Electronic Supplementary Material (ESI) for Lab on a Chip.

Supplementary Information for the manuscript:

Hydrogen peroxide concentration by pervaporation of a ternary liquid solution in microfluidics

Iwona Ziemecka*, Benoît Haut and Benoit Scheid

Appendix

x [m]-*coordinate along micro-channels*

L_P [m] –length of the micro-channel

P [bar] – pressure in the vapour channel

T [^{o}C] - temperature in the liquid channel

w_0 - molar fractions of H_2O in the solution introduced in the chip

m_0 - molar fractions of MeOH in the solution introduced in the chip

h_0 - molar fractions of H_2O_2 in the solution introduced in the chip

$w_l(x)$ - molar fractions of H_2O in the liquid at the position x in the liquid channel

$m_l(x)$ - molar fractions of MeOH in the liquid at the position x in the liquid channel

$h_l(x)$ - molar fractions of H_2O_2 in the liquid at the position x in the liquid channel

$i_g(x)$ - molar fractions of inert gas at the position x in the vapour channel

$w_g(x)$ - molar fractions of H_2O at the position x in the vapour channel

$m_g(x)$ - molar fractions of MeOH at the position x in the vapour channel

$h_g(x)$ - molar fractions of H_2O_2 at the position x in the vapour channel

$G(x)$ [mol/s] – molar flow rate of gas at the position x in the liquid channel

W [µm] – width of the liquid channel

H [µm]- thickness of the membrane

$J_w(x)$ [mol/s/m^2]- molar flux of H_2O across the membrane at position x

$J_m(x)$ [mol/s/m^2]- molar flux of MeOH across the membrane at position x

$J_h(x)$ [mol/s/m^2]- molar flux of H_2O_2 across the membrane at position x

P_w – permeability coefficient of liquid H_2O across the PDMS membrane

P_m - permeability coefficient of liquid MeOH across the PDMS membrane

P_h - permeability coefficient of liquid H_2O_2 across the PDMS membrane

$P_{\mathrm{sat},w}(T)$ [Pa] - saturation pressures of water

$P_{\mathrm{sat},m}(T)$ [Pa] - saturation pressures of methanol, MeOH

$P_{\mathrm{sat},h}(T)$ [Pa] - saturation pressures of hydrogen peroxide, H_2O_2

L_0 [mol/s] - molar flow rate of liquid introduced to the chip

NMR measurement

Hydrogen peroxide reacts with acetone therefore NMR measurements were performed directly after preparation of the samples. A typical ^1H NMR spectrum of a H_2O_2/ H_2O/ MeOH mixture in acetone-d6, measured at -25^{o}C is shown Fig. 1S. Due to low temperature of measurement the reaction between H_2O_2 and acetone is kinetically decreased. At this temperature chemical shifts related to protons from hydroxyl group and from methyl group of methanol can be distinguished by two separated signals. Note that it is not the case when measurement is taken at 25^{o}C (see Fig. 3S).

Kinetic measurements (see Fig. 2S) were realized to find out the stoichiometry of the reaction between hydrogen peroxide and acetone such as we could include concentration of byproduct into initial concentration of hydrogen peroxide. We observe that from 1 mol of H_2O_2 (2 protons) we obtain 1 mol (1 proton) of product with chemical shift at 10.4 ppm and 1 mol (1 proton) of product at 5.4 ppm. Products were not identified but stoichiometry of the reaction is preserved with respect to the error of the measurement.

We did also NMR of the sample using a coaxial tube filled with toluene but since internal solution was our pure sample the concentration of hydrogen peroxide was high and exchange of proton between H_2O_2 and H_2O molecule was fast which was causing broadening of the peak and increasing of the error of peak integration.

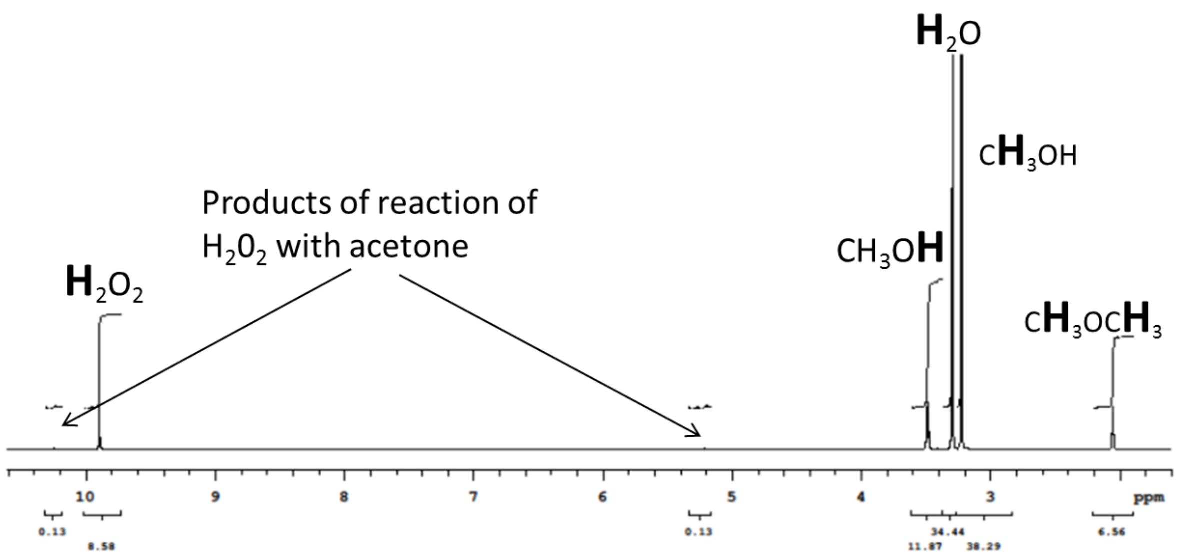

Fig. 1S Typical ^1H NMR spectra of mixture H_2O_2/ H_2O/ MeOH in acetone-d6 measured at -25^{o}C.

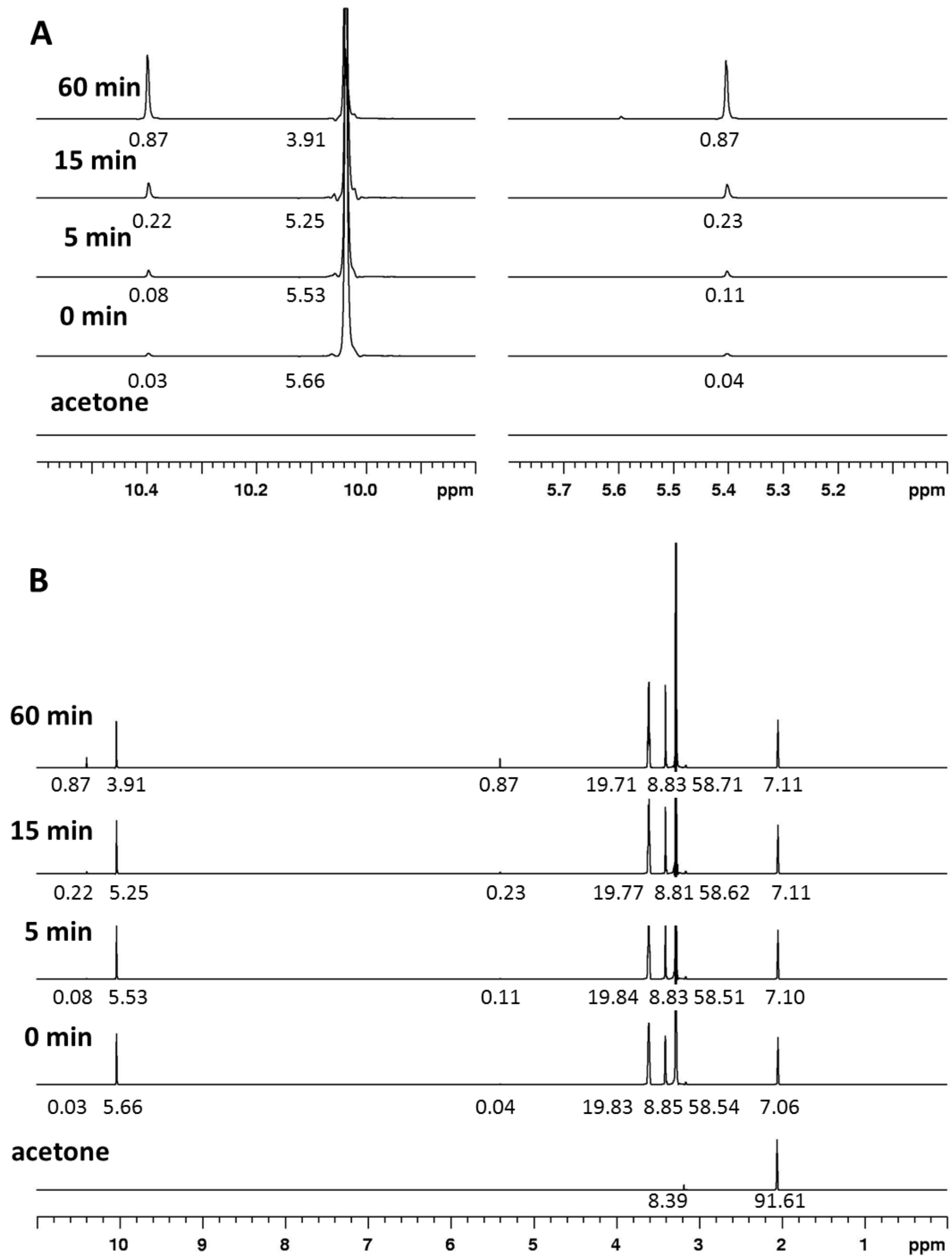

Fig. 2S Kinetic measurements of reaction between H_2O_2 and acetone, A: zoom showing decrease of signal from H_2O_2 at 10 ppm and increase of signals from products at 10.4 ppm and 5.4 ppm, B: full spectra.

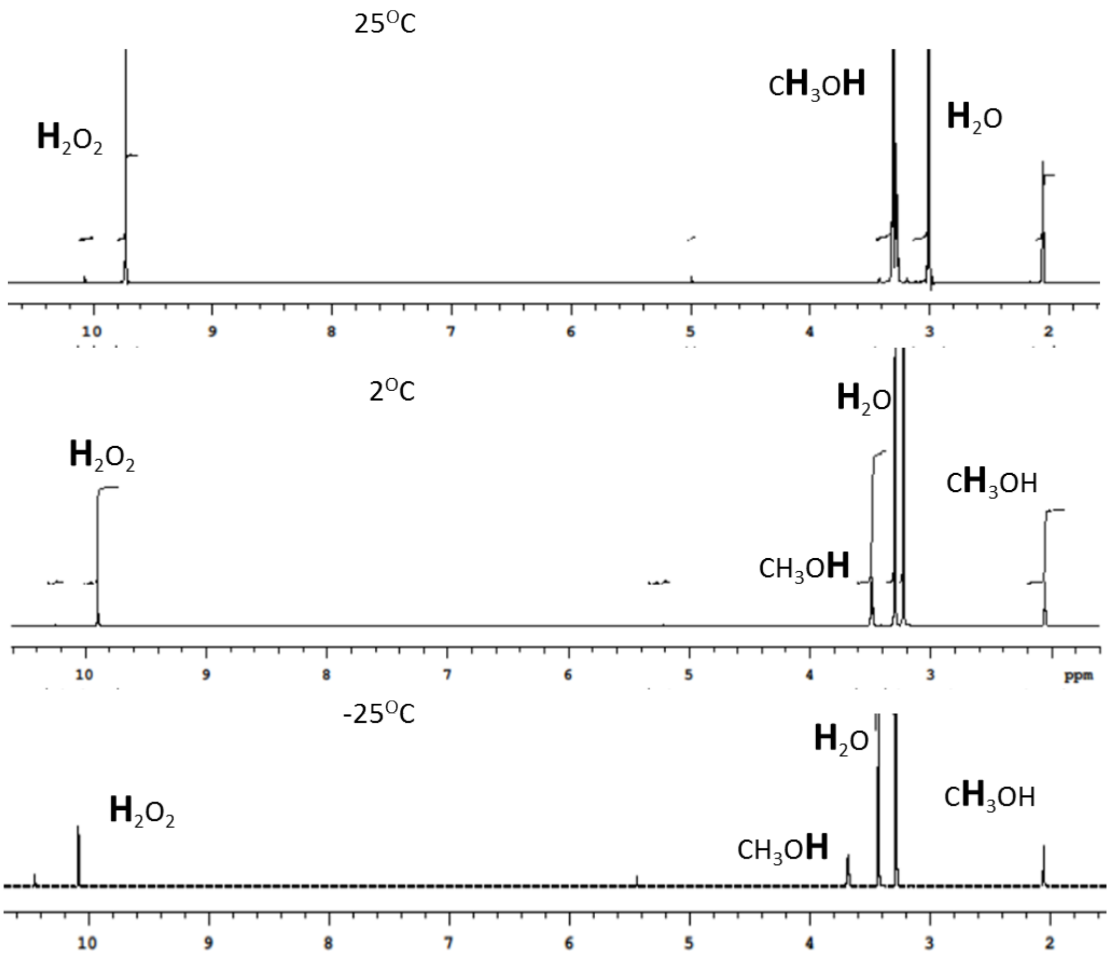

Fig. 3S Typical [1]H NMR spectra of mixture H_2O_2/ H_2O/ MeOH in acetone-d6 measured at 25^{O}C, 2^{O}C and -25^{o}C.

MODEL:

```
Off[General::spell1];


(*Physico-chemical properties*)

rlist = {

   Rg → 8.314,
   MMH2O → 18 × 10^-3,
   MMH2O2 → 34 × 10^-3,
   MMCH3OH → 32 × 10^-3,
   ρH2O → 1000,
   ρCH3OH → 800,
   ρH2O2 → 1000,
   Pm → Exp[-25],
   Pw → Exp[-25],
   Ph → Exp[-25]


  };

PsatH2O[T_] = Exp[13.7 - 5120/(T + 273.15)] 101325;
PsatCH3OH[T_] = 133 × 10^(8.8 - 2002/(T+273.15));
PsatH2O2[T_] = Exp[A + B T] /. N[Solve[{Log[10000] == A + B 90, Log[1000] == A + B 45}, {A, B}][[1]]];




(*Operating parameters*)

buffer = {

   ml0 → 0.35,
   hl0 → 0.02,
   P → 101325 - 0.5 × 101325,
   W → 300 × 10^-6,
   H → 170 × 10^-6 ,
   Lpuce → 0.9



  };

oper = Join[buffer, {L0 → 0.1 × 10^-9 1/((ml0 MMCH3OH)/ρCH3OH + (hl0 MMH2O2)/ρH2O2 + (1 - ml0 - hl0) MMH2O/ρH2O) /. rlist /. buffer,
```

$G0 \rightarrow 0.0001 \times 10^{-9} \frac{1}{\frac{m10\, MMCH3OH}{\rho CH3OH} + \frac{h10\, MMH2O2}{\rho H2O2} + (1 - m10 - h10) \frac{MMH2O}{\rho H2O}}$ /. rlist /. buffer}];

```
MatrixForm[rlist]
MatrixForm[oper]
```

$$\begin{pmatrix} Rg \rightarrow 8.314 \\ MMH2O \rightarrow \frac{9}{500} \\ MMH2O2 \rightarrow \frac{17}{500} \\ MMCH3OH \rightarrow \frac{4}{125} \\ \rho H2O \rightarrow 1000 \\ \rho CH3OH \rightarrow 800 \\ \rho H2O2 \rightarrow 1000 \\ Pm \rightarrow \frac{1}{e^{25}} \\ Pw \rightarrow \frac{1}{e^{25}} \\ Ph \rightarrow \frac{1}{e^{25}} \end{pmatrix}$$

$$\begin{pmatrix} m10 \rightarrow 0.35\text{`} \\ h10 \rightarrow 0.02\text{`} \\ P \rightarrow 50662.5\text{`} \\ W \rightarrow \frac{3}{10000} \\ H \rightarrow \frac{17}{100000} \\ Lpuce \rightarrow 0.9\text{`} \\ L0 \rightarrow 3.843197540353575\text{`*^-6} \\ G0 \rightarrow 3.843197540353575\text{`*^-9} \end{pmatrix}$$

```
(*Characterestic length and mass fluxes through the membrane*)

Lcar = (L0/2 H)/(P Pm W) /. oper /. rlist

ϵ = 0.00001;

Jm[x_] = Pm/H (PsatCH3OH[T] * ml[x] - P * mg[x]);
Jw[x_] = Pw/H (PsatH2O[T] * wl[x] - P * wg[x]);
Jh[x_] = Ph/H (PsatH2O2[T] * hl[x] - P * hg[x]);
ig[x_] = G0 (1 - 3 ϵ) / G[x] /. oper;
wg[x_] = 1 - (mg[x] + hg[x] + ig[x]);
wl[x_] = 1 - (ml[x] + hl[x]);

1.54763

(*Equations*)

eq1 = L'[x] ml[x] + L[x] ml'[x] == -W * Jm[x] /. rlist /. oper;
eq2 = L'[x] hl[x] + L[x] hl'[x] == -W * Jh[x] /. rlist /. oper;
eq3 = L'[x] wl[x] + L[x] wl'[x] == -W * Jw[x] /. rlist /. oper;
eq4 = G'[x] mg[x] + G[x] mg'[x] == -W * Jm[x] /. rlist /. oper;
eq5 = G'[x] hg[x] + G[x] hg'[x] == -W * Jh[x] /. rlist /. oper;
eq6 = G'[x] wg[x] + G[x] wg'[x] == -W * Jw[x] /. rlist /. oper;

sol[p1_, p2_, p3_, p4_] := NDSolve[{eq1 /. T → p4, eq2 /. T → p4, eq3 /. T → p4, eq4 /. T → p4, eq5 /. T → p4, eq6 /. T → p4, G[Lpuce] == G0 /. oper, mg[Lpuce /. oper] == ϵ, hg[Lpuce /. oper] == ϵ,
    ml[Lpuce /. oper] == p3, hl[Lpuce /. oper] == p2, L[Lpuce /. oper] == p1}, {ml, hl, mg, hg, G, L}, {x, 0, Lpuce /. oper}];

cout[p11_?NumericQ, p12_?NumericQ, p13_?NumericQ, p14_?NumericQ] := (L[0] - L0)^2 / L0^2 + (ml[0] - ml0)^2 / ml0^2 + (hl[0] - hl0)^2 / hl0^2 /. oper /. sol[p11, p12, p13, p14][[1]];

cout[1.5 * 10^-6, 0.1, 0.35, 75]

6.37425

liquidmod = {};
vapormod = {};

Toper = 75;
valmin = NMinimize[{cout[p1, p2, p3, Toper], p2 > 0, p3 > 0}, {p1, p2, p3}];
solfin = sol[p1 /. valmin[[2]], p2 /. valmin[[2]], p3 /. valmin[[2]], Toper][[1]];
liquidmod = Join[liquidmod, {{Toper, hl[Lpuce /. oper], wl[Lpuce /. oper], ml[Lpuce /. oper]}} /. solfin];
vapormod = Join[vapormod, {{Toper, hg[0], wg[0], mg[0]}} /. solfin];
```

Mass balance

Example of mass balance calculated for pervaporation result performed for each mixture at different temperature.

Inlet composition	H 3.4%, W 50.4%, M 46.1%			
Temperature	Phase	Mass [g]	Phase composition	Total
75°C	V	0.0161	H 0.3%, W 28.6%, M 71.1%	H 3.7%, W 54.4%, M 41.9%
	L	0.1549	H 4.0%, W 57.1%, M 38.9%	
80°C	V	0.0306	H 0.1%, W 26.1%, M 73.8%	H 3.6%, W 52.9%, M 43.5%
	L	0.1389	H 4.3%, W 58.8%, M 36.9%	
85°C	V	0.0678	H 0.1%, W 28.1%, M 71.8%	H 3.5%, W 52.6%, M 43.9%
	L	0.1245	H 5.4%, W 65.9%, M28.7%	
90°C	V	0.0576	H 0.2%, W 35.8%, M 64.0%	H 3.0%, W 50.5%, M 46.5%
	L	0.0665	H 5.5%, W 63.2%, M31.3%	

Inlet composition	H 8.6%, W 46.4%, M 45.5%			
Temperature	Phase	Mass [g]	Phase composition	Total
75°C	V	0.0168	H 0.3%, W 33.7%, M 66.6%	H 9.6%, W 51.7%, M 38.8%
	L	0.1178	H 10.9%, W 54.2%, M 34.9%	
80°C	V	0.019	H 0.2%, W 31.5%, M 68.3%	H 8.9%, W 51.5%, M 39.6%
	L	0.0601	H 11.6%, W 57.8%, M 30.5%	
83°C	V	0.042	H 0.3%, W 27.6%, M 72.1%	H 9.1%, W 49.6%, M 41.2%
	L	0.1014	H 12.8%, W 58.7%, M28.4%	
85°C	V	0.0298	H 0.3%, W 30.4%, M 69.3%	H 9.4%, W 50.8%, M 39.8%
	L	0.0662	H 13.5%, W 60.0%, M26.5%	
87°C	V	0.0574	H 0.3%, W 27.4%, M 72.3%	H 9.2%, W 50.1%, M 40.7%
	L	0.1159	H 13.7%, W 61.3%, M25.0%	
90°C	V	0.060	H 0.3%, W 29.5%, M 70.1%	H 8.1%, W 47.7%, M 44.2%
	L	0.0691	H 14.9%, W 63.4%, M 21.6%	

Inlet composition	H 13.0%, W 9.1%, M 77.9%			
Temperature	Phase	Mass [g]	Phase composition	Total
70°C	V	0.027	H 0.2%, W 11.0%, M 88.8%	H 13.2%, W 13.9%, M 72.9%
	L	0.054	H 19.7%, W15.3%, M 65.0%	
75°C	V	0.0345	H 0.5%, W 7.2%, M 92.3%	H 13.2%, W 11.4%, M 75.4%
	L	0.0500	H 22.0%, W 14.3%, M 63.7%	
80°C	V	0.0679	H 0.5%, W9.5%, M 90.0%	H 13.0%, W 12.0%, M 75.0%
	L	0.087	H 22.7%, W 14.0%, M63.3%	
85°C	V	0.0399	H 1.1%, W 11.1%, M 87.8%	H 12.8%, W 13.2%, M 74.0%
	L	0.0504	H 22.1%, W 14.9%, M63.0%	
90°C	V	0.0802	H 1.5%, W 12.3%, M 86.1%	H 11.3%, W 13.3%, M 75.4%
	L	0.0849	H 20.5%, W 14.1%, M65.4%	