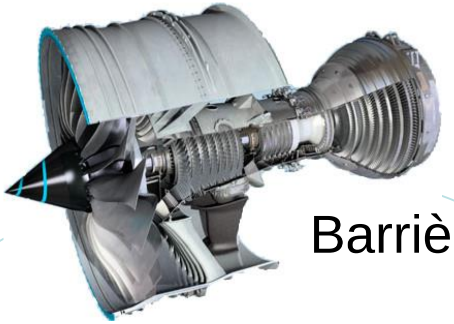
Injection synchrone de précurseurs liquides dans un plasma d'arc pulsé

SPCTS (UMR7315)
Science des Procédés Céramiques et Traitements de Surface
Limoges

Fabrice Mavier, Jean-François Coudert, V. Rat

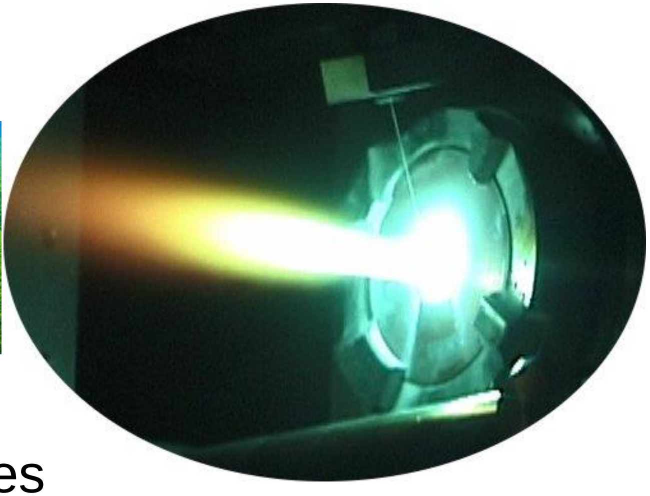
Louise Lemesre, Marguertite Bienia, Martine Lejeune

Projection plasma de liquide (suspensions/solutions)



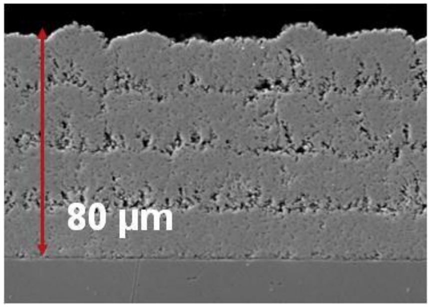
Barrières thermiques

Dépôts photocatalytiques



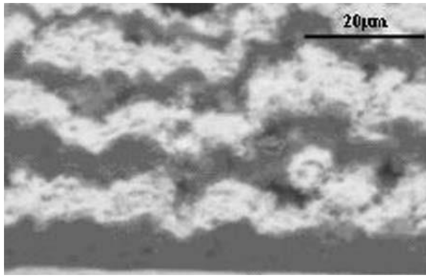
Biomatériaux

Anti-usure



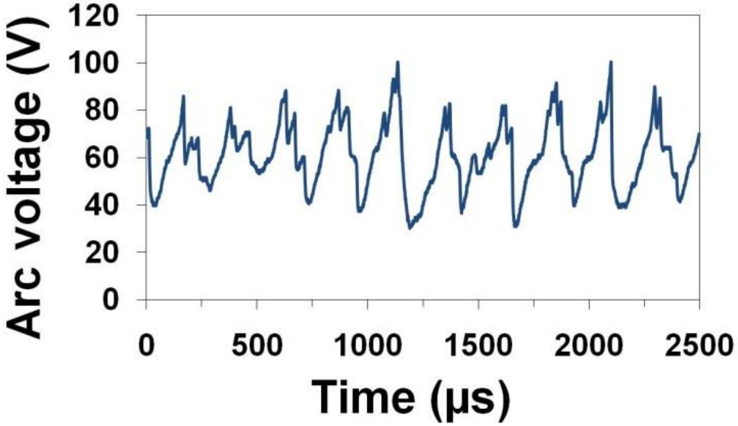
Contrôle des microstructures,

des structures et composition chimique

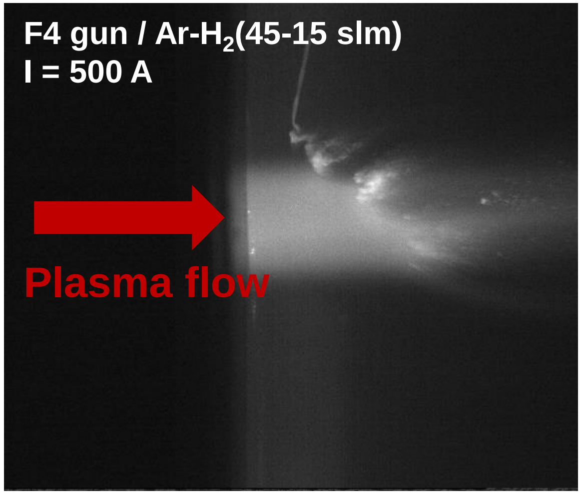


Instabilités de l'arc dans les torches dc

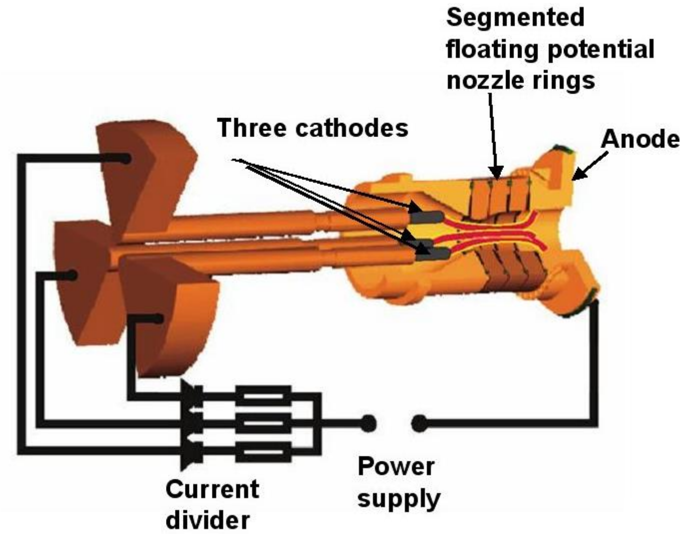
- **Torche conventionnelle - P_{elec} ~ 35 kW**

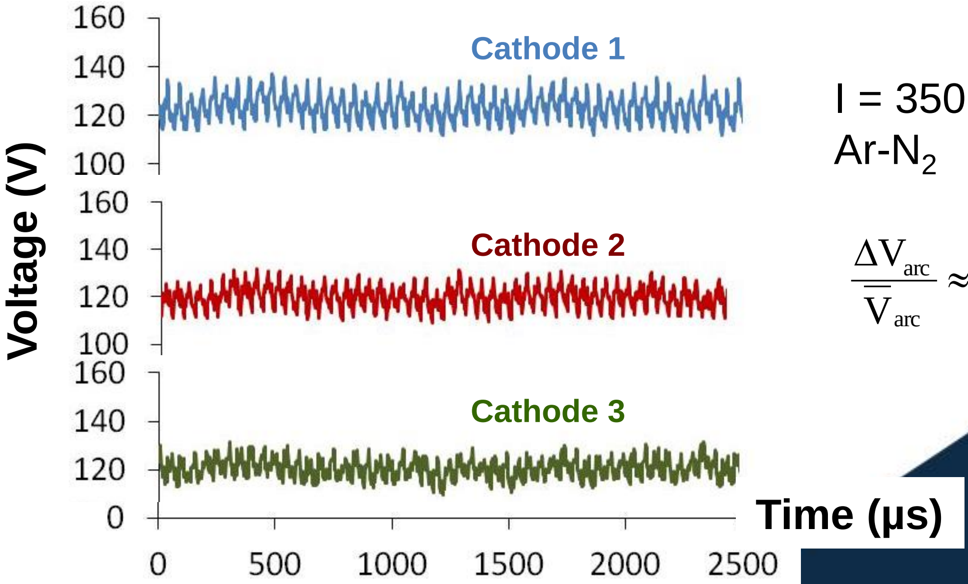


$$\frac{\Delta V_{arc}}{\overline{\overline{V}}_{arc}} \approx 0.9$$



- **Réduire les instabilités: torches multi-électrodes - P_{elec} ~ 40-100 kW**



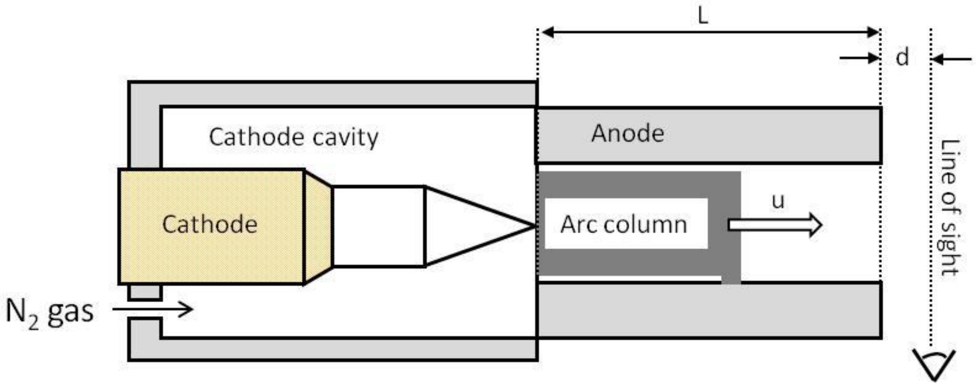


I = 350 A
Ar-N_2

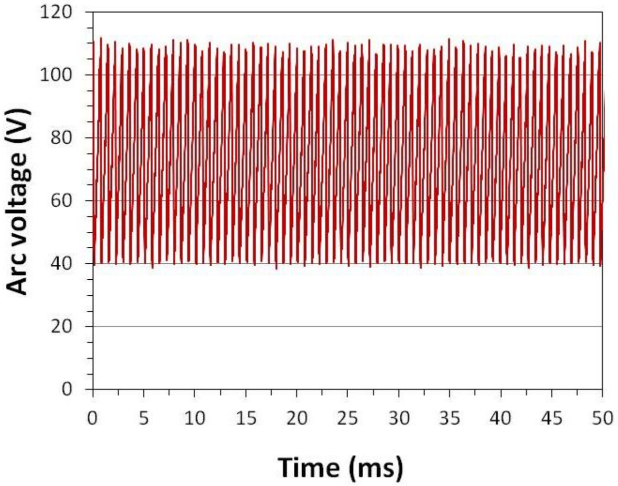
$$\frac{\Delta V_{arc}}{\overline{\overline{V}}_{arc}} \approx 0.2$$

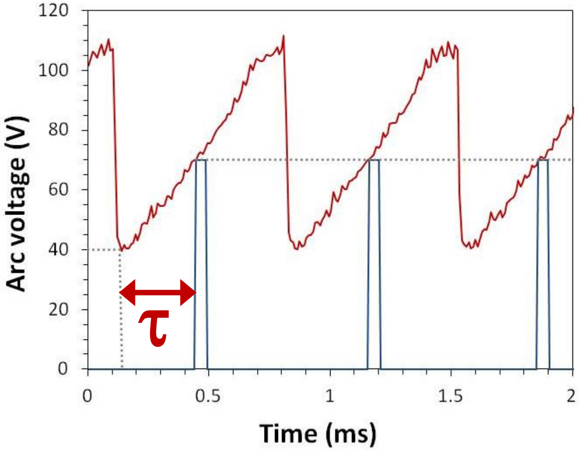
Torche pulsée

- **DC, I = 15 A – faible puissance- N_2 – Pression atmosphérique**



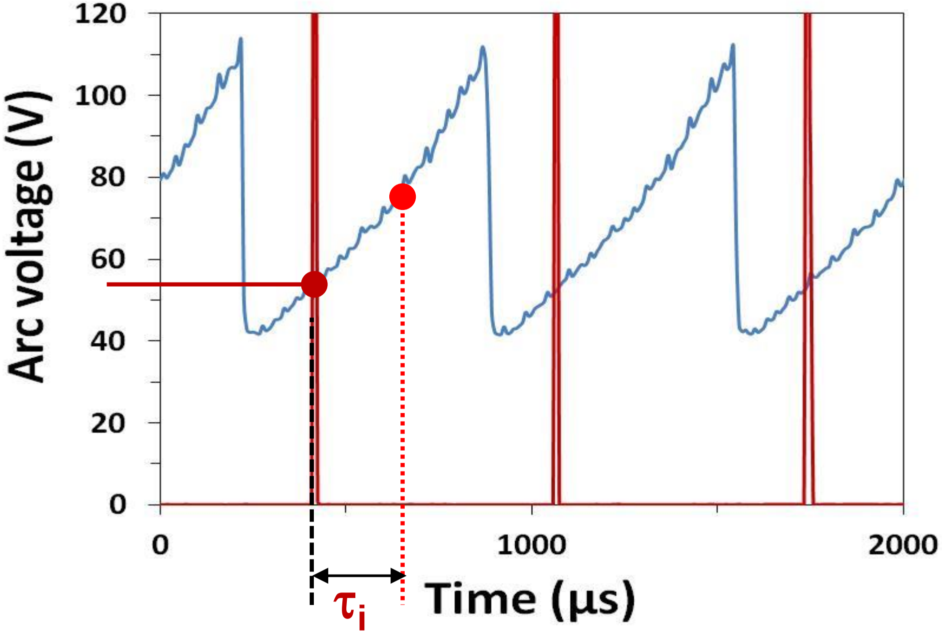
f_0 ~ 1.4 kHz



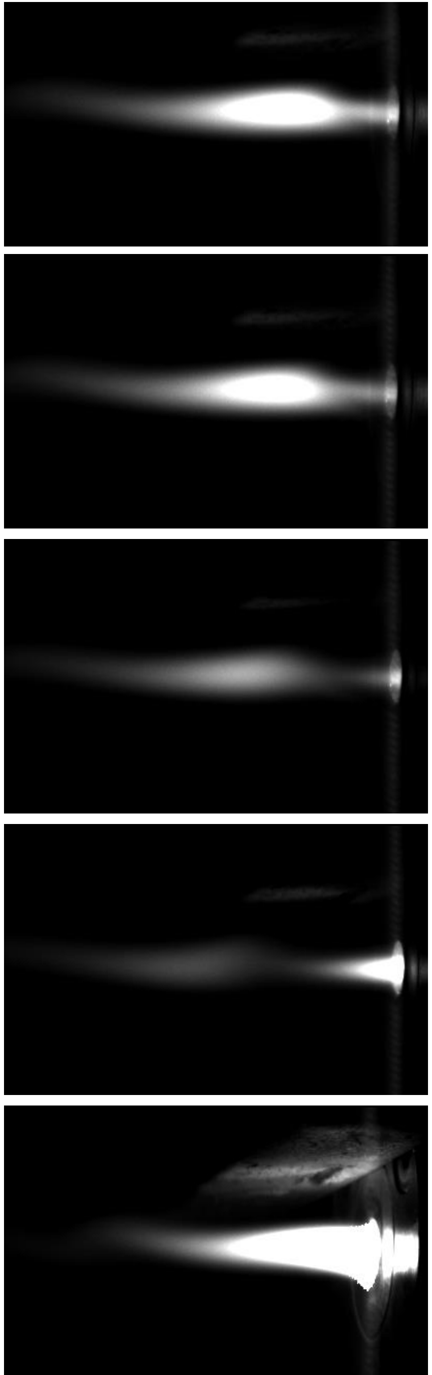


- **Délai de déclenchement τ_i**

I = 15 A, N_2 plasma, 3 slpm,



h_{moy}=13.3 MJ.kg^{-1}

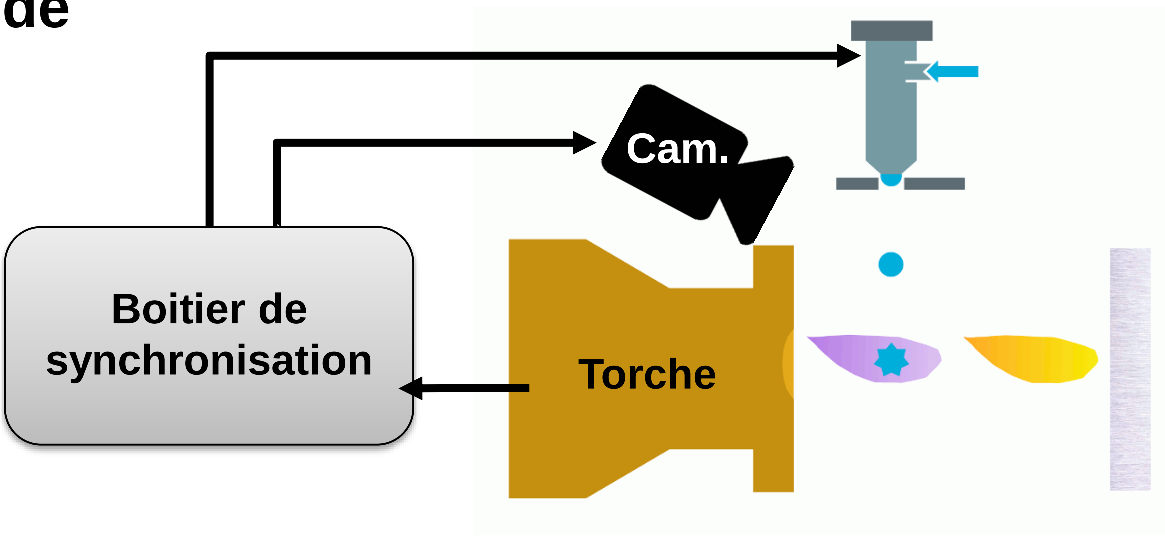


Exposition = 60 µs

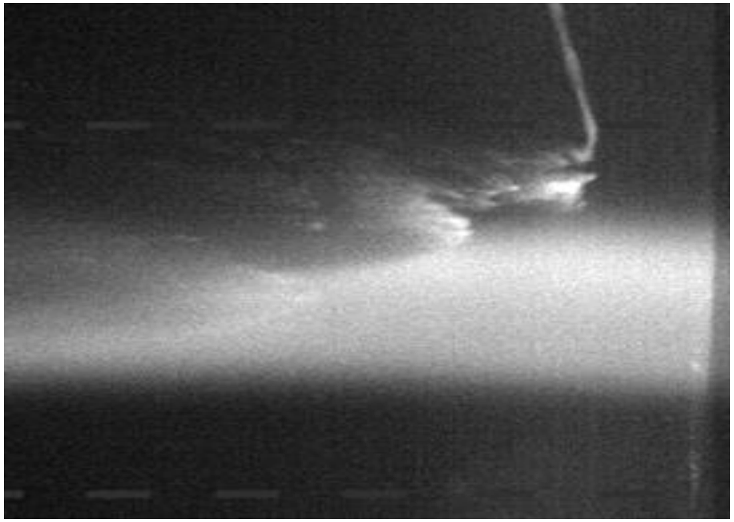
1 Période : 700 µs

f ~ 1.4 kHz

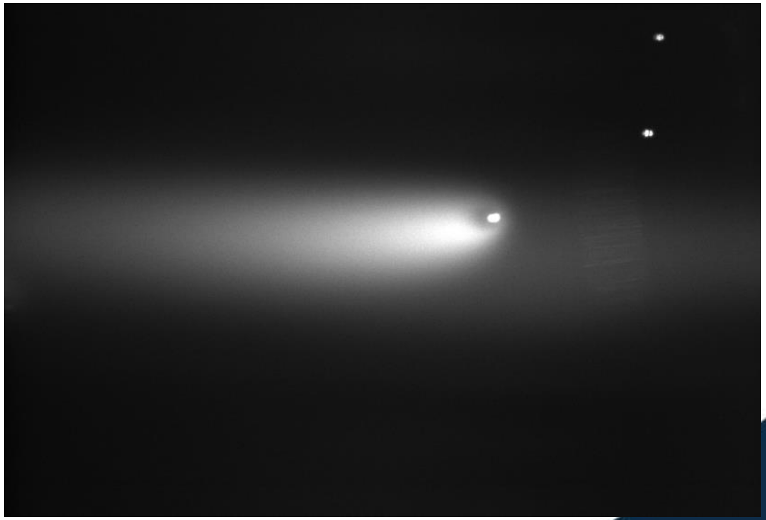
Synchronisation de l'éjection



Injection mécanique non contrôlée avec torche F4



Injection synchronisée avec torche pulsée



Projet AAE : Les livrables

➢ Sans injection de précurseurs:

- Identification des espèces et des systèmes par OES pour différents z et τ –T_{rot} (N_2^+)
- Lien avec enthalpie massique en mode pulsé mode libre et forcé I=f(t)

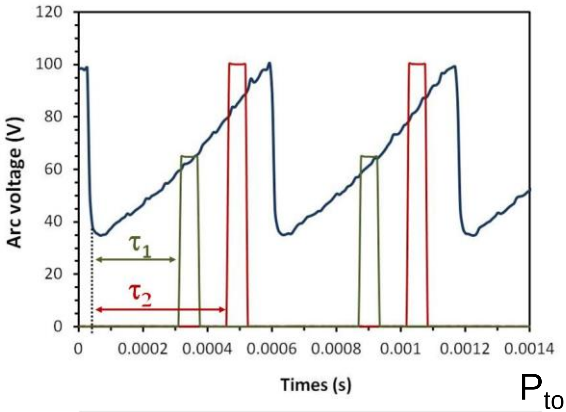
$$I(t) = I_0(1+\alpha\sin(2\pi f_0 t))$$

➢ Avec injection de précurseurs:

- Mise en place d'une monobuse
- Identification des espèces par OES (z et τ)
- Comparaison avec le cas sans injection

➢ Collecte/dépôt

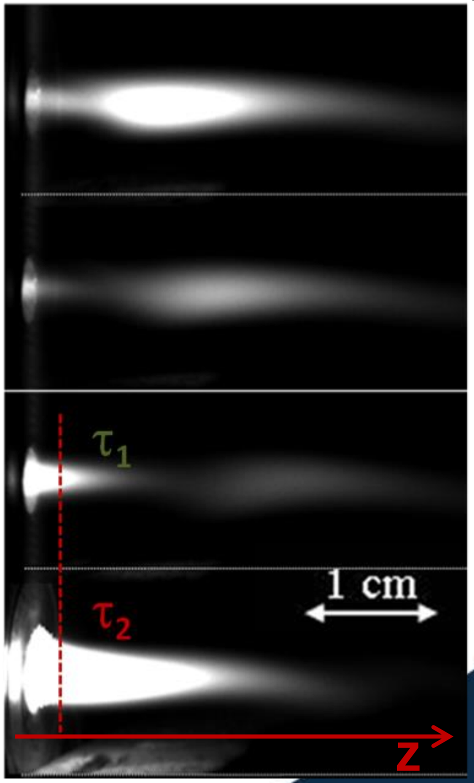
- Microstructure/structure des matériaux déposés (MEB, RX)



P_{torche}~1 kW

N_2

p_{atm}



Torche

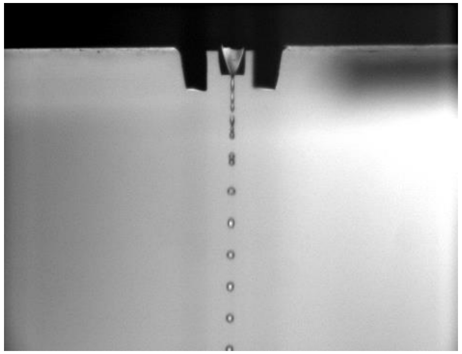
1) Compréhension du fonctionnement de la torche
   Lien entre tension et propriétés (enthalpie, vitesse)
   mesures / modèle simplifié en mode libre

2) Etude de l'influence de la modulation du courant sur la stabilité de la torche

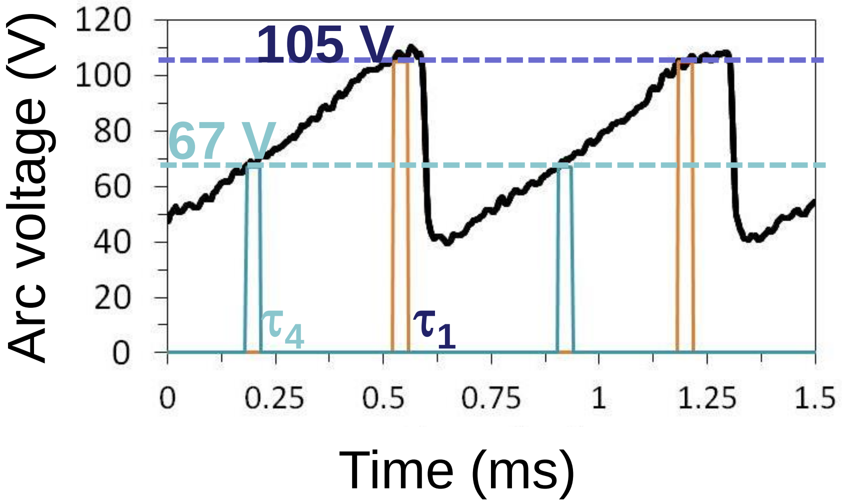
Monobuse

3) Installation de la monobuse

4) Optimisation des propriétés des encres



Modulation de l'enthalpie

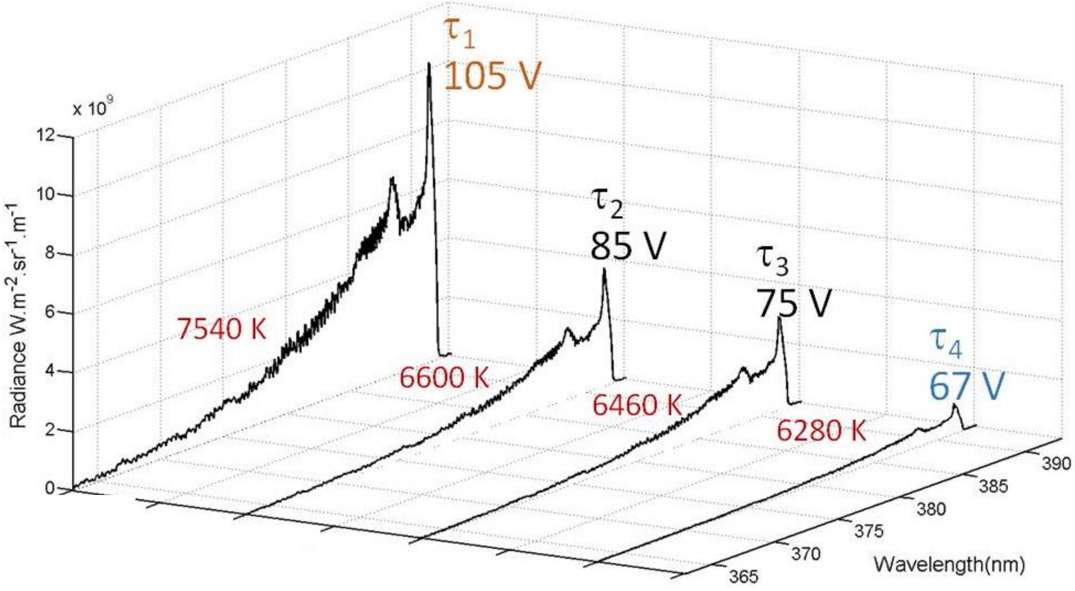


I = 15 A - constant

d = 1 mm

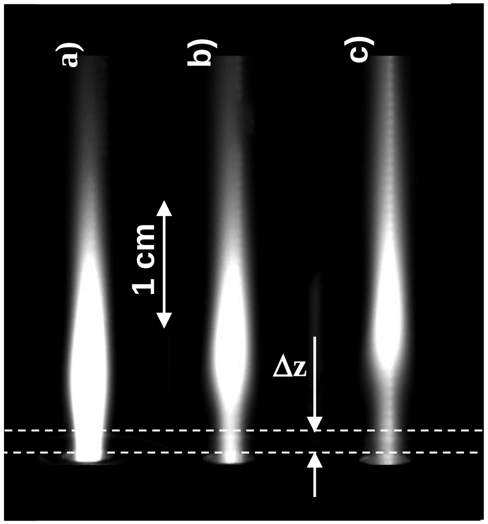
Premier système négatif de N_2^+

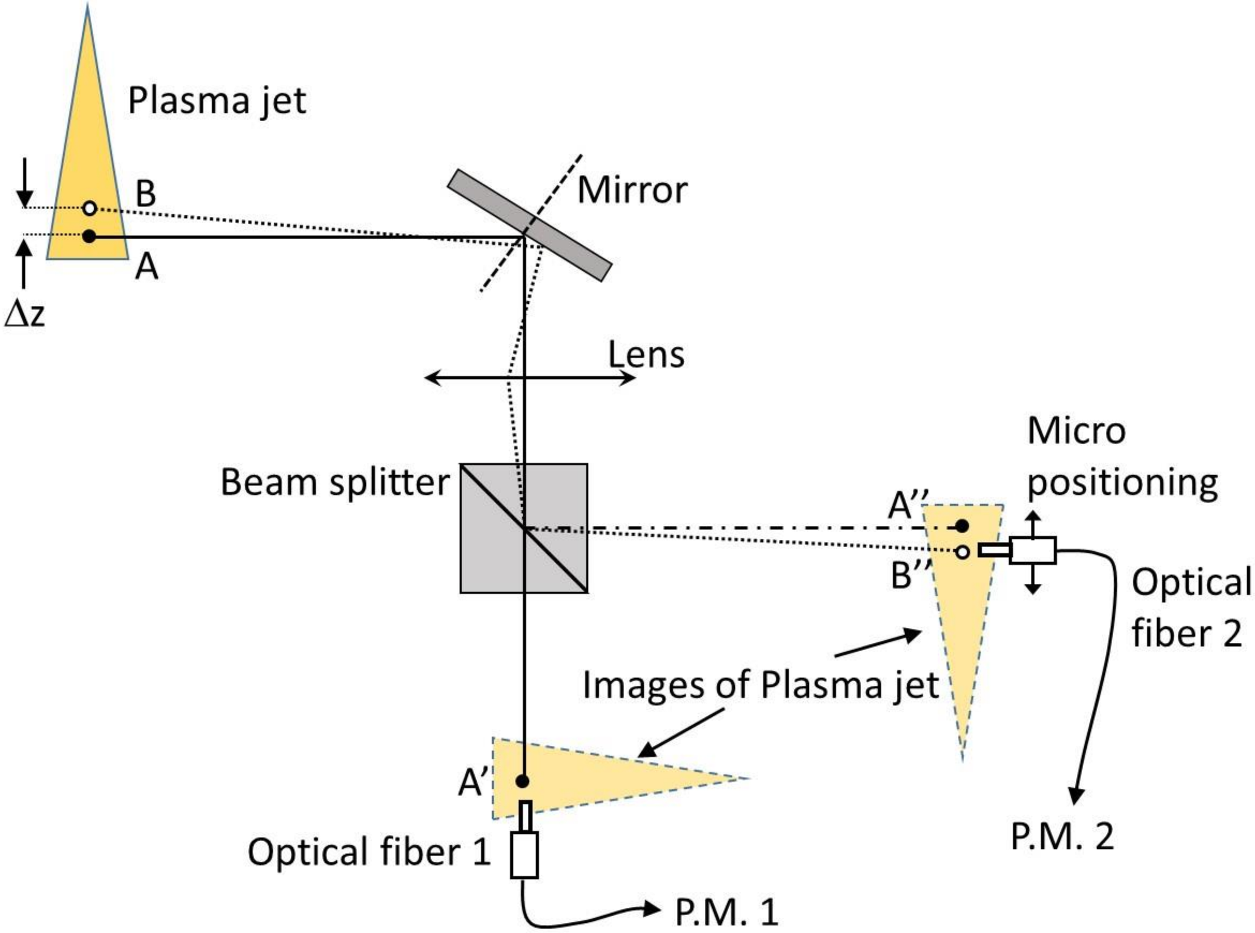
$$\bar{T} = \frac{\int \varepsilon_{N_2^+}^{(0,0)}(x,y)T(x,y)dxdy}{\int \varepsilon_{N_2^+}^{(0,0)}(x,y)dxdy}$$

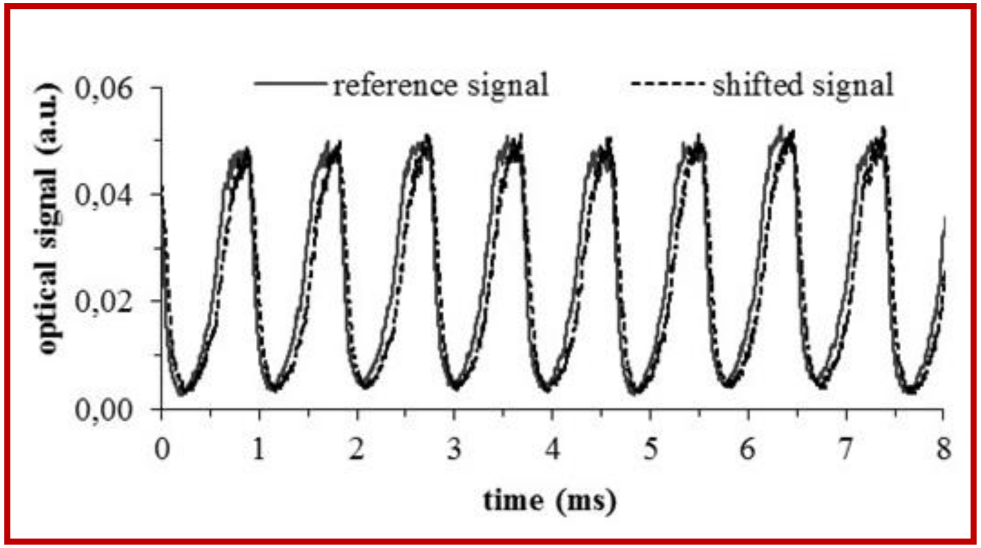


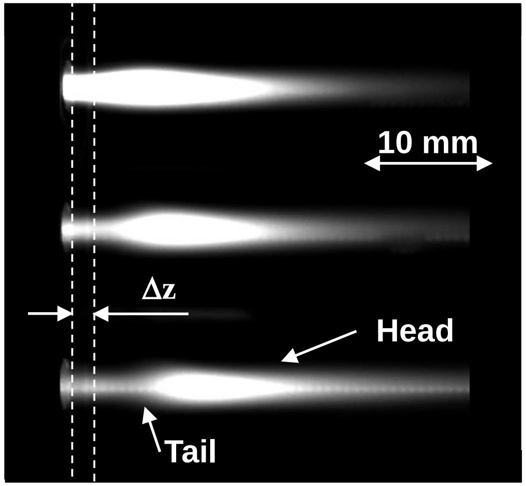
h_{moyen} = 9 - 25MJ.kg^{-1}

Mesure de la vitesse du plasma

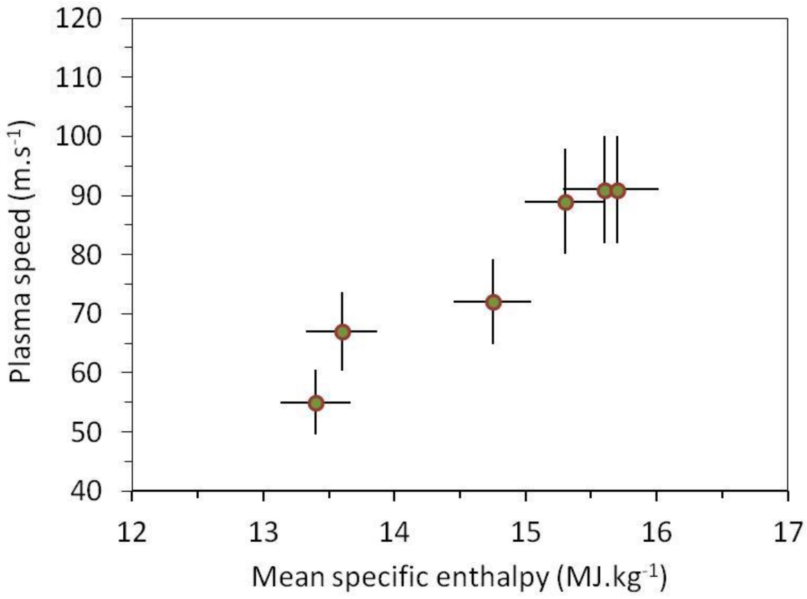




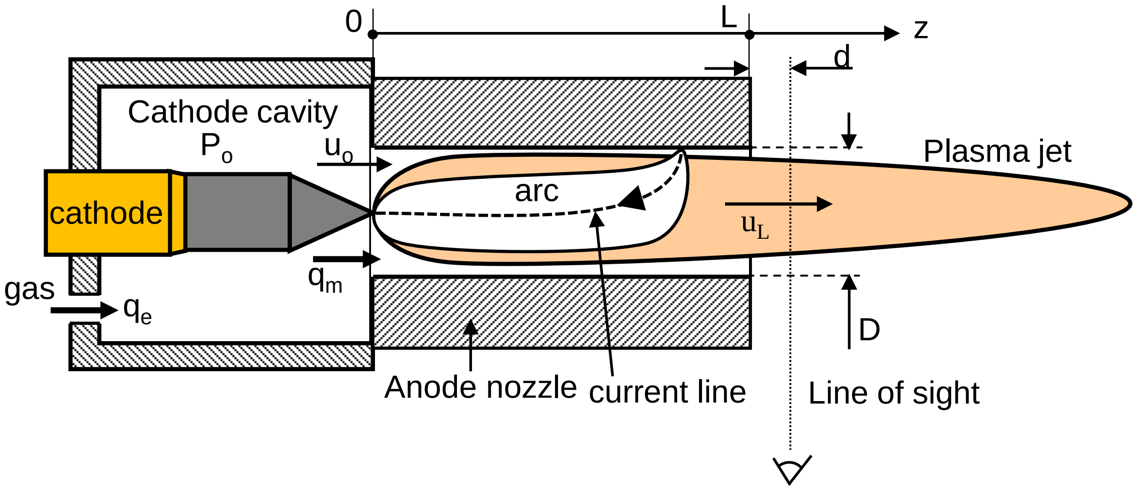




- Fonction d’intercorrélation
- Décalage temporel
- Vitesse moyenne $u = \frac{\Delta z}{\tau_0}$



Parameter coupling in a dc plasma torch



- *Input parameters*: torch geometry, plasma forming gases, arc current
  Arc voltage
- *Output parameters*: plasma specific enthalpy and speed
  mass flow rate, gas pressure inside the cathode cavity
- Properties averaged over the channel cross at nozzle exit
- 0D, transient, linear, analytical model

Integrating 1-D time dependent conservation equations over the axial distance z
L : nozzle length

Energy equation

$$m_p \frac{dh_L}{dt} + q_m (h_L - h_0) = -\alpha_{cr} L h_L \qquad q_m h_0 = (V_{arc} - V_{elec}).I$$

Momentum equation

$$L \frac{dq_m}{dt} + (u_L - u_0) q_m = -S(P_L - P_0) - \frac{L q_m}{\tau_f}$$

Mass balance in the cathode cavity

$$q_e - q_m = V_{cav} \left(\frac{\partial \rho}{\partial P} \right)_{cav} \frac{dP_0}{dt}$$

Fundamental frequency

$$\omega_0^2 = \left(\frac{\partial \rho}{\partial P} \right) \frac{S}{L V_{cav}}$$

Linearizing conservation equations $x = \bar{x} + x'$ $x = \{\ q_m \quad u_L \quad P_0 \quad \rho_L \quad h_L \quad V_{arc}\ \}$

Non-dimensional fluctuating components $h = -\rho$ $u = q - \rho = q + h$

Conservation equations

$$\dot{h} + \frac{h}{\tau} = \frac{v}{\tau} - \frac{q}{\tau_{res}} \qquad \ddot{q} + \frac{\dot{q}}{\tau_{cav}} + \omega_0^2 q = -\frac{\dot{h}}{\tau_{res}}$$

Characteristic times:

$$\frac{1}{\tau} = \frac{1}{\tau_{res}} + \frac{1}{\tau_{tr}} \qquad \frac{1}{\tau_{cav}} = \frac{2}{\tau_{res}} + \frac{1}{\tau_f}$$

Residence time

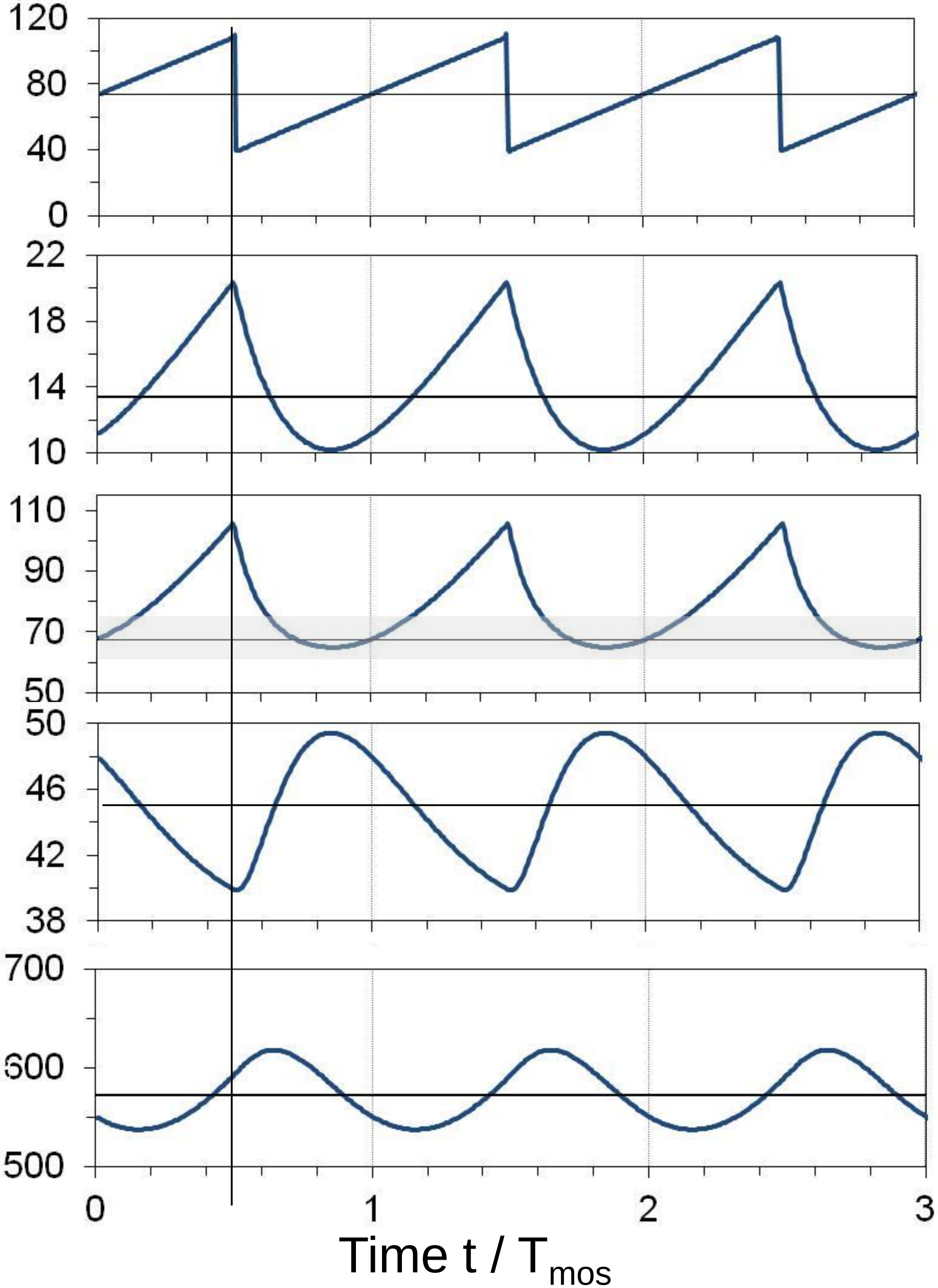
Heat transfer time

Viscosity effect

Fourier expansion

$$v(t) = \sum_{n=1}^{\infty} V_n \sin(\omega_n t)$$

Consistent with measurements



Arc voltage (V)

Enthalpy ($MJ.kg^{-1}$) $h_L(t)$

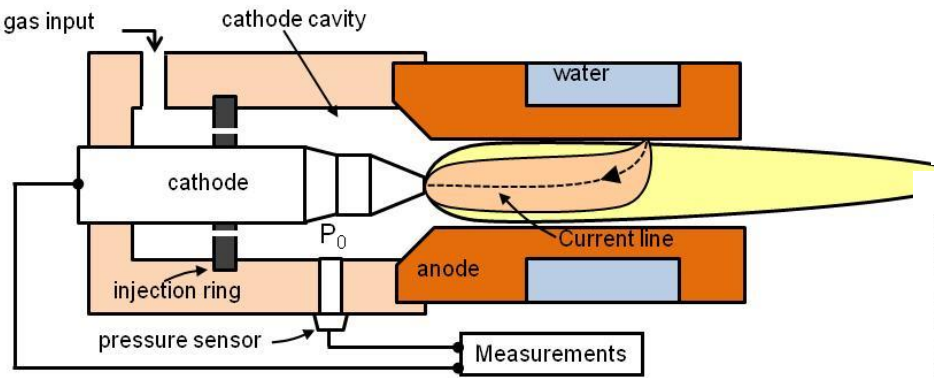
Plasma speed ($m.s^{-1}$) $u_L(t)$

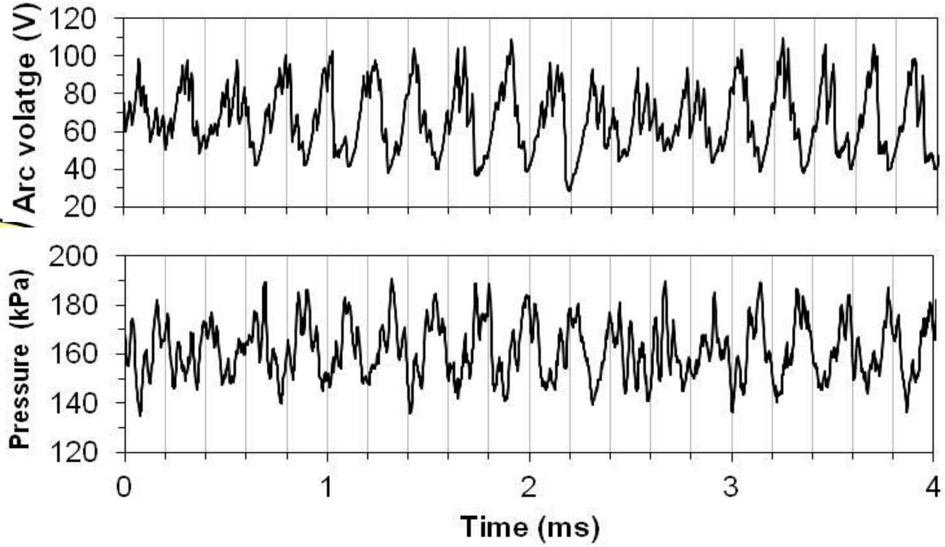
Mass flow rate ($mg.s^{-1}$) $q_m(t)$

Gas pressure in cavity (Pa)

$P_0(t)$

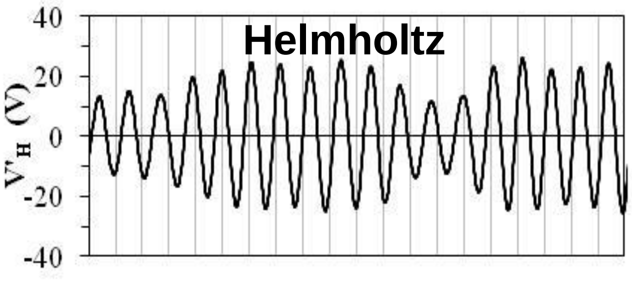
Coupling of arc voltage/pressure in dc arc torches

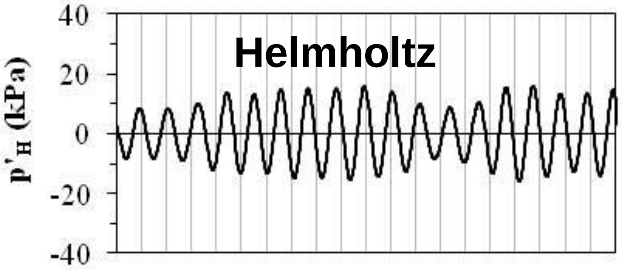




$$v(t) = \bar{v} + v_H(t) + v_R(t) + v_A(t)$$

$$P_0(t) = \bar{P}_0 + p_H(t) + p_R(t) + p_A(t)$$





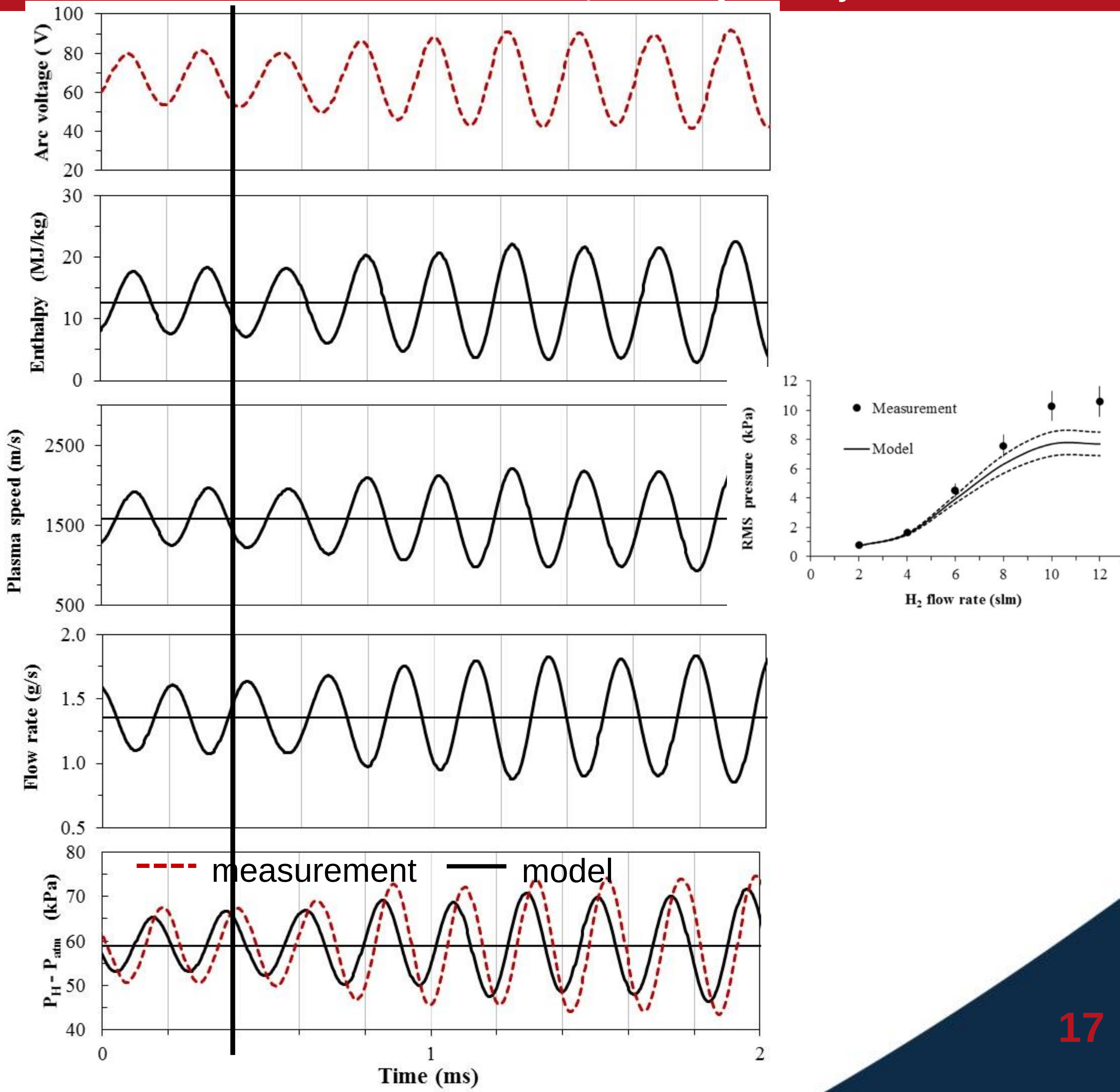
Helmholtz component after filtering (V)

Enthalpy (MJ.kg^{-1})

Plasma speed (m.s^{-1})

Mass flow rate (g.s^{-1})

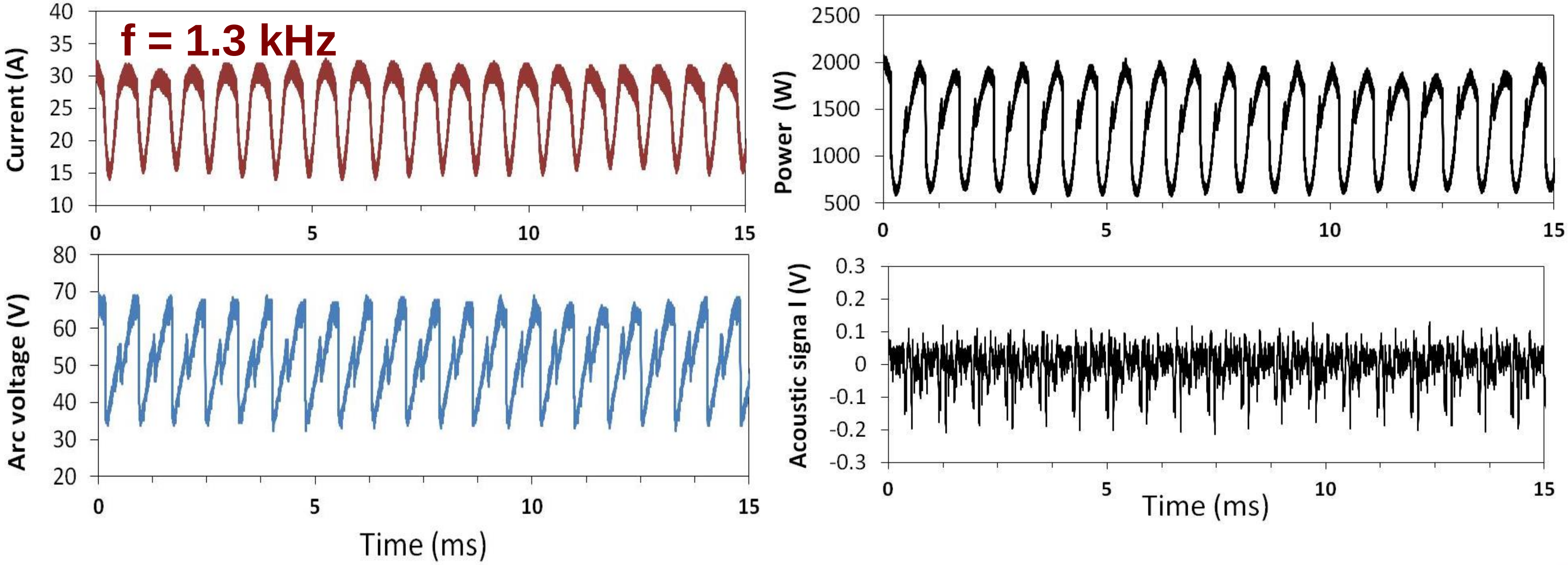
Pressure (kPa)
$\Delta P_H = P_H - P_{atm}$



What is the influence of the application of a time-dependent arc current ?

$$I(t) = I_0\left(1 + \alpha \sin\left(2\pi f_0 t\right)\right)$$

- Is a resonance effect favored by arc current oscillations ?

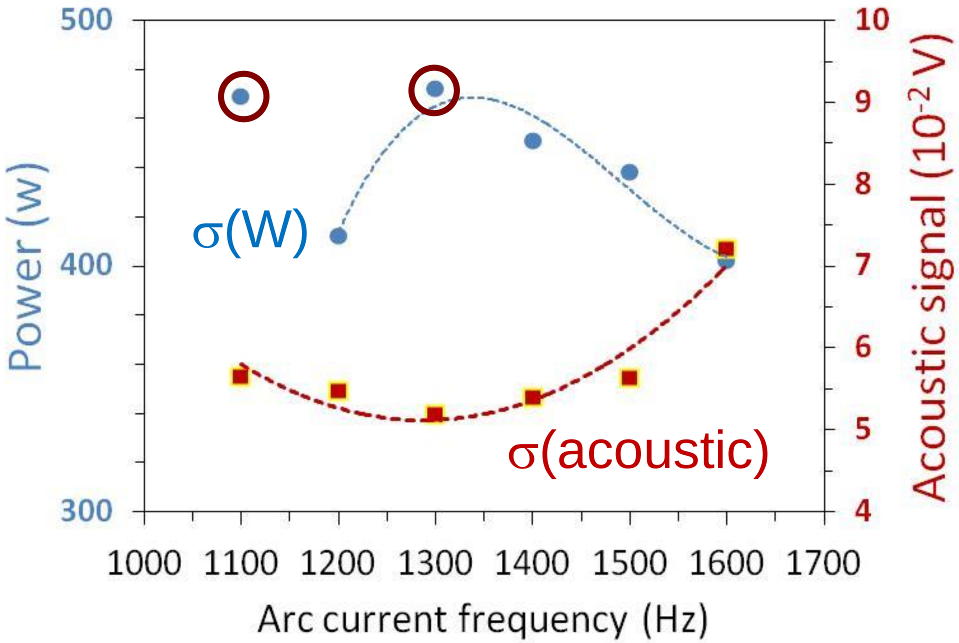


Acoustic emission: Fitaire law

$$a(t) \propto \frac{dP}{dt}$$

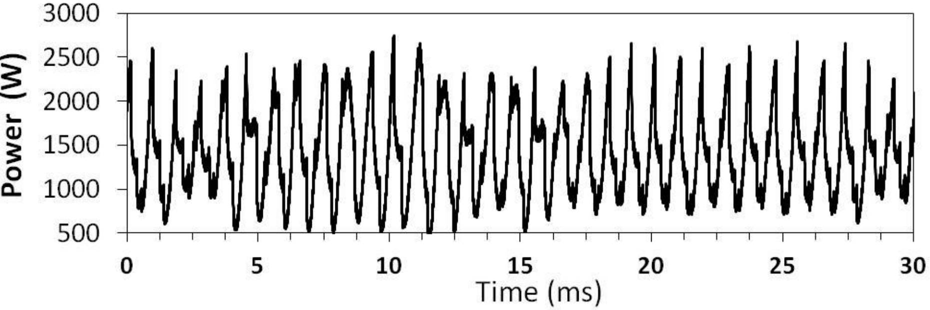
Influence of the arc current frequency applied

$\bar{I} = 25A \qquad \sigma(I) \sim constant$

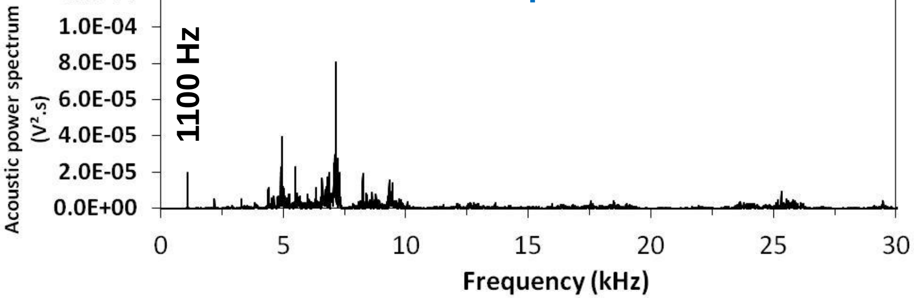


1100 Hz

Power

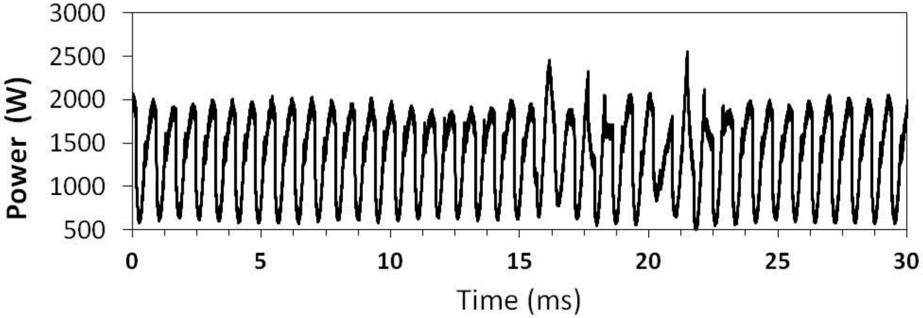


Acoustic spectrum

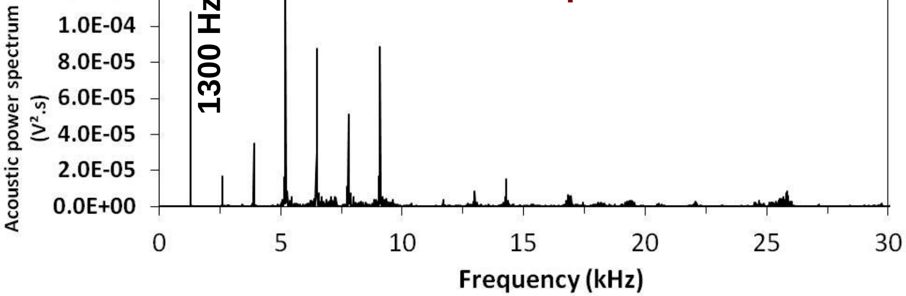


1300 Hz

Power



Acoustic spectrum



$$\sigma_a^2 = \int_0^{f_{max}} \Phi_a(f)\,df$$

- ➢ **the arc current frequency affects the arc oscillation : stabilizing mechanism of resonant mode**

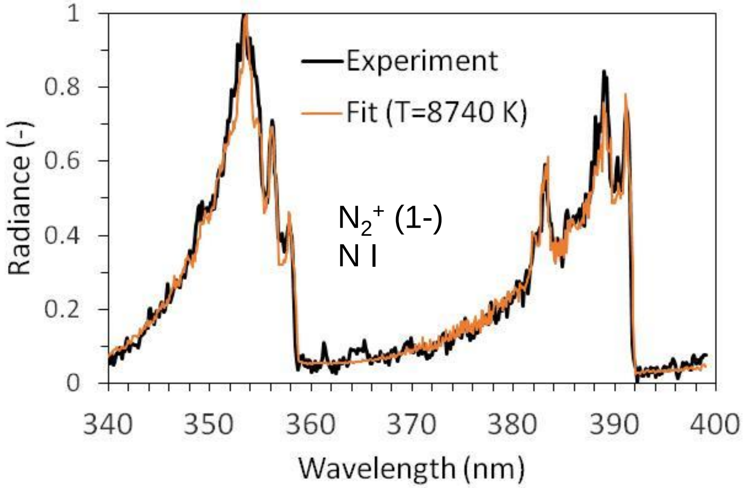
Enthalpy modulation : temperature measurements

Arc current frequency 1300 Hz

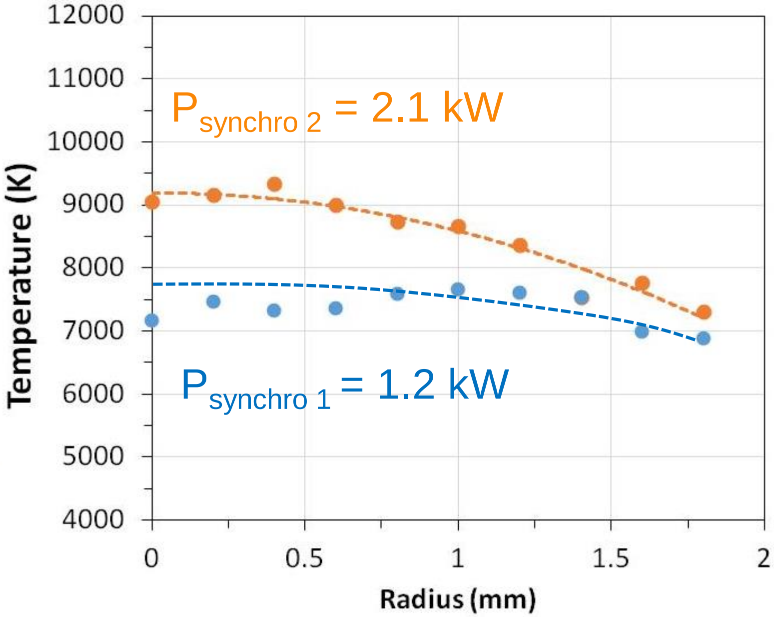
2 trigger times : **$P_{synchro\ 1}$ = 1.2 kW** =and **$P_{synchro\ 2}$ = 2.1 kW**

Exposure time 30 µs + accumulation N_{acc} ~ 50-200

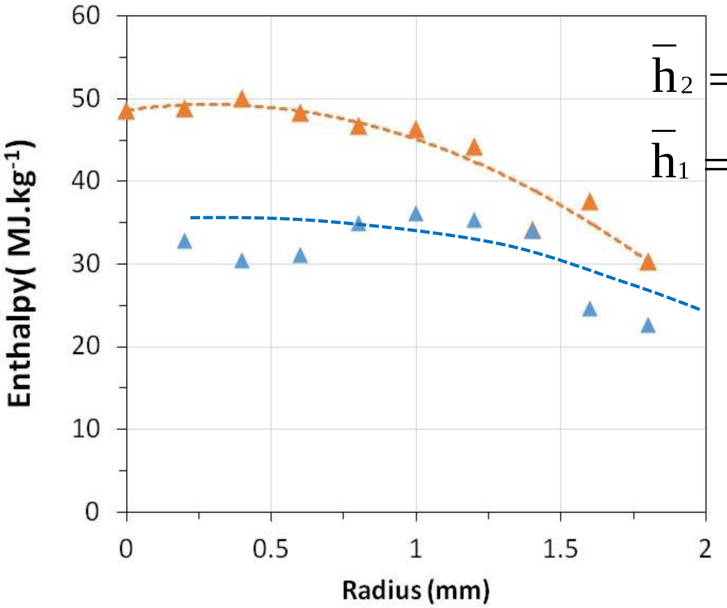
Abel inversion



Temperature profile



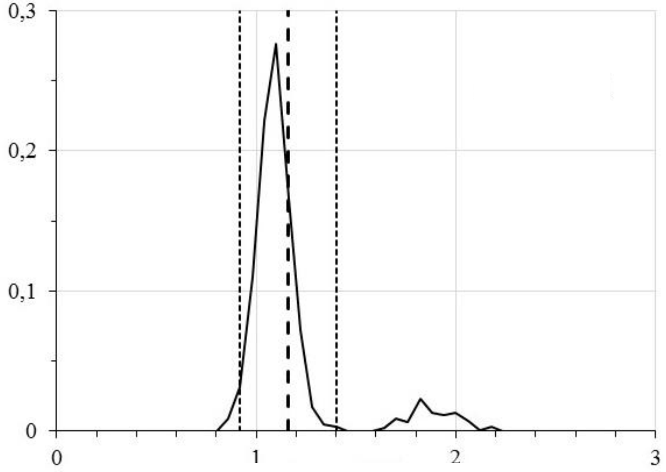
Enthalpy profile



$$\bar{h}_2 = 35.76\ \mathrm{MJ.kg^{-1}}$$

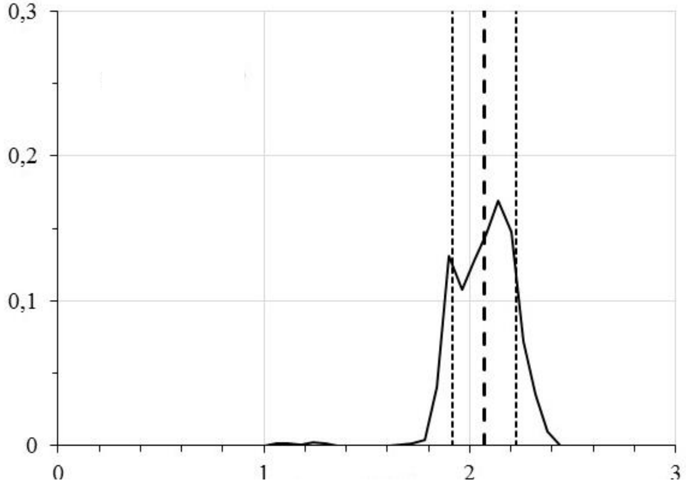
$$\bar{h}_1 = 27.15\ \mathrm{MJ.kg^{-1}}$$

$$\overline{P}_{\text{synchro}\,1} = 1.19\ \text{kW} \qquad \sigma\left(\overline{P}_{\text{synchro}\,1}\right) = 0.24\ \text{kW}$$



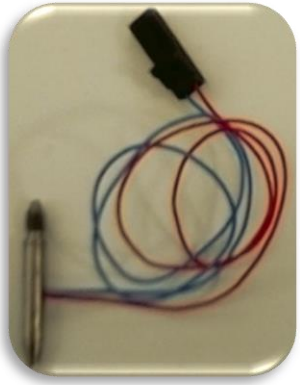
$P_{\text{synchro}\ \mathbf{1}}$ (kW)

$$\overline{P}_{\text{synchro}\,2} = 2.10\ \text{kW} \qquad \sigma\left(\overline{P}_{\text{synchro}\,2}\right) = 0.15\ \text{kW}$$

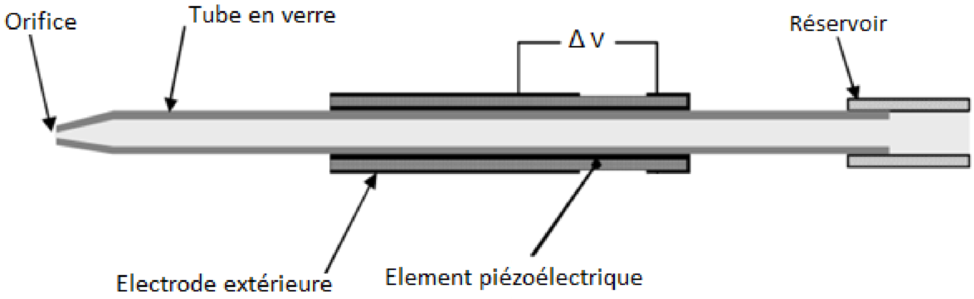


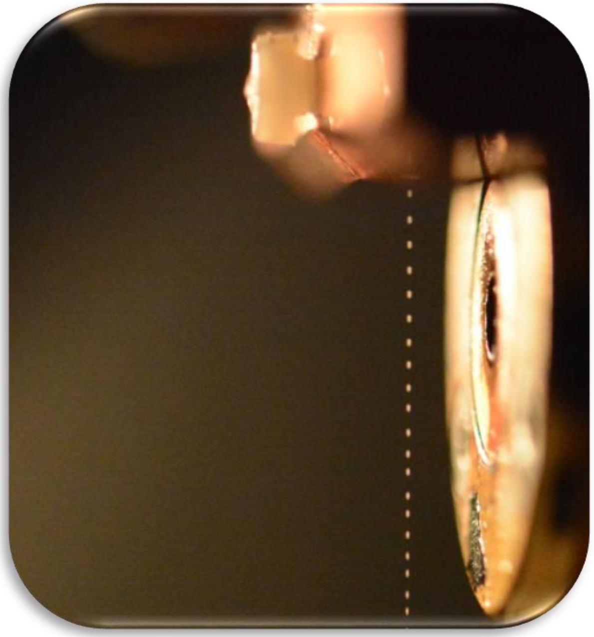
$P_{\text{synchro}\ \mathbf{2}}$ (kW)

Dispositif d'injection jet d'encre drop-on-demand



Monobuse





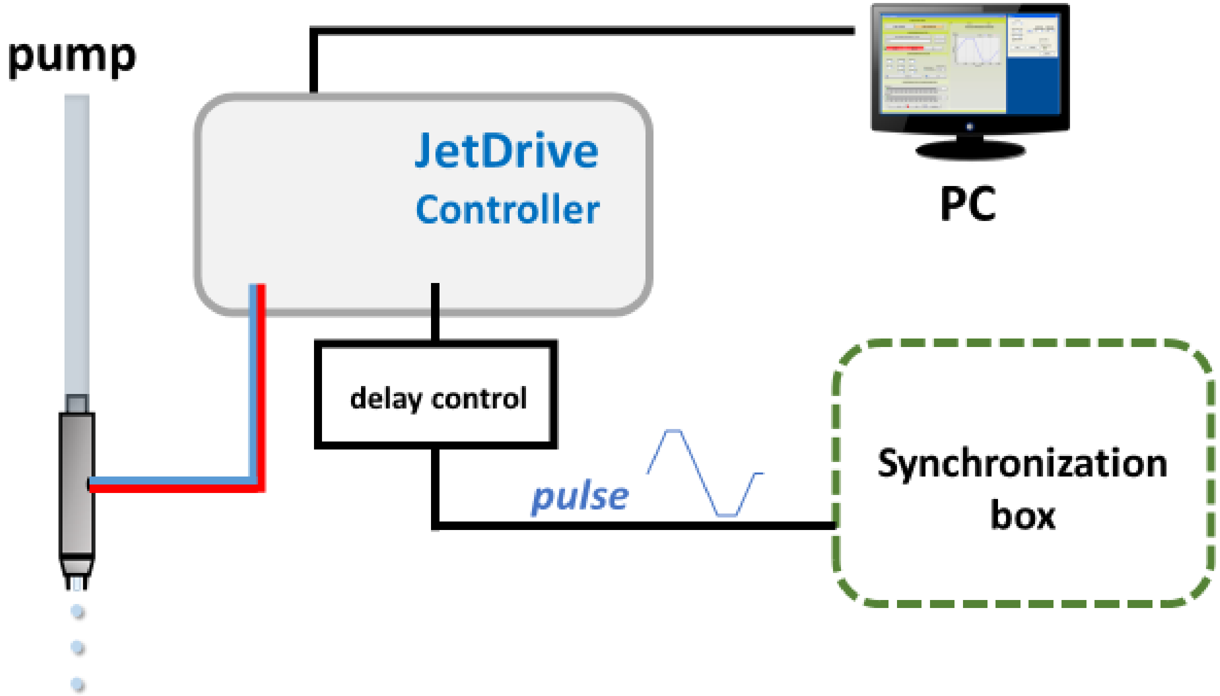
➢ Recommandations du fabricant

Diamètre de l'orifice	80 µm +/- 1 µm
Température maximale du fluide	50 °C
Tension de surface du fluide	30 - 50 mN/m
Viscosité du fluide	4 – 8 mPa.s
pH du fluide	2 – 11

➢ Rapport d'éjection

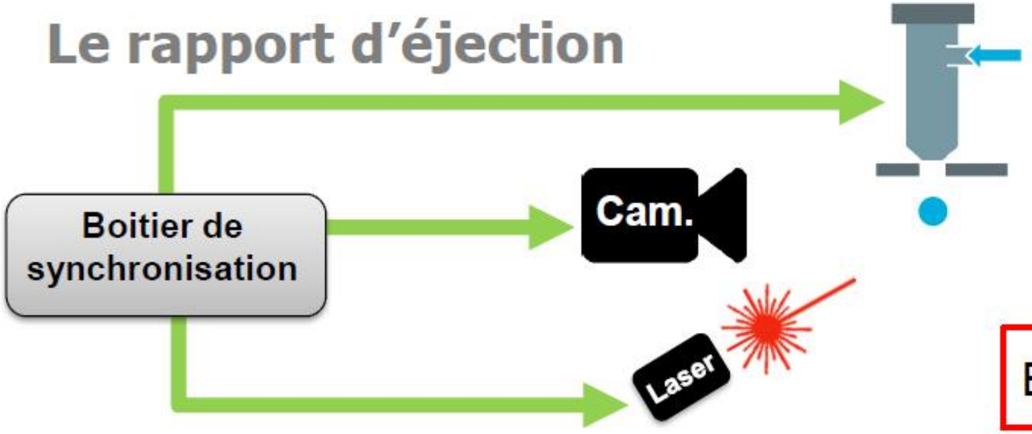
$$Z = \frac{Re}{\sqrt{We}} = \frac{\sqrt{\boldsymbol{\rho\,\gamma\,r}}}{\boldsymbol{\eta}}$$

monobuse piézo-électrique



- Temps de réponse du piézoélectrique
  (mesure vitesse du son)

Le rapport d'éjection



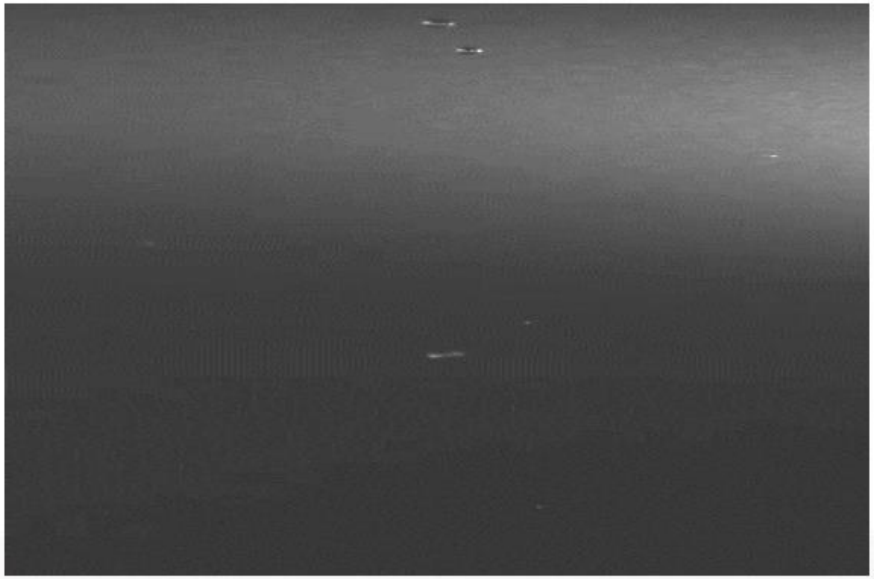
Boitier de synchronisation

Cam.

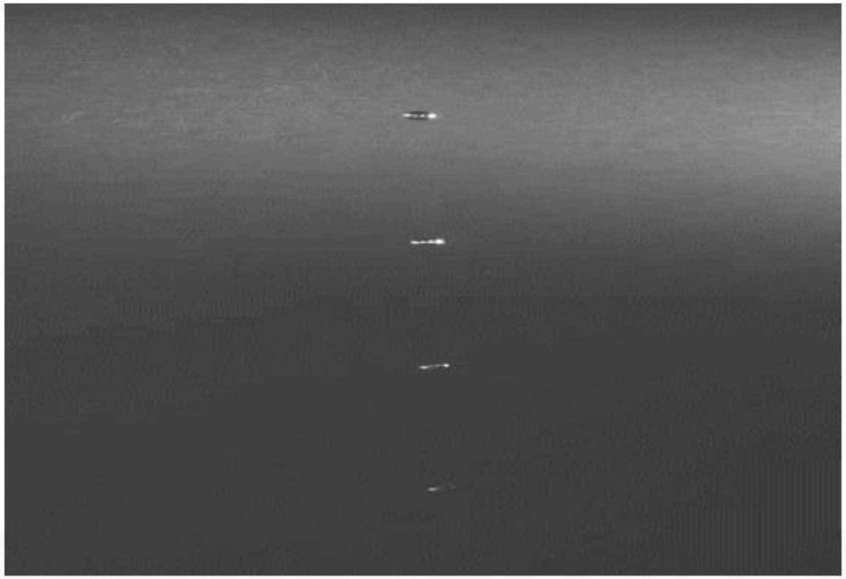
Laser

- Viscosité **η**
- Tension de surface **γ**
- Masse volumique **ρ**
- Rayon de l'orifice **r**

Éjection stable → $1 < Z < 10$



Z =14



Z =8

Formulations

Milieu aqueux

Tension de surface trop grande → ajout de tensio-actif (BRIJ 58)
Viscosité trop faible → ajout de glycérol ($C_3H_8O_3$)

- **Solution étalons**

Avec différentes quantités de glycérol (23 à 55 % volumique)

- **Suspension d'anatase (TiO_2)**

Commerciale 20 % massique
Taille des particules 20 nm

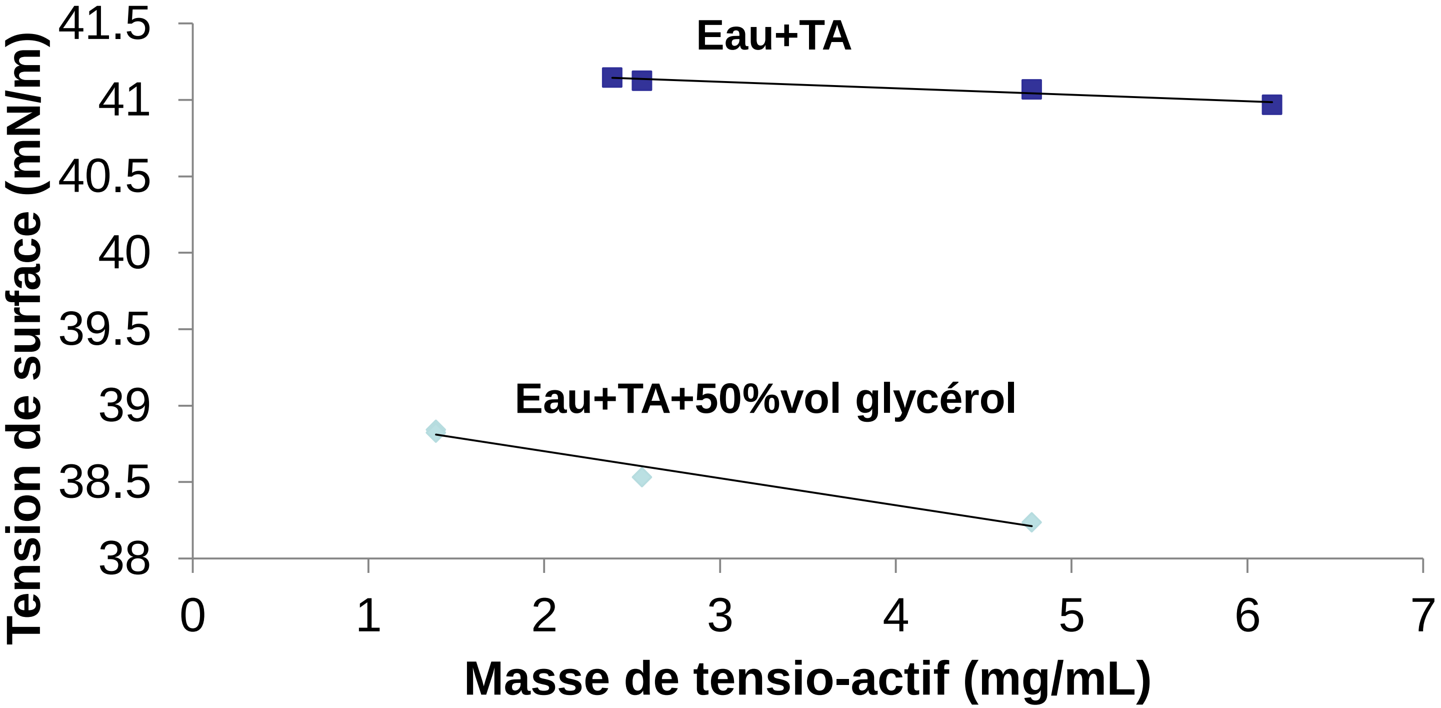
- **Solution de nitrate d'aluminium ($Al(NO_3)_3$)**

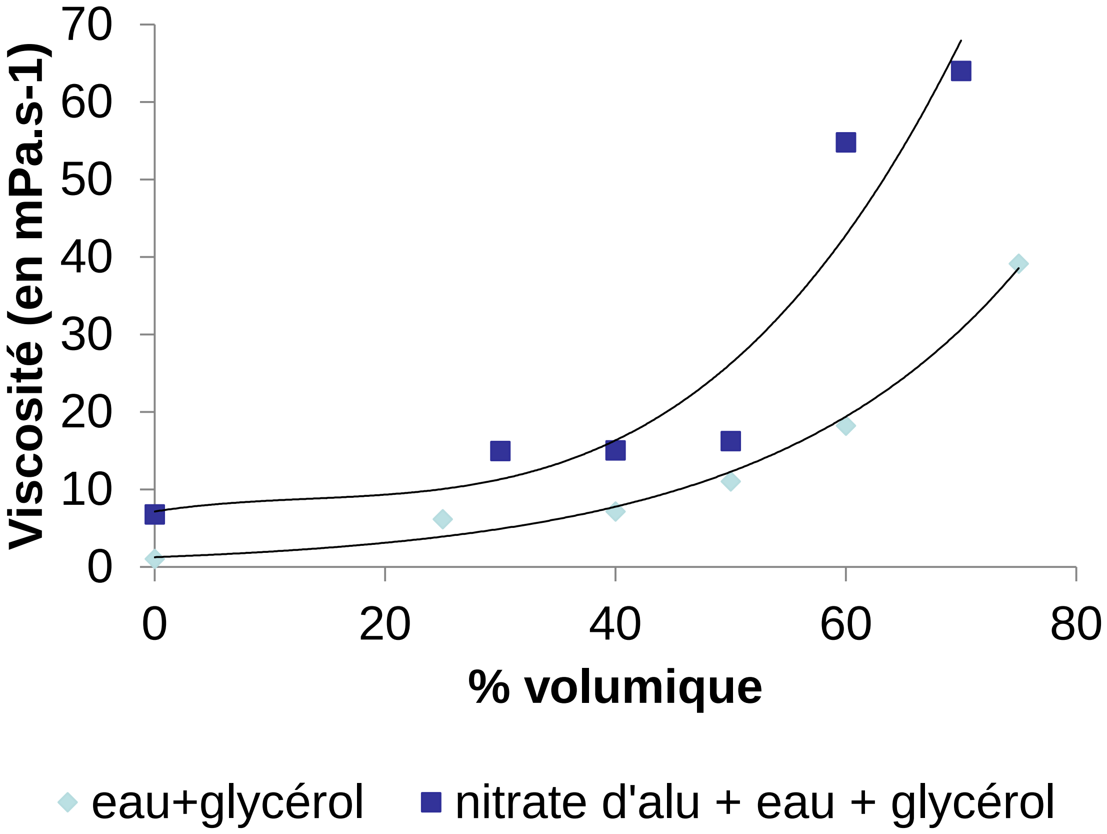
[Eau + TA (<0.1%mass)] + nitrate d'aluminium (39 %mass) + glycérol (31% mass) + NaOH (PH, <1%mass)

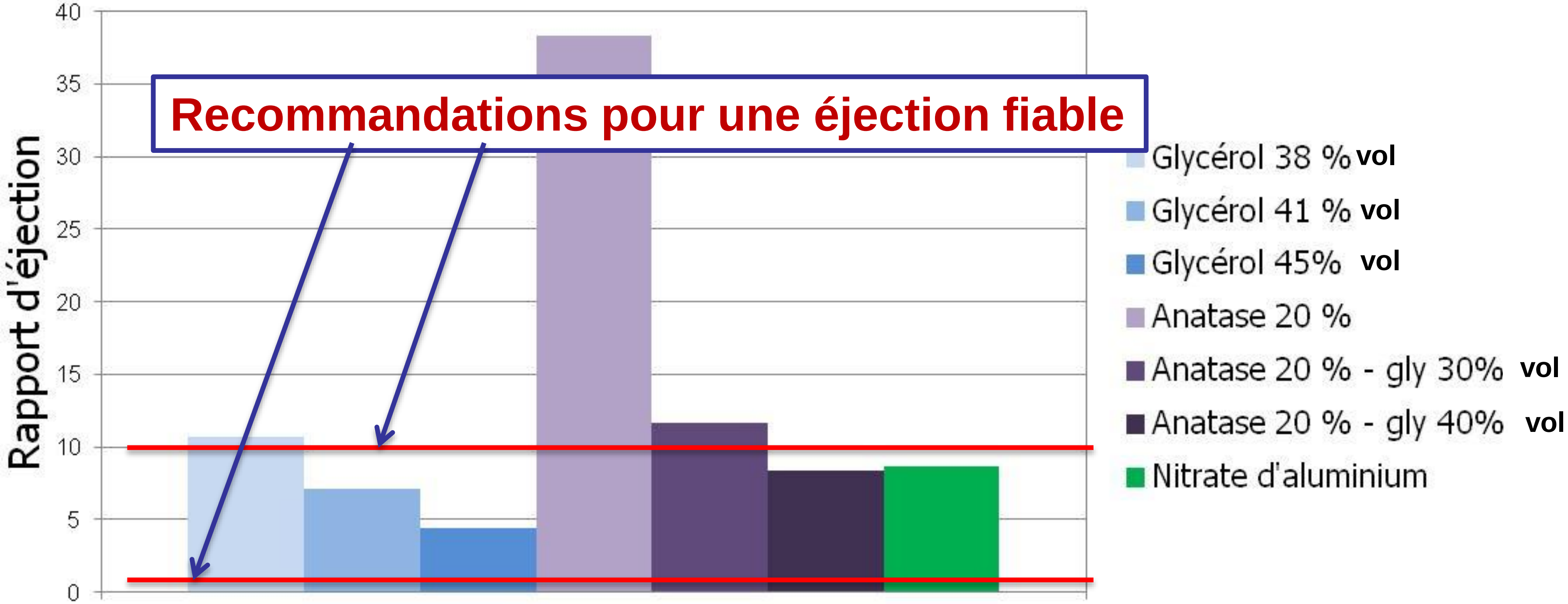
Elaboration solution de nitrate d'aluminium

Sans tensio-actif : mélanges eau + glycérol [63-70 mN.m^{-1}]

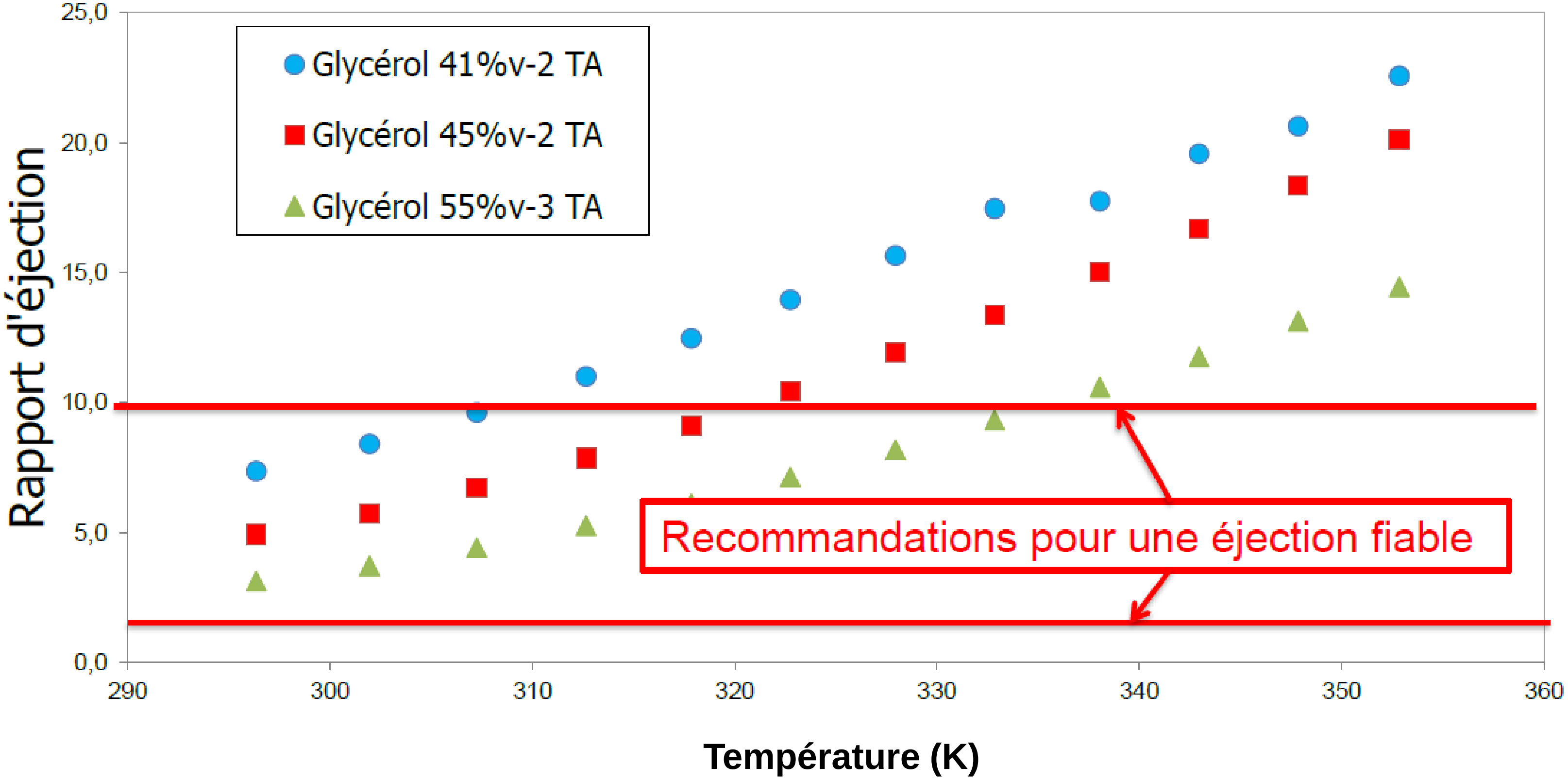
- **Brij58 - tensio-actif - $HO(CH_2CH_2O)_{20}C_{16}H_{33}$**
- **L'ajout de sel de nitrate d'aluminium modifie peu la tension de surface**




Viscosité (en mPa.s-1)
70
60
50
40
30
20
10
0
0
20
40
60
80
% volumique
◆ eau+glycérol
■ nitrate d'alu + eau + glycérol

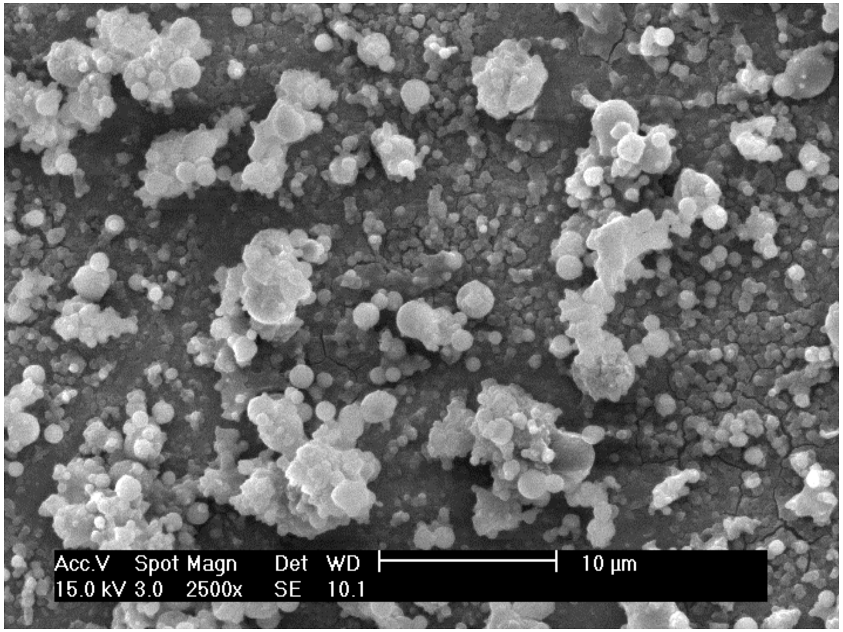


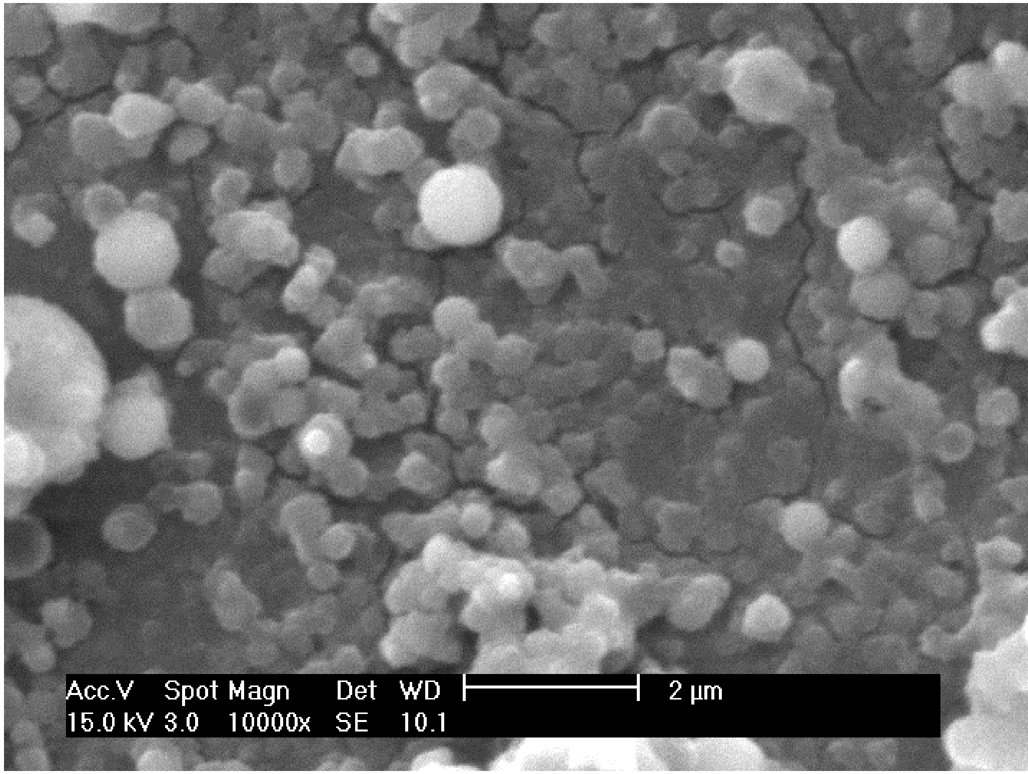
Recommandations pour une éjection fiable

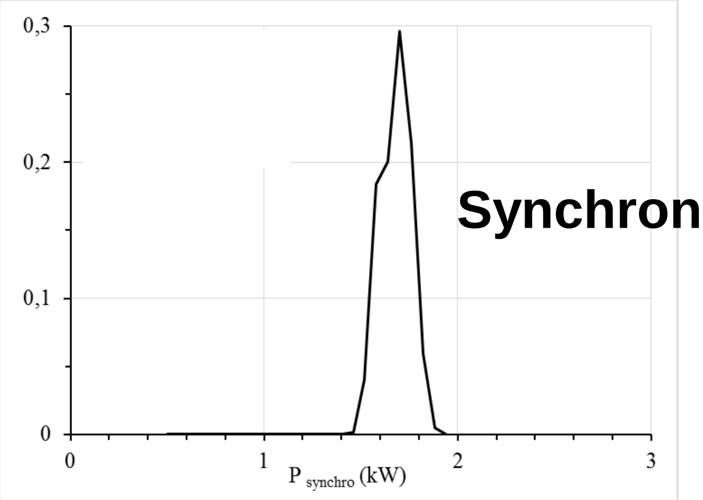


Recommandations pour une éjection fiable

Projection de la solution de nitrate d’aluminium







Synchrone

Projection de la solution de nitrate d’aluminium

Non synchrone