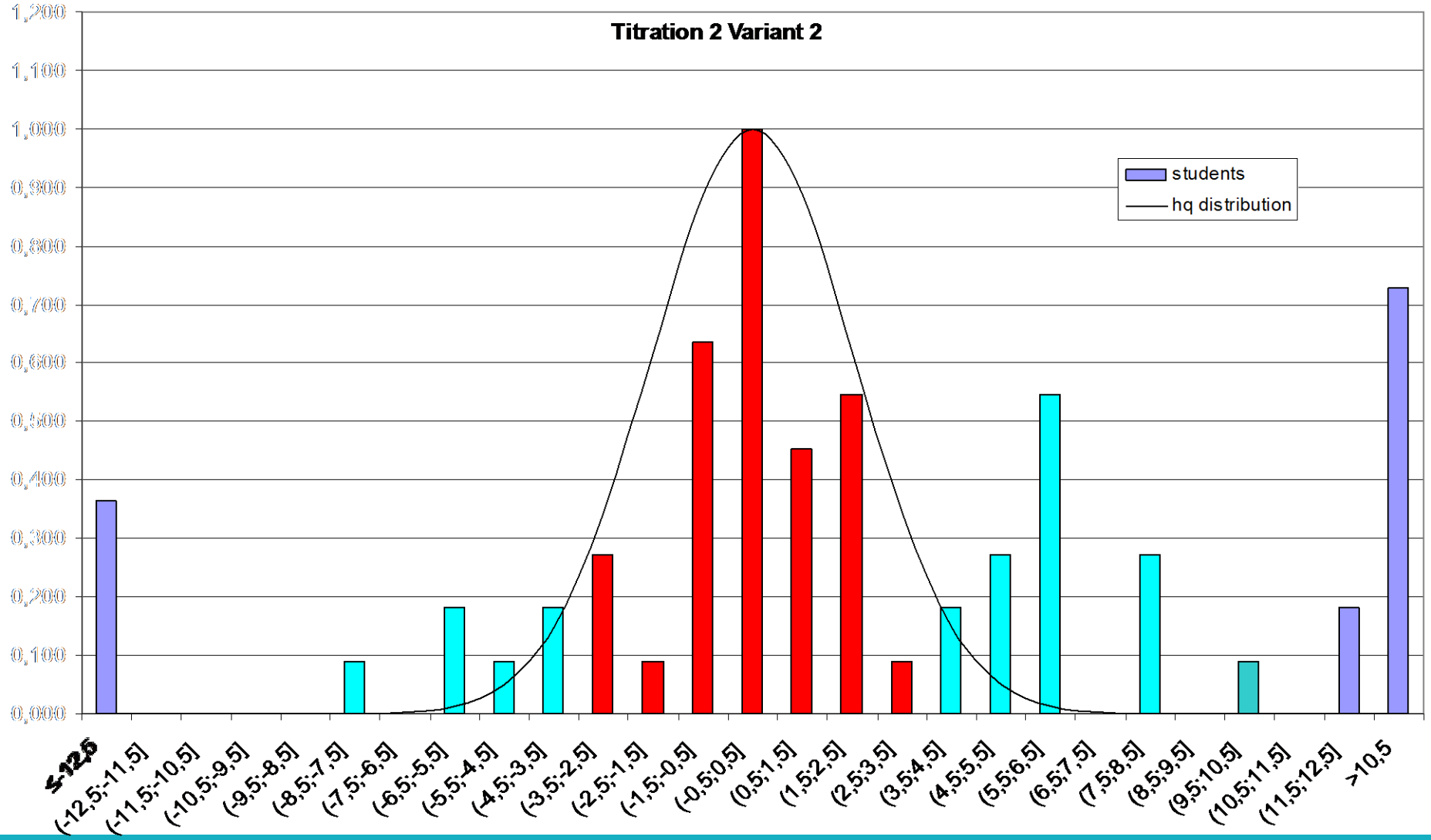
T2. Statistical results
Titration 1 Variant 4



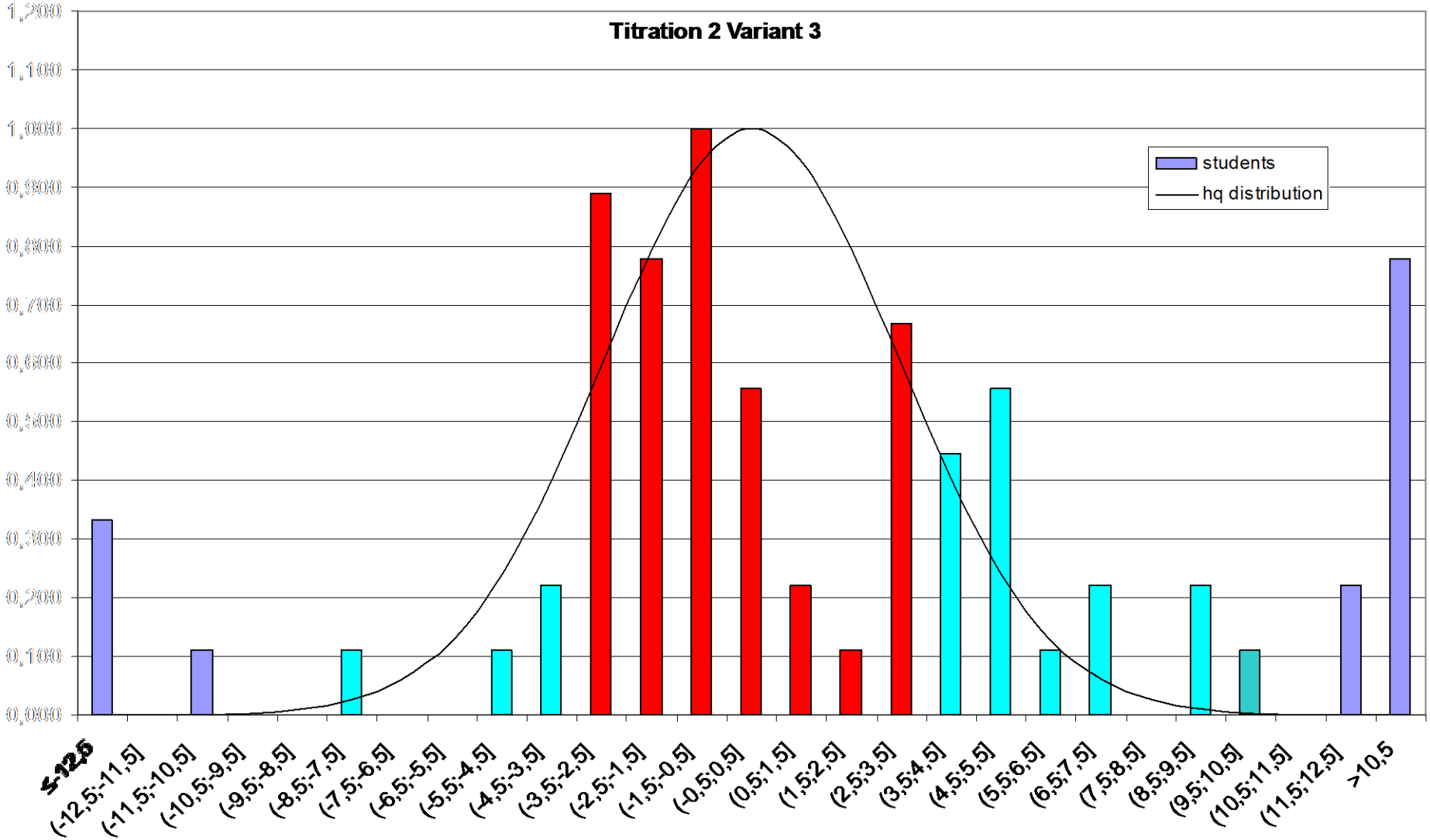
T2. Statistical results
Titration 2 Variant 1



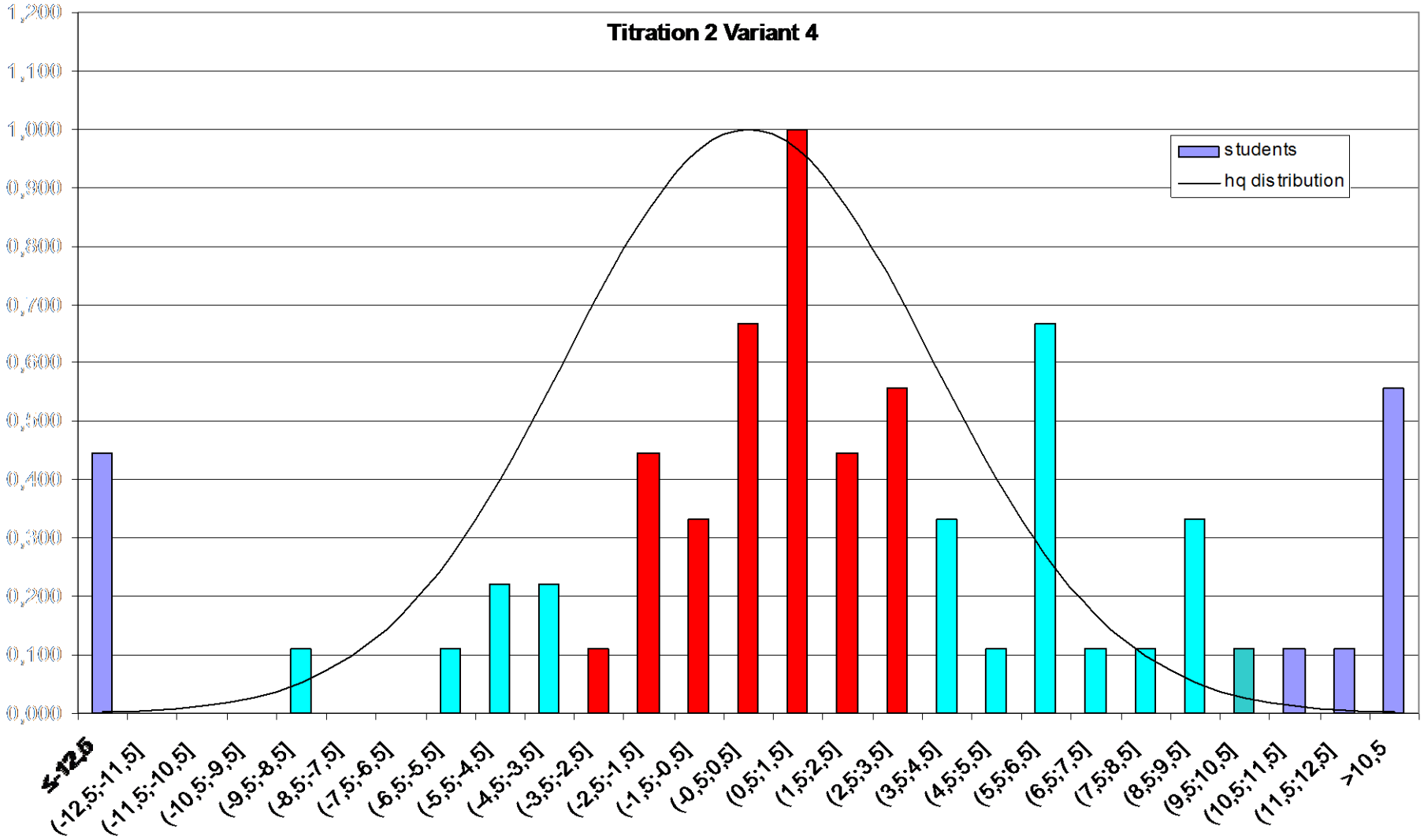
T2. Statistical results
Titration 2 Variant 2



T2. Statistical results
Titration 2 Variant 3



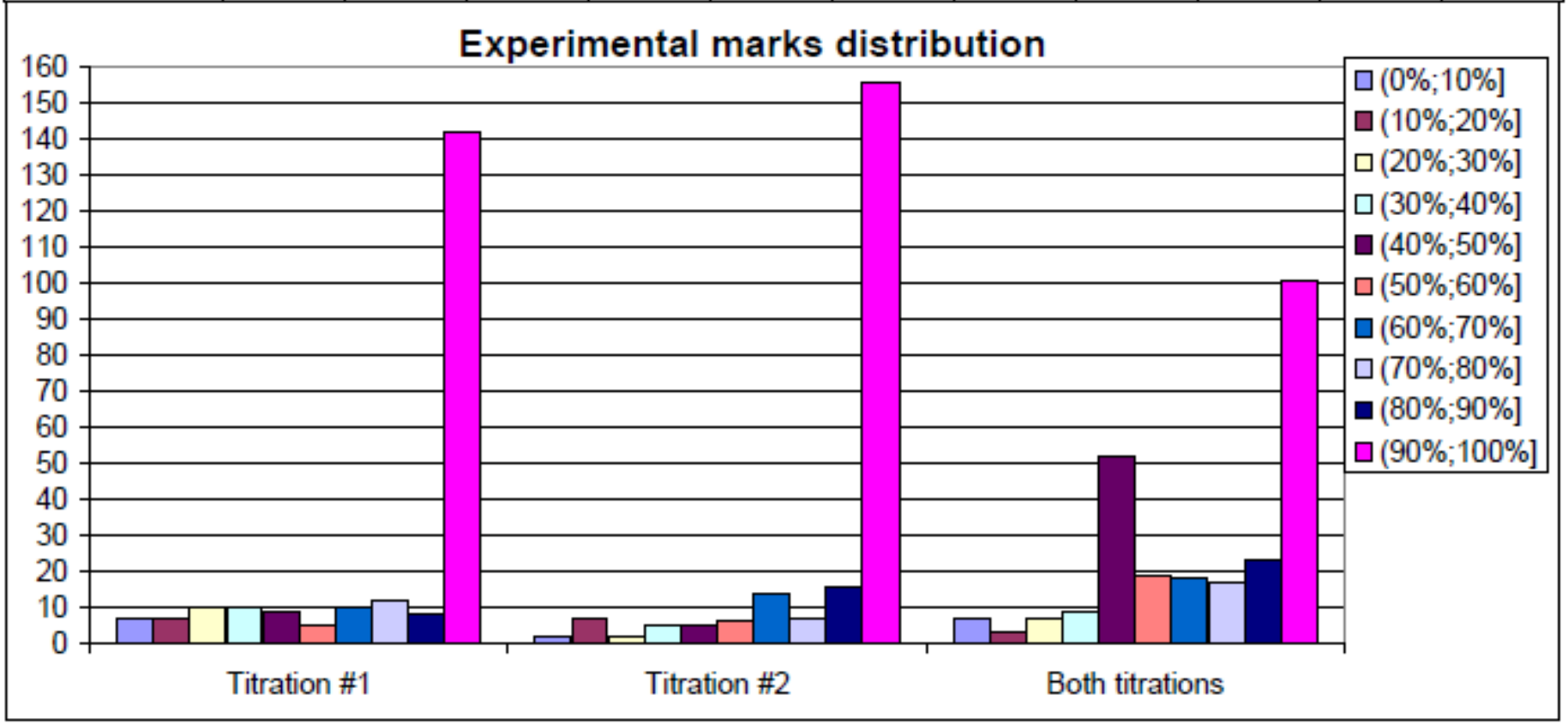
T2. Statistical results
Titration 2 Variant 4



T2. Statistical results

Statistical data for experimental part of problem #2

Variant	Titration #1					Titration #2					Both titrations
	V1	V2	V3	V4	Total	V1	V2	V3	V4	Total	
Count	72	73	74	71	290	72	73	74	71	290	290
Non-zero	53	58	59	50	220	55	55	56	54	220	256
Full mark	35	26	35	34	130	40	33	38	32	143	80
Zero mark	19	15	15	21	70	17	18	18	17	70	34
Average (excl. 0's)	27,7	23,3	26,4	26,5	25,9	29,2	27,3	28,8	26,5	27,9	46,3



T3. Statistical data

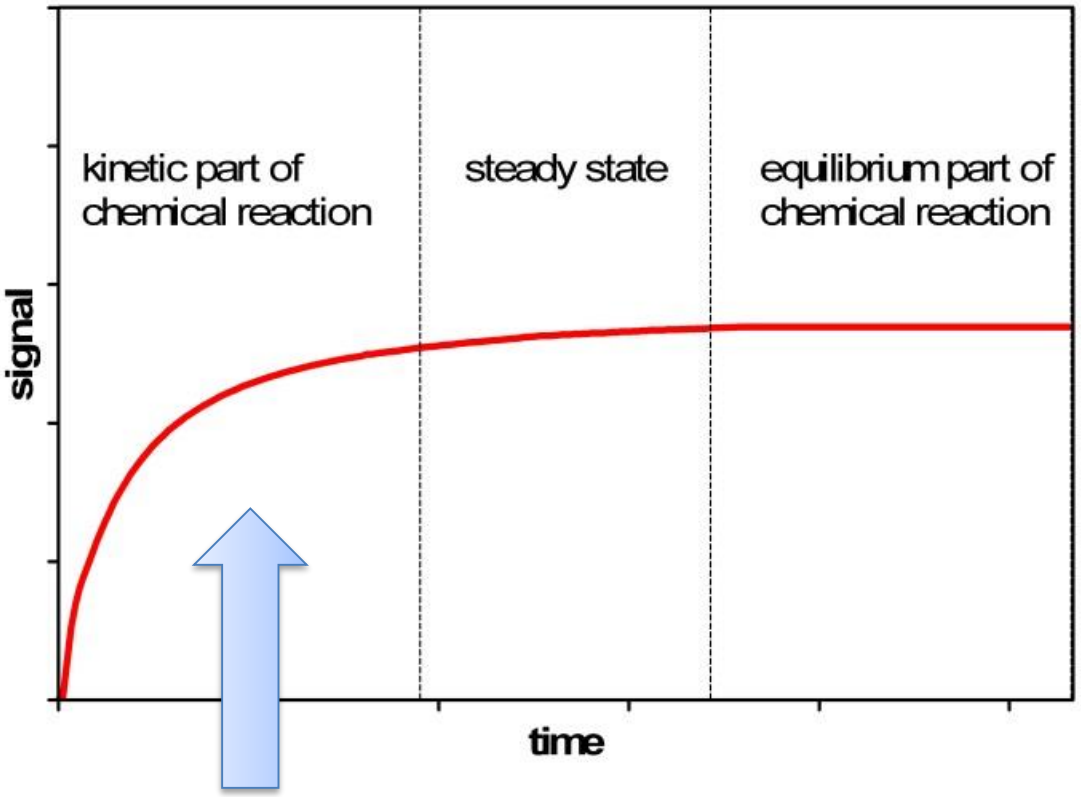
Kinetic determination of Diclofenac (DCF)

Total amount of participants – 290

Amount of memory sticks with <u>any</u> data (.txt, .xlsx) saved – 220

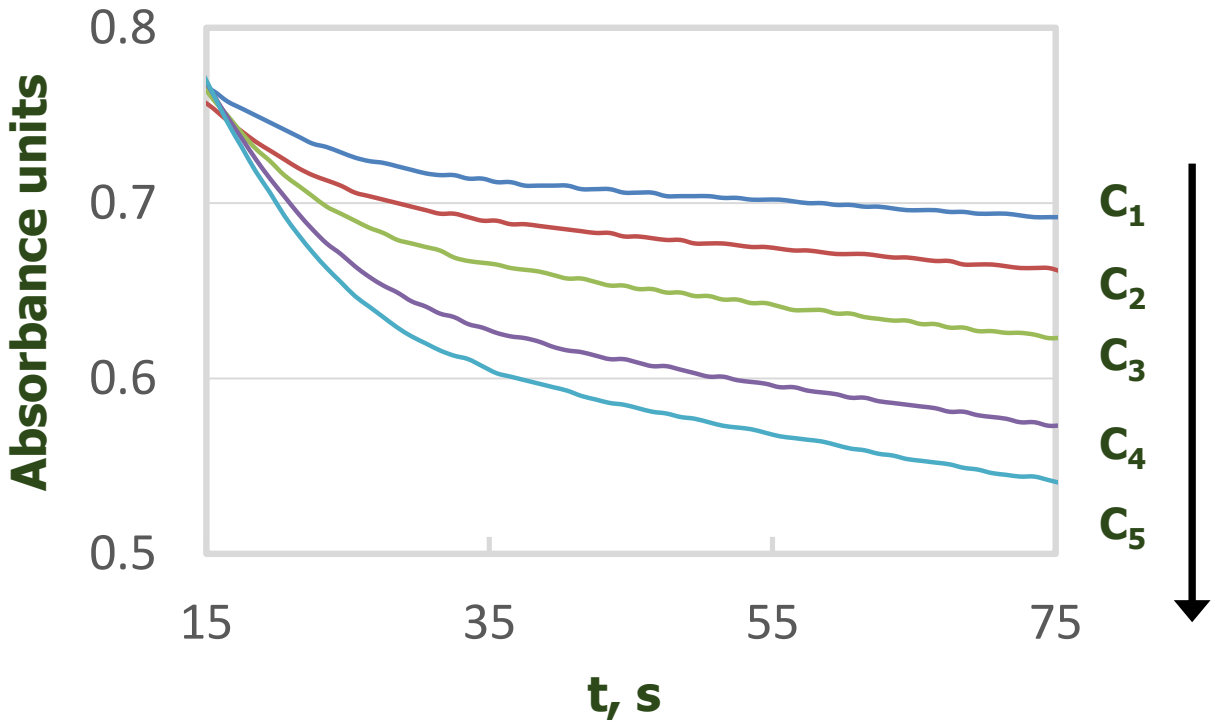
T3. General idea

T3. General idea



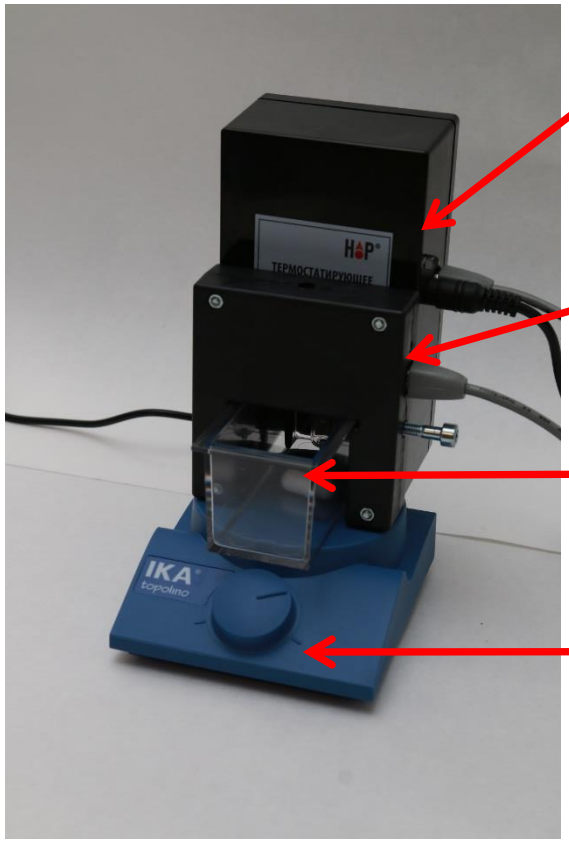
Experimental check-in of the methodology

T3. General idea



Increase of analyte concentration

T3. Equipment

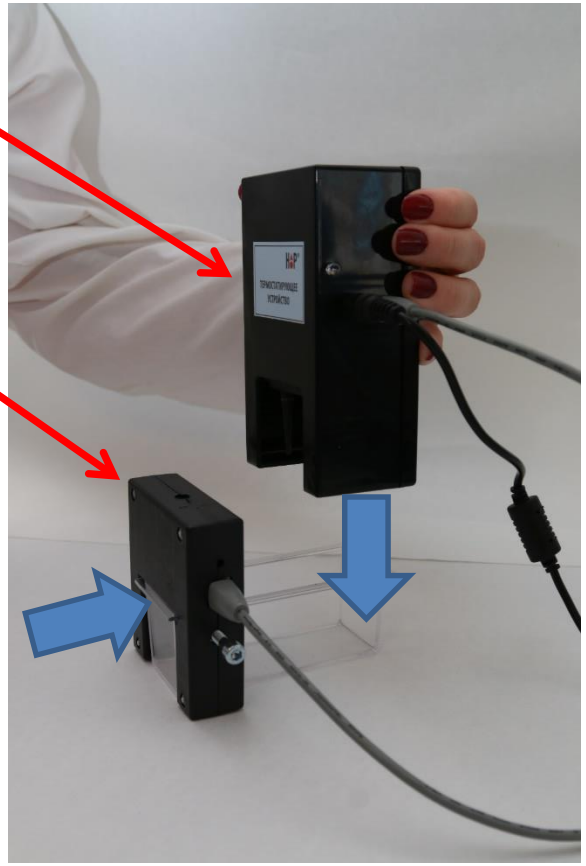


Thermostat (to be set at 30 °C)

Photometer 525 nm

Cuvette with a stir-bar

Magnetic stirrer

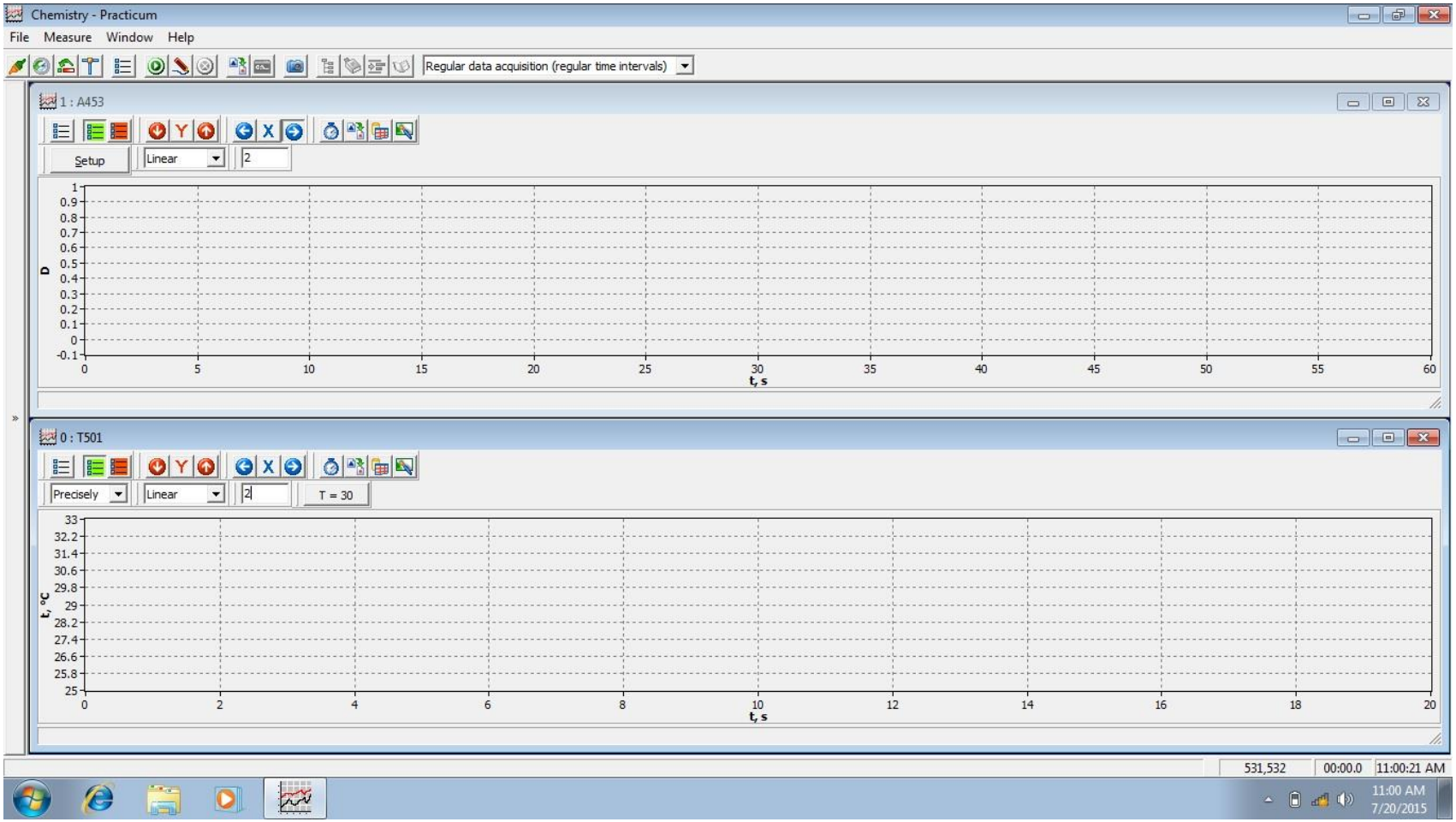


Thermostat allows avoiding of minor differences of room temperature during the practical examination. Test group fixed the maximum deviation of the temperature ± 0.2 °C.

T3. Software

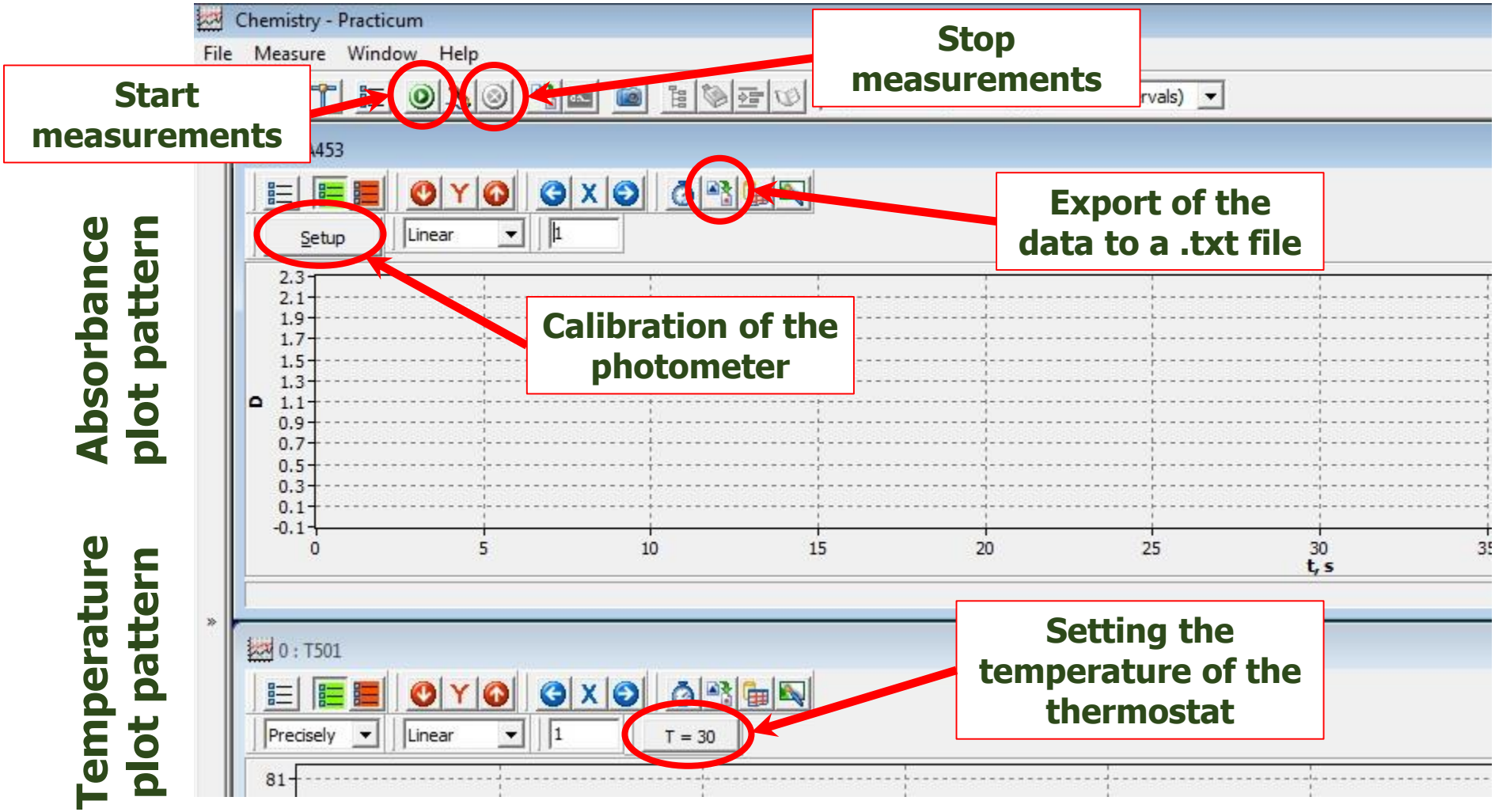
Absorbance plot pattern

Temperature plot pattern



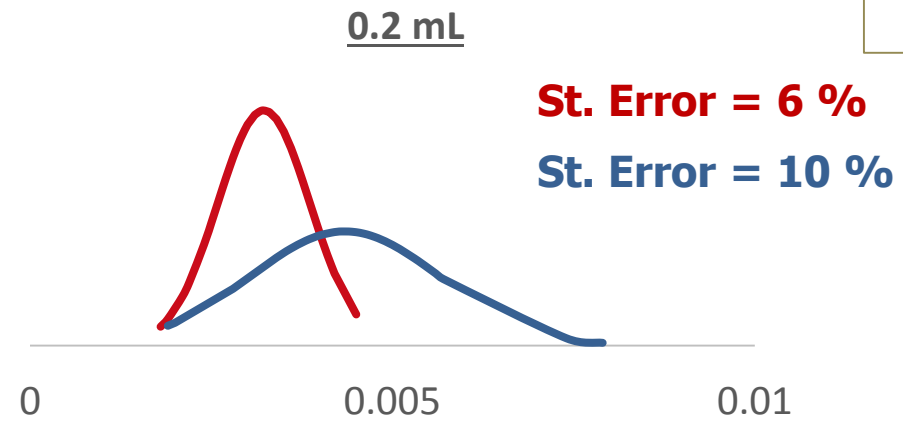
“Chemistry-Practicum” software window

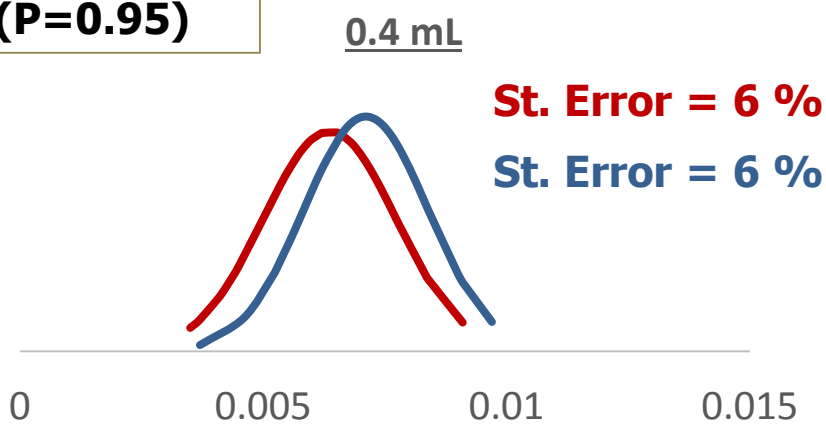
T3. Software

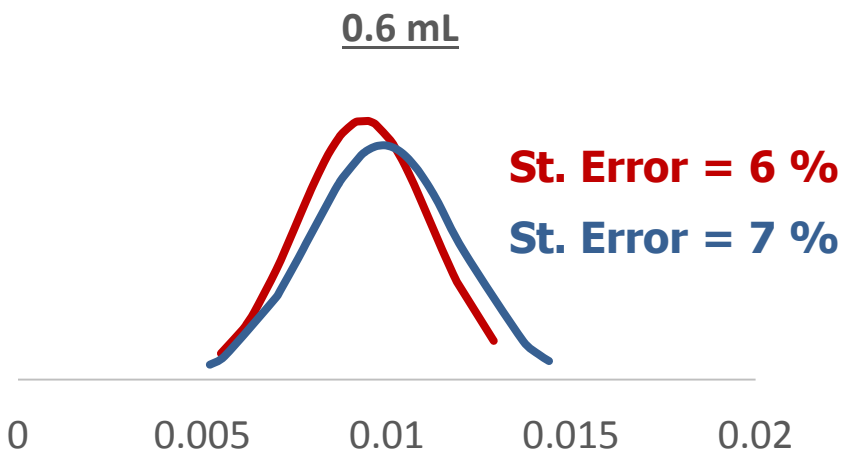

Chemistry - Practicum
File
Measure
Window
Help
Start measurements
Stop measurements
Export of the data to a .txt file
Calibration of the photometer
Setting the temperature of the thermostat
Absorbance plot pattern
Temperature plot pattern
Setup
Linear
D
t, s
0 : T501
Precisely
T = 30

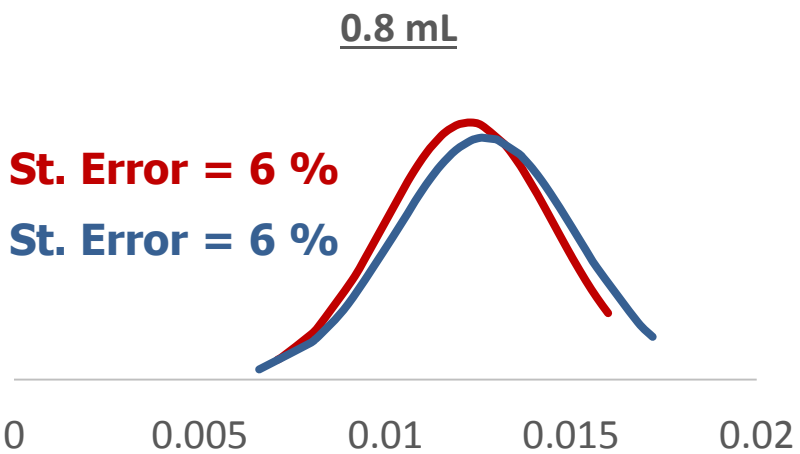
T3. Statistical data – Estimation of initial rates

t_x (P=0.95)









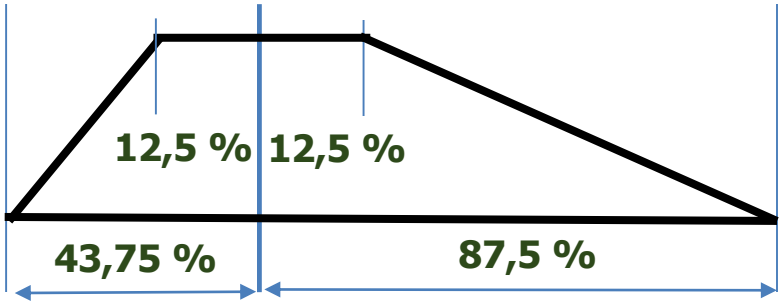
Highly qualified team
45 experiments

Test team
39 experiments, 1 failed

T3. Grading of initial rates

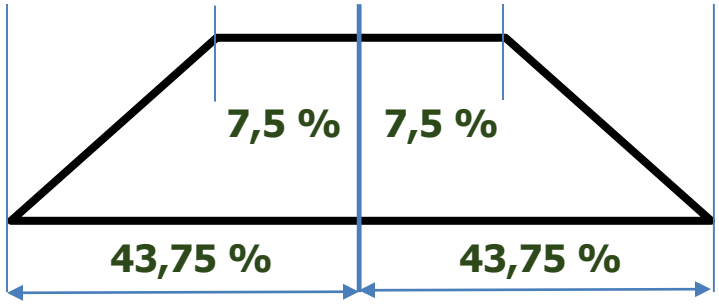
0.2 mL

Master value



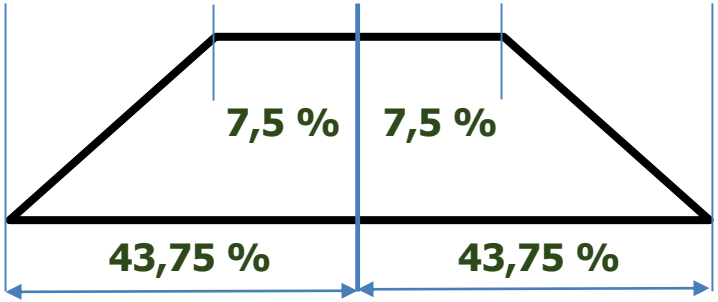
0.4 mL

Master value



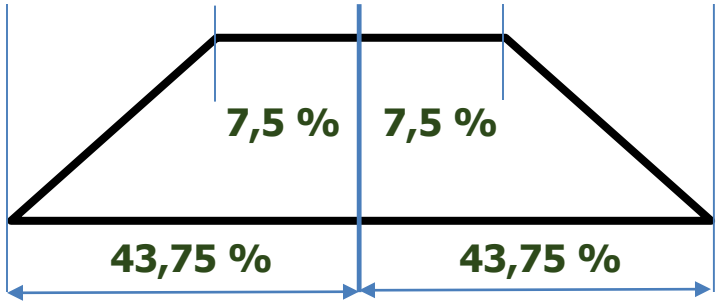
0.6 mL

Master value

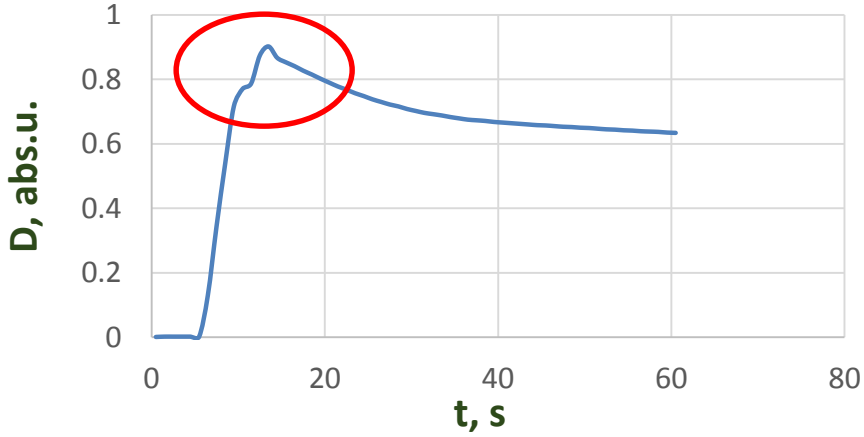


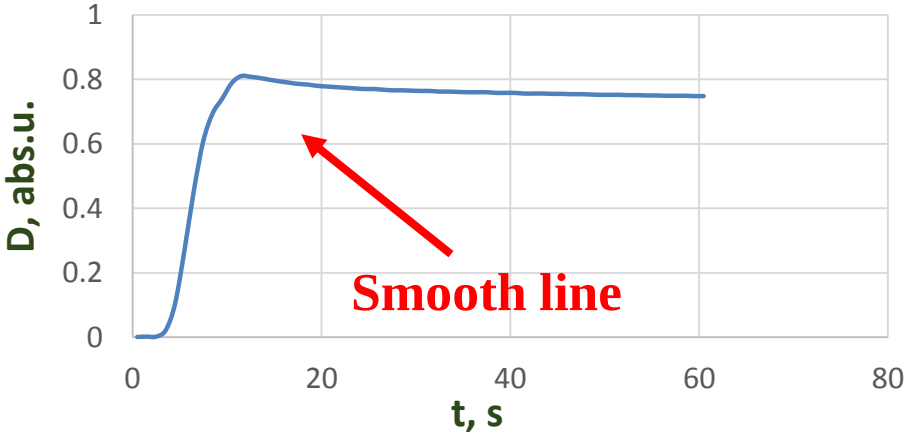
0.8 mL

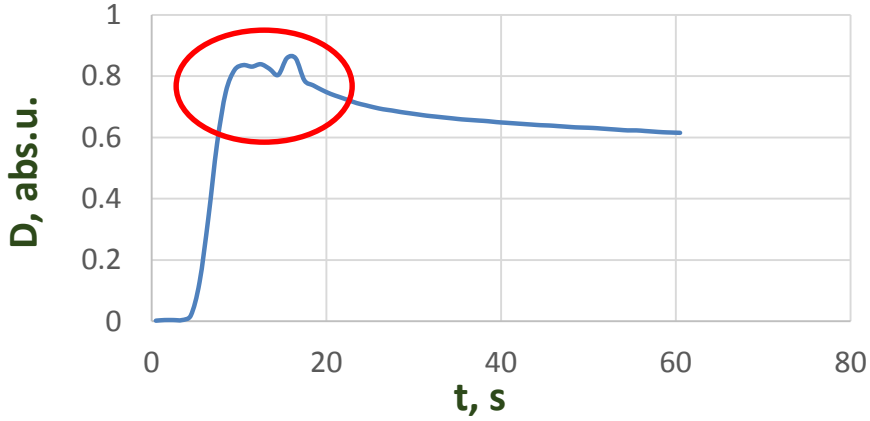
Master value



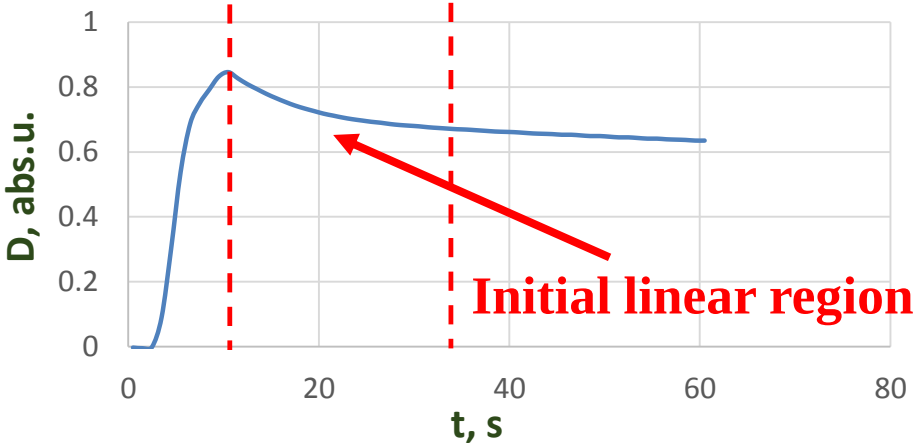
T3. Typical experimental curves





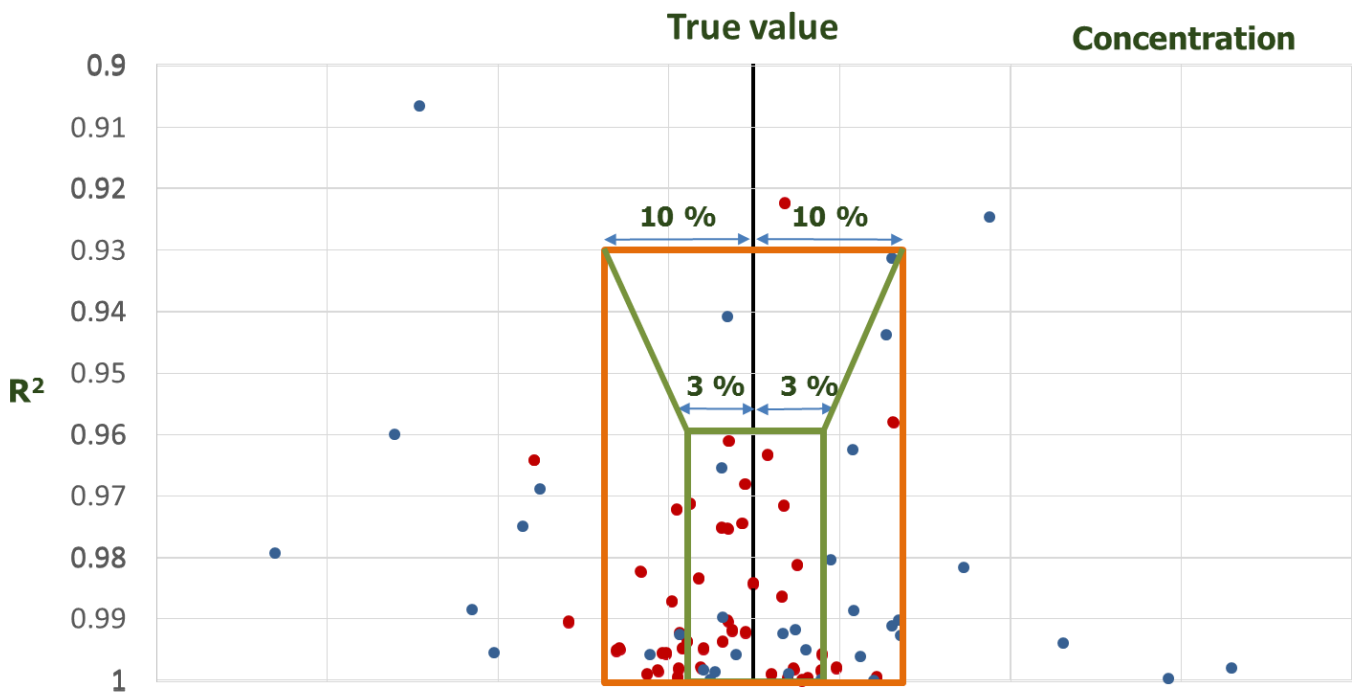


Inaccurate measurements



Accurate measurements

T3. Grading of concentration

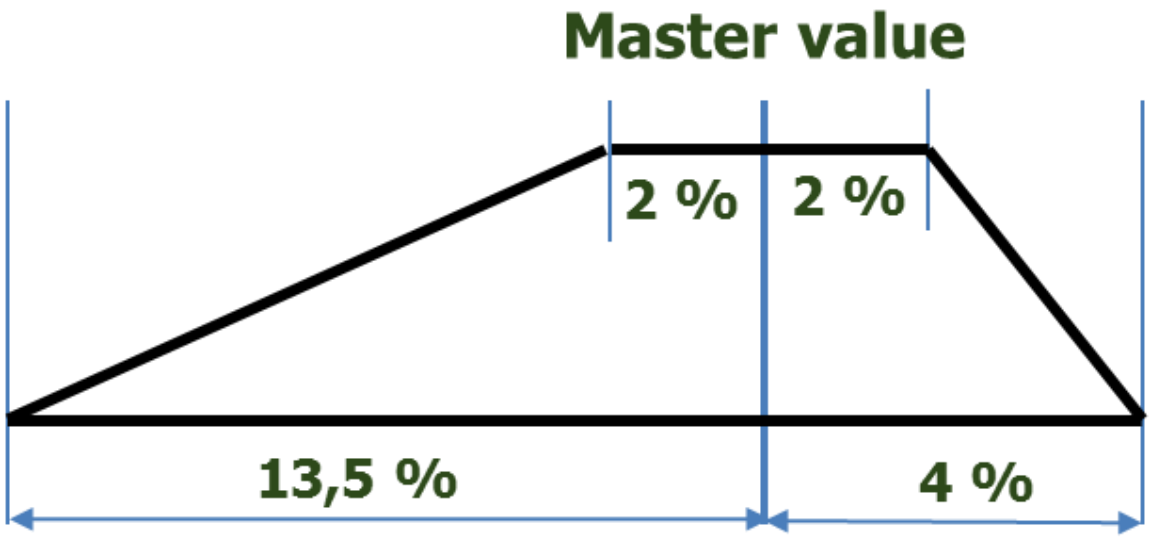


The grading scheme takes into account two values re-measured by the Science Committee: R-squared value (R^2) and obtained concentration of the control solution (Conc).

- If the value obtained is within region A, 100% of 12 marks
- If the value obtained is within region B, 0.1926*Conc-154.2857 (%) of 12 marks
- If the value obtained is within region C, 400*R^2-372 (%) of 12 marks
- If the value obtained is within region D, -0.1926*Conc+188.5714 (%) of 12 marks

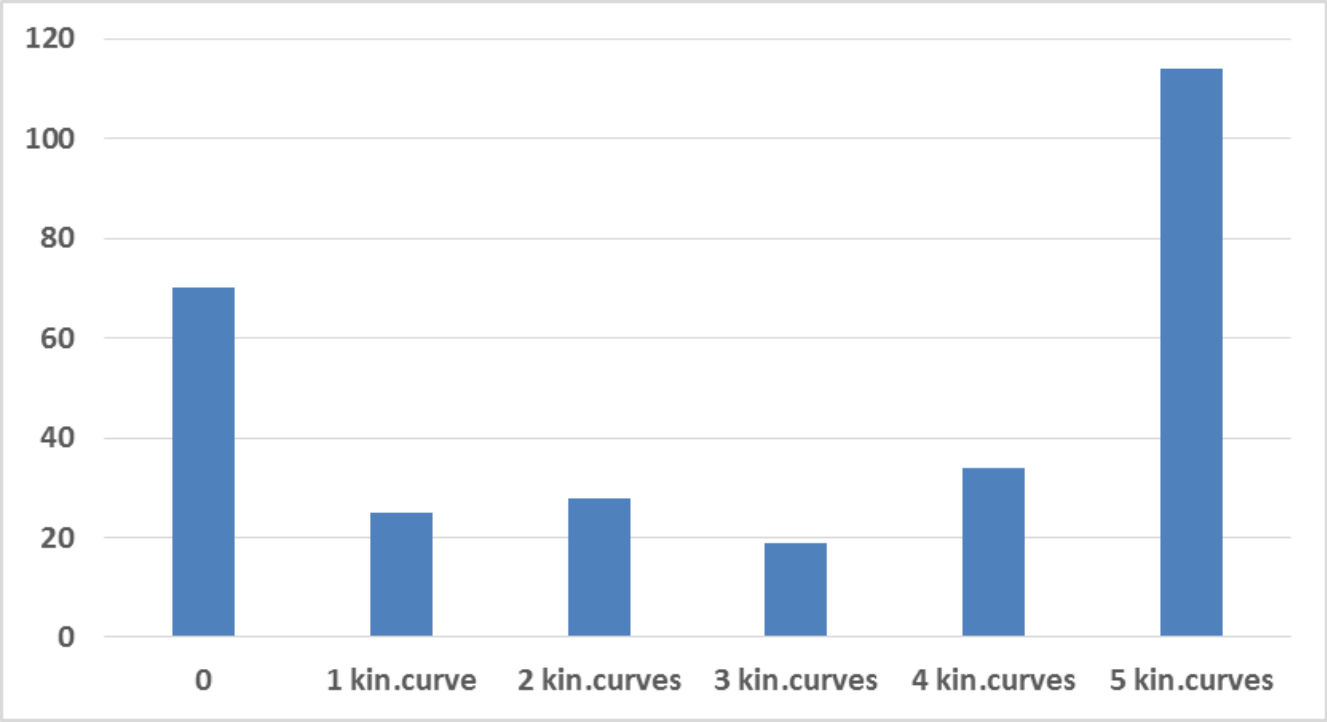
Master value – 890.1 mg/L

T3. Grading of reaction order



T3. Statistical data

Number of participants



T3. Typical mistakes

1) Photometer was not calibrated with “Setup” button

2) Linear parts of the curves were chosen incorrectly

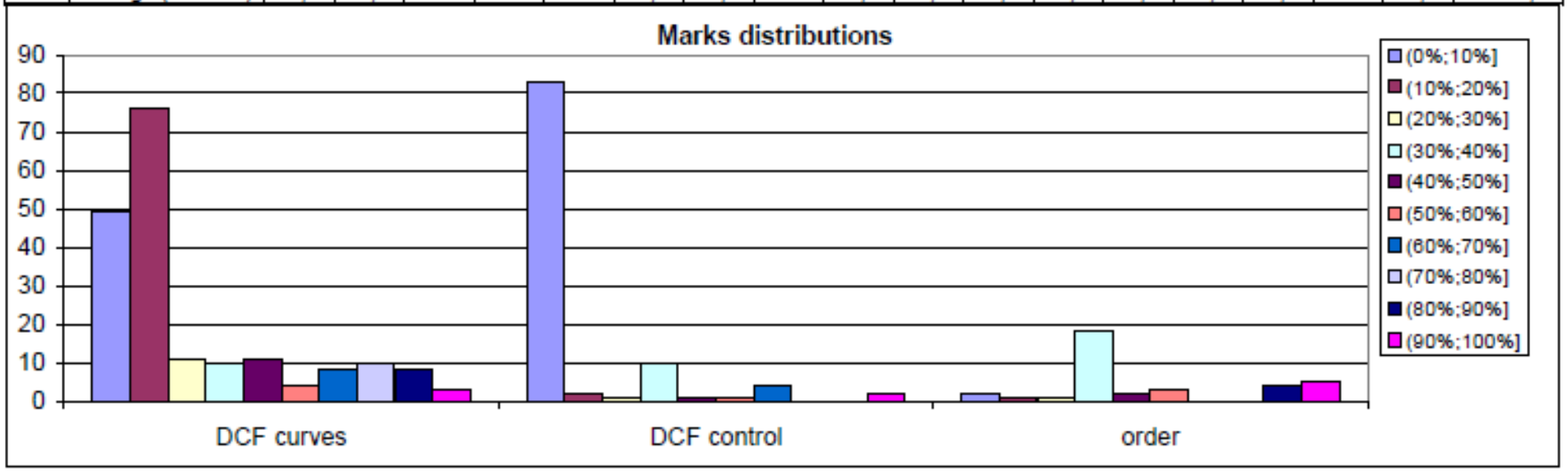
3) Calculations

- concentration in the cuvette
- slope of the calibration line
- data for the reaction order

T3. Statistical results

Statistics for problem #3 by room

	Room #	8	36	42	26	41	3	37	43	25	49	27	2	7	35	30	47	52	Total
DCF curves	Count	15	12	10	15	5	7	10	3	12	28	20	8	17	17	15	9	17	220
	Non-zero	13	12	9	13	5	6	8	3	12	23	13	7	16	15	15	8	12	190
	Full mark	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Zero mark	2	0	1	2	0	1	2	0	0	5	7	1	1	2	0	1	5	30
	Average (excl. 0's)	17,69	11,88	8,40	6,41	5,20	11,96	10,66	3,33	15,35	14,05	6,93	16,39	14,17	11,19	10,13	6,58	9,24	11,30
DCF control	Count	15	12	10	15	5	7	10	3	12	28	20	8	17	17	15	9	17	220
	Non-zero	10	7	4	3	1	5	6	1	8	18	4	4	8	10	8	2	5	104
	Full mark	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	2
	Zero mark	5	5	6	12	4	2	4	2	4	10	16	4	9	7	7	7	12	116
	Average (excl. 0's)	4,34	4,53	2,00	2,00	2,00	5,60	5,00	2,00	3,52	3,09	3,21	6,01	2,75	2,60	4,25	2,00	2,00	3,54
order	Count	15	12	10	15	5	7	10	3	12	28	20	8	17	17	15	9	17	220
	Non-zero	5	5	0	0	0	1	2	0	2	5	2	5	1	1	2	0	5	36
	Full mark	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	2
	Zero mark	10	7	10	15	5	6	8	3	10	23	18	3	16	16	13	9	12	184
	Average (excl. 0's)	5,04	5,22				4,00	2,40		9,16	4,71	7,72	5,20	4,00	4,00	7,00		3,82	5,12



Total practical skills success rate.