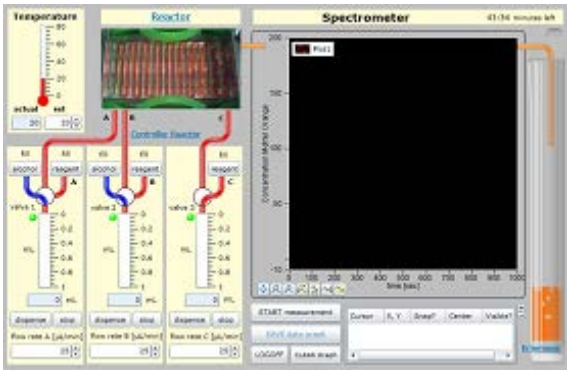
Manual

Chemical web experiment
Online synthesis of methyl orange



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online chemical web experiment

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1. Introduction

This manual describes a web experiment based on the technique of micro scale flow chemistry. A micro reactor is used to synthesise methyl orange. The conditions of this synthesis can be controlled online, so the mechanisms and the overall reaction yield can be studied. Online analysis of the product is performed by a spectrometer.

The experimental setup is located at the VU University, Amsterdam. The web experiment can be accessed from any location in the world, provided the user's system meets the minimum system requirements as listed in Appendix A (page 14).
Before starting the experiment it is recommended to formulate a research plan to work as productively as possible.

2. Synthesis and analysis of methyl orange

2.1 Synthesis of methyl orange: chemistry in a micro reactor

Micro scale flow chemistry provides a reliable platform for reactions of many types, including very exothermic reactions, like the synthesis of methyl orange. In flow chemistry experiments two or three liquid reagents flow through the micro channels (0,3 mm diameter) of a micro reactor.

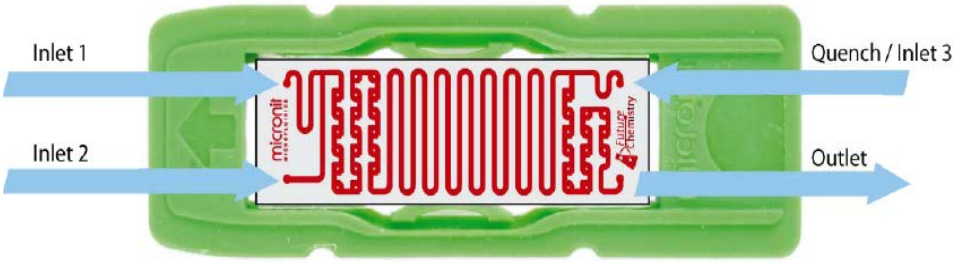


Fig. 1 – Four-channel micro reactor (FutureChemistry©), overall length appr. 5 cm

The synthesis of methyl orange requires three reagents, each of which is pumped into the inlets 1, 2 and 3. The micro reactor's outlet collects the product into an erlenmeyer.

2.2 Detection of methyl orange: using a spectrometer

A spectrometer is used to determine the yield of the product. Because of methyl orange's bright colour it is suitable to measure the optical properties of the solution that leaves the micro reactor.
The concentration of methyl orange can be related to the transparency of the solution leaving the micro reactor.

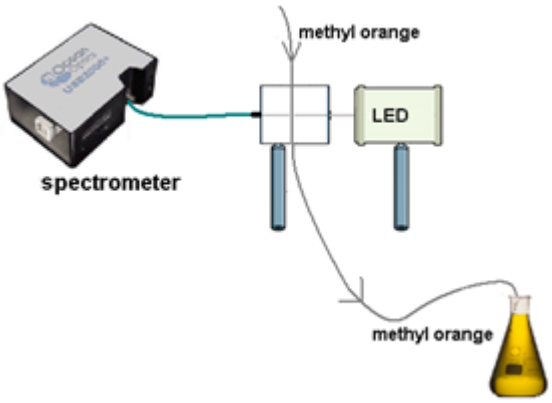
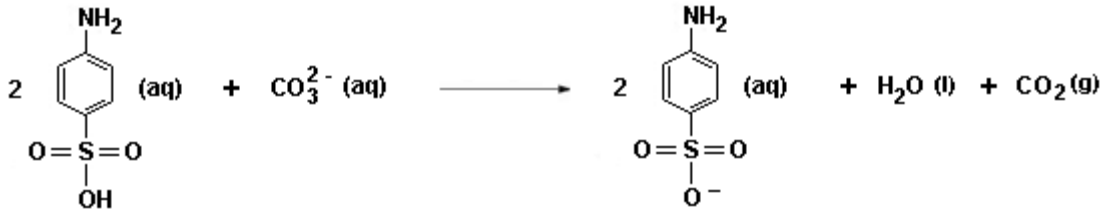


Fig. 2 – Spectrometer detecting the transparency

2.3 Synthesis of methyl orange: a multiple-step reaction

The synthesis of methyl orange is an exothermic 4-step reaction.

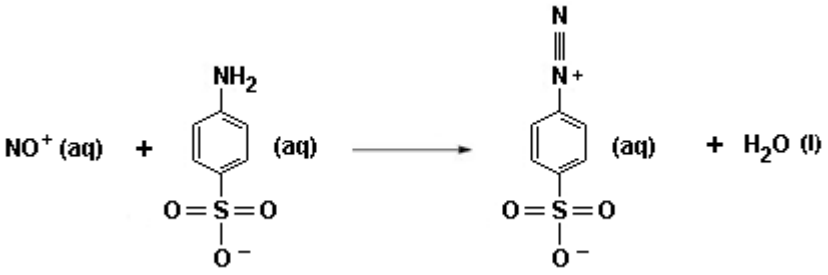
Step 1
Sodium carbonate reacts with sulfanilic acid, making the acid more soluble:



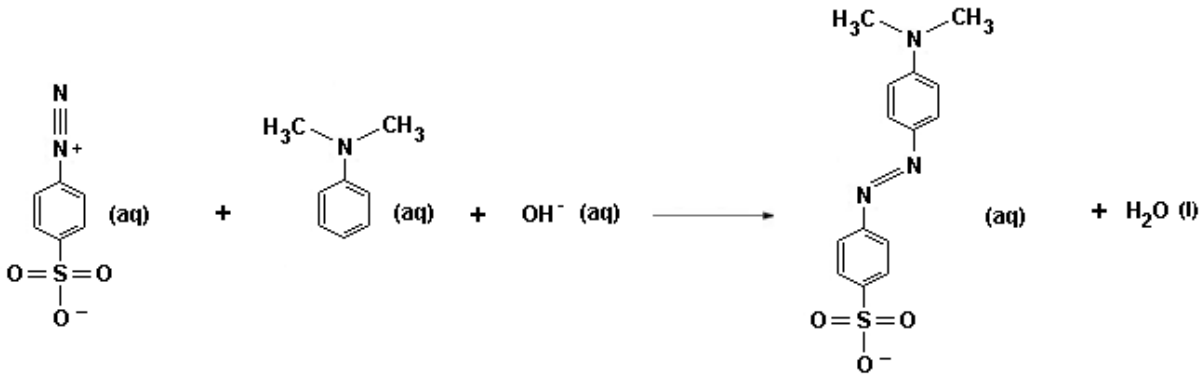
Step 2
Sodium nitrite and hydrochloric acid react to produce water and the NO^+ (nitrosonium) ion:

$$2\ H_3O^+\ (aq) + NO_2^-\ (aq) \rightarrow 3\ H_2O\ (l) + NO^+\ (aq)$$

Step 3
The nitrosonium ion reacts with the amino of the sulfanilic acid, attaching a second N-atom at the sulfanilic acid (making it a diazonium salt),



Step 4
The diazonium salt reacts with N,N-dimethylaniline and the hydroxide ion to produce methyl orange.



More details can be found in this manual's appendix B (page 13).

2.4 Synthesis of methyl orange: outline of the experimental setup

All reagents flow into the micro reactor's channels:
- Inlet 1: reagent A – solution of sodium carbonate, sulfanilic acid and sodium nitrite
- Inlet 2: reagent B – solution of N,N-dimethylaniline and hydrochloric acid
- Inlet 3: reagent C – solution of sodium hydroxide

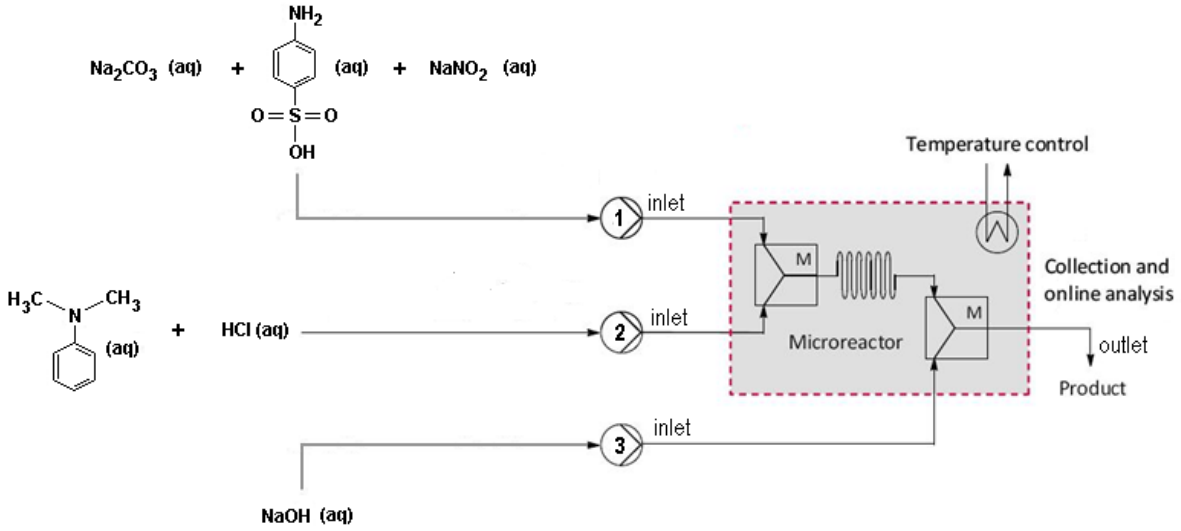


Fig. 3 – Outline of the experimental setup

The product is analysed using an Ocean Optics spectrometer.

2.5 Synthesis of methyl orange: experimental setup

This picture of the experimental setup at the VU University Amsterdam shows most of the essential parts.

Fig. 4 – Experimental setup

1. Temperature display
2. Syringes with valves V1, V2, V3, resp.
3. Stock: reagents A, B and C
4. Webcam controller
5. Webcam micro reactor
6. Detection of methyl orange (details below)
7. Webcam erlenmeyer
8. Erlenmeyer collecting methyl orange

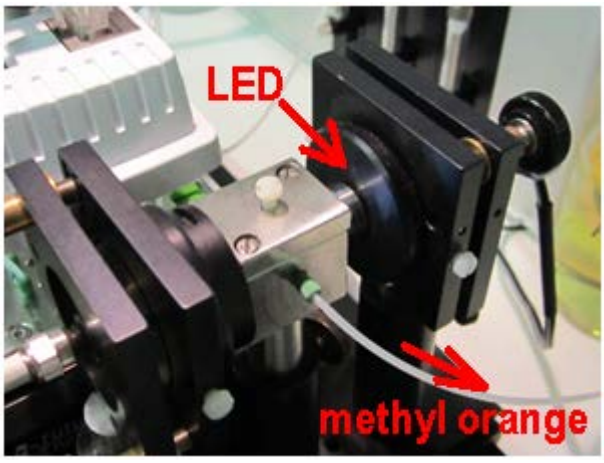


Fig. 5 – Methyl orange passing the spectrometer

3. The web experiment

3.1 – Access and login

Access

If you haven't done this experiment before, you can choose 'MAKE A RESERVATION' to book one hour for your experiment (50 minutes effectively).

If you made a reservation already, you can choose the 'LOGIN for experiment' button. In that case, you can skip the 'Reservation'.

An automatic cleaning procedure can make the experiment offline for 10 minutes.

Access to the web experiment:
ask Hans van Dijk

Reservation

Select (in the lower part of the screen):
- the month and
- the day of the month

at which you want to perform your experiment.

The,green bar tells you which period is available (red: not available, yellow indicates your reservation settings.

Select:
- the starting time of your experiment.

Important: you can only make a reservation for 1 hour, of which the first 50 minutes are available for the experiment. After 50 minutes, a 10 minutes cleaning procedure is performed automatically. By then you are logged off - after a 10-minutes warning.
So, be sure you saved your data!

Type (PERSONAL DETAILS):
- your e-mail address,
- your full name,
- the name of your school,
- the city/town of your school.

Press 'Confirm reservation'.

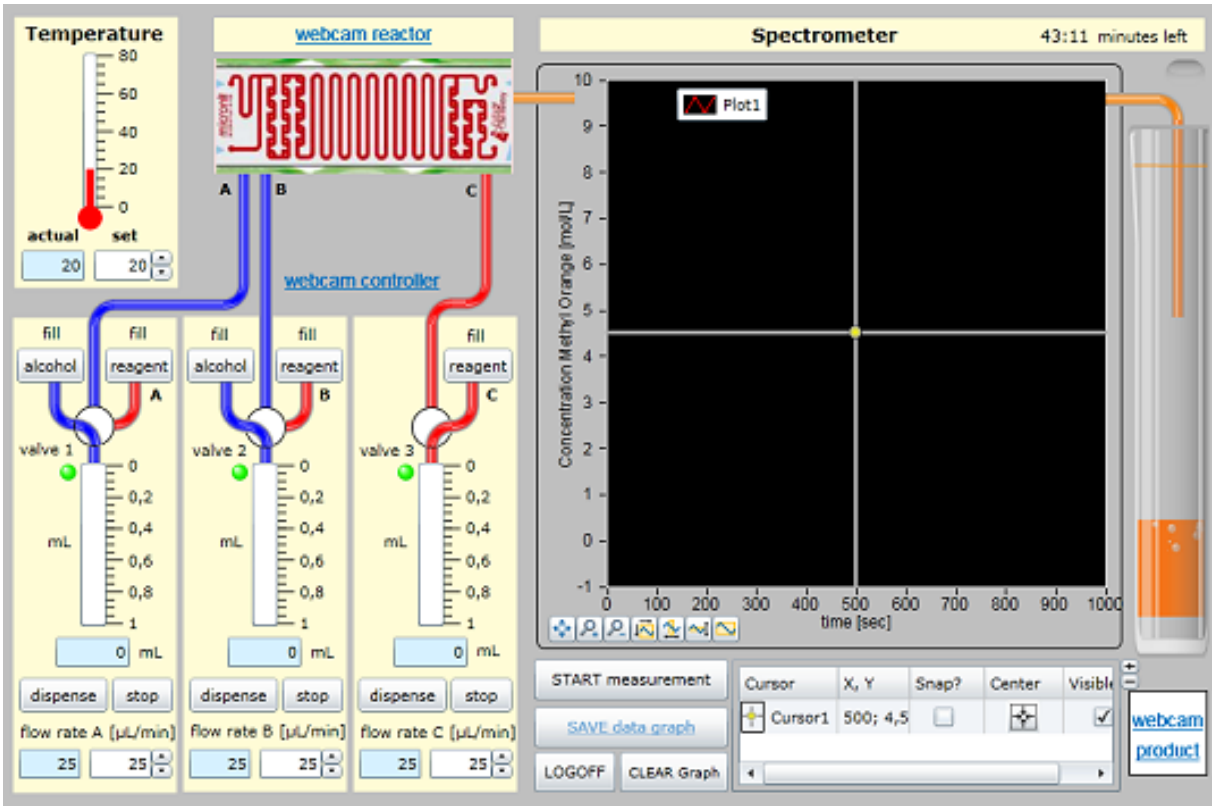
A unique password will be sent to you (by e-mail) which you can use to log in for the experiment.

Note: of course you can make a two hours reservation.

Login You can access the experiment by typing your e-mail address and the unique password which you received by e-mail. Press the 'START experiment' button. *From this moment you have 50 minutes working time!*	

3.2 – Interface of the web experiment

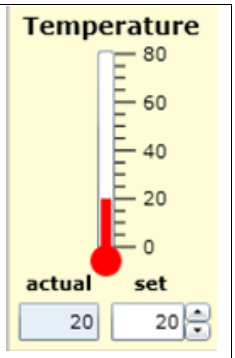
The interface of the web experiment provides you with all controls to
- set and control the reaction's circumstances,
- monitor the reaction's progress,
- detect the yield of the product.



All controls are described in the table on the next pages.

Control: temperature

The 'set'-box enables you to set the temperature of the reaction. You can type a temperature in this 'set'-box or use the up- and down arrows. The thermo controller allows temperatures of 8 °C minimum and 80 °C maximum.
The thermometer shown indicates the actual temperature (also visible in the 'actual'-box).



Controls: syringes

Three syringes (1000 µL = 1.000 mL) can be filled with either reagents or alcohol. Alcohol is used to clean the micro reactor.

Select:
- alcohol or a reagent to fill the syringe,
- the flow rate (range 1 µL/min to 1500 µL/min).

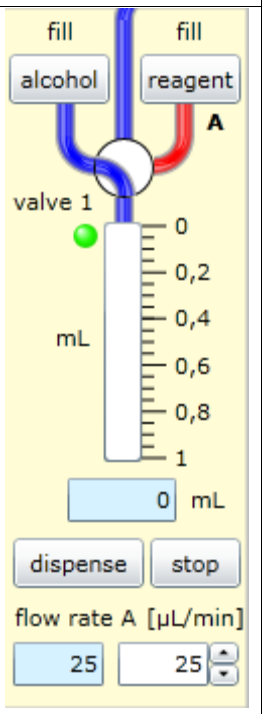
Press the 'dispense' button to empty the syringe at the flow speed you selected. Changing any of the flow rates requires pressing the 'dispense' button again to confirm the change(s).
The volume of the alcohol or reagent in the syringe is indicated graphically (blue = alcohol, red = reagent).

Syringe 1 can be filled with either alcohol or reagent A
(solution of sodium carbonate, sulfanilic acid and sodium nitrite).
Syringe 2 can be filled with either alcohol or reagent B
(N,N-dimethylaniline and hydrochloric acid).
Syringe 3 can be filled with reagent C (solution of sodium hydroxide).

Note 1: you can fill the syringes whenever you want.
Note 2: before you fill a syringe with reagent, there might be some alcohol left!

For a detailed description of the reagents' contents: see appendix C (page 14).

When cleaning the micro reactor (you can do that whenever you want), use syringe A as well as syringe B. Cleaning with alcohol (at a recommended flow speed of 200 – 500 µL/min) is much faster when the temperature is 70-80 ºC.
Check the cleaning process with the webcam of the micro reactor! The micro reactor should be clear (colourless) after cleaning.

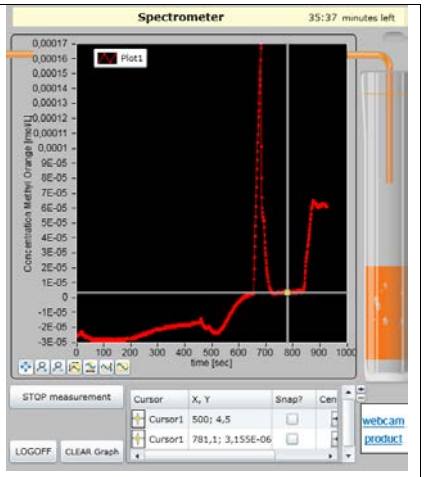


Control: spectrometer

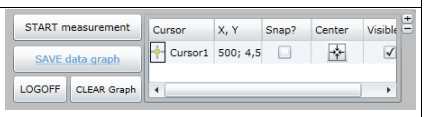
A spectrometer is used to measure the transparency of the product (the methyl orange solution). This transparency is related to the concentration (mol/L) of the methyl orange. The spectrometer's window of the interface shows the time (seconds, x-axis) and the concentration ($molL^{-1}$, y-axis) of the product.

The orange coloured test tube on the right side of the spectrometer control indicates how much time you have consumed (the test tube fills up while experimenting).
At the upper right corner you can see how much time is left for your session. A bulb blinking just below the 'minutes left' bar will tell you that there are 10 minutes left.
So save your data in time!

Remember that after these 50 minutes a cleaning sequence starts automatically and your data will be lost!



Control: spectrometer-details (1)



Button 'START measurement': the spectrometer is switched on.
The spectrometer's graph shows the concentration of the methyl orange produced in the last 1000 s period. So, if your measurement takes more time, the time-basis will shift automatically. In that case former data will be lost!

Button 'LOGOFF' ends the connection with the online experiment. If you log off (for what reason), the experiment you have started continues! If you log in again you can see the latest results of the experiment.

Button 'CLEAR Graph' clears all data.

Button 'SAVE data graph' saves the data in a text-file that can be opened in an EXCEL-sheet. Appendix D (page 13) provides you with information about transforming these data into a graph.
Important: if you only want to save (a part of) the graph, you can also make a screendump (hardcopy of your screen). Doing this you don't have access to the numeric data.

Button '+' adds two perpendicular straight lines. You can put the intersection of these lines (the cursor) at one point of the graph to read the values of the data at that point.

Button '-' deletes a cursor.

Button 'snap' attaches the cursor to the graph. When moving the intersection, the cursor is always attached to one point of the graph.

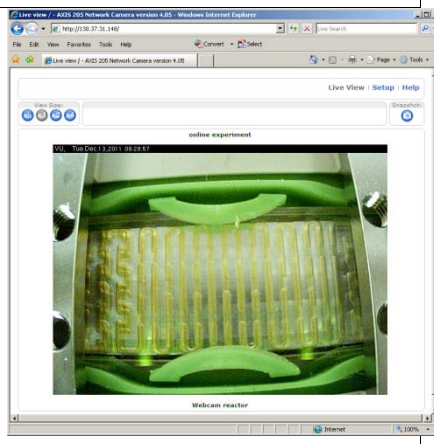
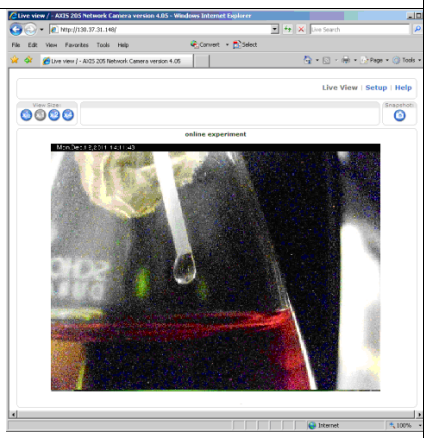
Button 'Cursor' enables you to select one of the cursors.

Button 'center' sets the cursor to the center of the spectrometer's window.

Button 'visible' makes the cursor visible/invisible.

Control: spectrometer-details (2)

From left to right:
button #1 – 'Pan' for moving the graph
button #2 – 'ZoomInClick' for zooming in (requires a click on the spectrometer's window)
button #3– 'ZoomOutClick' for zooming out (requires a click on the spectrometer's window)
button #4 – 'ZoomInDrag' for zooming in (requires drawing a rectangular

shaped section) button #5 – 'ZoomHorizontalDrag' for zooming in at the horizontal axis (requires selecting a part of the horizontal axis) button #6 – 'ZoomVerticalDrag' for zooming in at the vertical axis (requires selecting a part of the vertical axis) button #7 – 'ZoomToFit' for automatic scaling of the graph	
Control: webcam #1 - controller of the micro reactor You can see the temperature settings and the movements of the syringes. **http://pc-021446.clients.vu.nl**	
Control: webcam #2 – micro reactor You can see what is happening in the micro reactor during the reaction by activating the 'webcam reactor' link. **http://pc-021445.clients.vu.nl**	
Control: webcam #3 - product You can see if any product is formed during the reaction. **http://pc-021447.clients.vu.nl**	

3.3 - How to do a measurement?

1. Check the micro reactor (using the webcam). Is it clean?
   If *not*….
   - fill up the syringes 1, 2 and 3 with alcohol,
   - set the temperature at 70 - 80 °C,
   - set the flow rates at 200 – 500 µL/min,
   - press 'dispense' (syringe 1, 2 and 3),
   - wait until the syringes are empty.

   Watch the micro reactor's webcam to see what happens.

2. Set the flow rates for your experiment (syringe 1, 2 and 3).

3. Set the temperature for your experiment.

4. Fill the syringes up with the reagents A, B and C.
   Note: you can see the syringes being filled up using the webcam 'controller'.

5. Start 'measurement' to activate the spectrometer.

6. Press 'dispense' (3x) to activate the syringes.
   Note 1: it takes some time before methyl orange is detected by the spectrometer. The tubes (appr. 100 µL) from the syringes to the micro reactor's inlets may contain alcohol, the micro reactor itself has a volume of appr. 100 µL), the tube from the outlet to the spectrometer has a length of 75 mm.
   Note 2: the spectrometer will first detect reagent 3, before any methyl orange is formed.
   Note 3: you can check if any methyl orange is formed using the webcam 'product'.

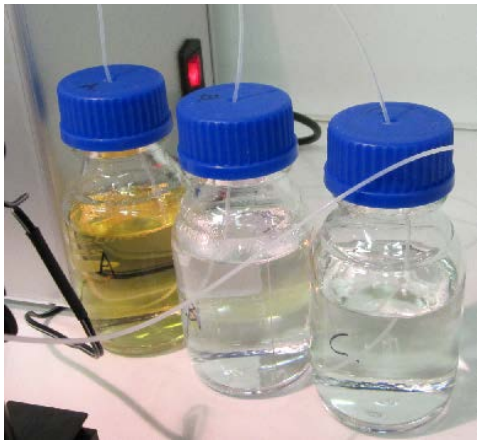
7. Wait until the spectrometer's output has a constant value. That is, the spectrometer's graph is horizontal again. The system has reached a stable situation, so you can measure the product's molarity.

8. Stop your measurement, so you can save your data.
   Important: depending on your operating system you may have to refresh (F5) your Excelsheet before importing new data.

4. APPENDICES

Appendix A – System requirements

Software: operating system WINDOWS
Additional plugins:
- Java (download here) and
- Silverlight (download here)



Appendix B – More about methyl orange

methyl orange (Wikipedia)
a synthesis of methyl orange
mechanism of the synthesis of methyl orange
All relevant documents:
http://www.chem.vu.nl/scheikunde-experiment

Appendix C - Composition of the reagents

solution A		molar mass (g/mol)	density (g/mL)	molarity (mol/L)	mass (g)	volume (mL)	mmol	conc. (mol/L)	conc. (g/L)
250 mL	sulfanilic acid	173.19			0.361		2.08	0.0083	1.44
	Na_2CO_3	105.99			0.221		2.09	0.0083	0.88
	$NaNO_2$	69			0.144		2.09	0.0083	0.58
	H_2O					168			
	ethanol					83			
solution B									
250 mL	N,N-dimethyl-aniline	121.18	0.956		0.378	0.395	3.12	0.012	1.51
	HCl	36.46		12.0	0.345	0.788	9.46	0.038	1.38
	H_2O					249			
solution C									
250 mL	NaOH	40.0			0.094		2.35	0.0094	0.38
	H_2O					64			
	ethanol					186			

Appendix D - How to make a graph with EXCEL

Saving data at the end of your session provides you with a text file containing many numeric data.
Important: depending on your operating system you may have to refresh (F5) your Excelsheet before importing new data.

So, what to do…..

- Save this text file.
- Open this text file with Excel.
- Select the column that contains these data.
- Choose ‘insert’ in the top toolbar.
- Select ‘line’ and a suitable chart type.
- And there it is!