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# Surface-Enhanced Raman Scattering for arsenic detection and speciation

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## Introduction

- Arsenic is the 20th most common element in Earth's crust. In natural water **we found** it as inorganic ions : As(3) and As(5). The World Health Organization (WHO) recommended an arsenic concentration of 10µg/L (10ppb)
- The table below is a comparison between the existing arsenic detection methods and our developing method (SERS sensor)

	Mass spectrometry induced coupled plasma (ICP-MS)	Gutzeit method	SERS sensor
<b>Advantages</b>	Reference technique As speciation	Rapid measurement Low cost	Instantaneous measurement Turnkey device As Speciation
<b>Inconveniences</b>	Expensive Sample treatment before analysis	Unreliable Arsine production No As speciation	No tested method Unknown speciation

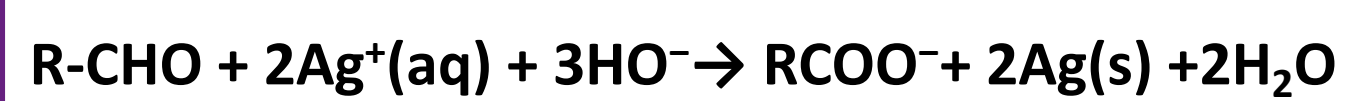
## Objectives

- Comparison of two SERS substrates : one made by chemical process (electroless substrate) and the other one by physical process (evaporation substrate)
- Arsenic detection by SERS substrates at the WHO recommendation (10µg/L) and discrimination of the two arsenic species (As(3) and As(5))

## SERS substrates elaboration and characterisation

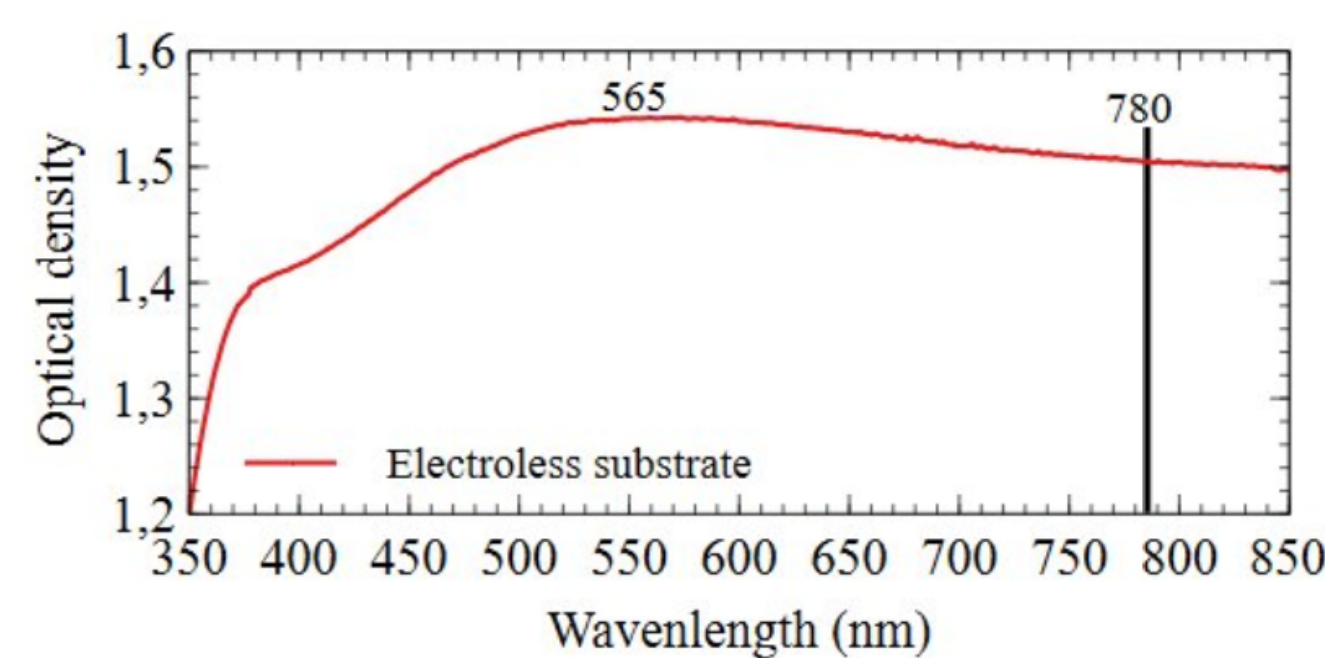
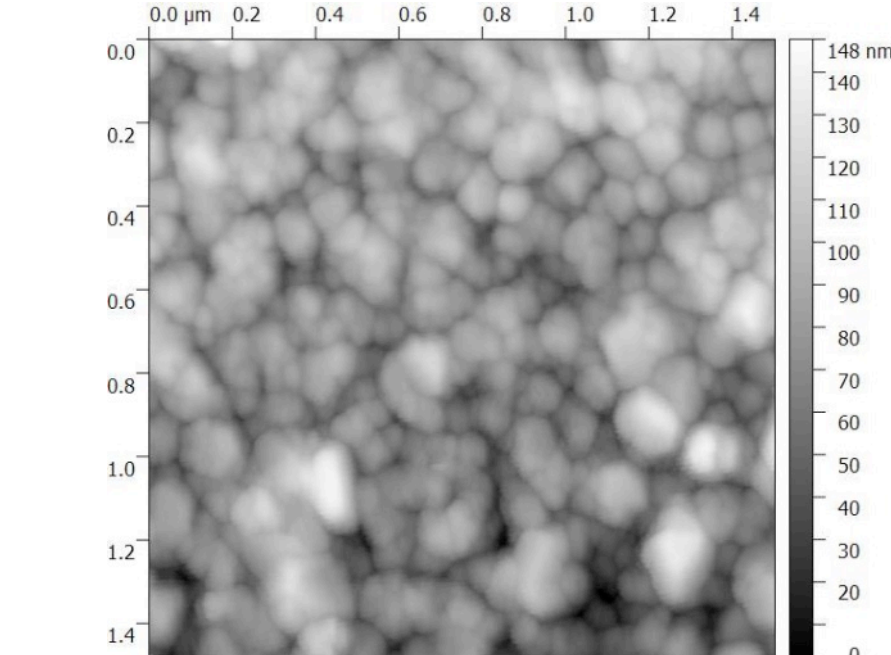
### 1. Electroless substrate:

Redox reaction without generator  
Aldehyde oxidation → carboxylic acid  
Ag<sup>+</sup> reduction → mirror coating

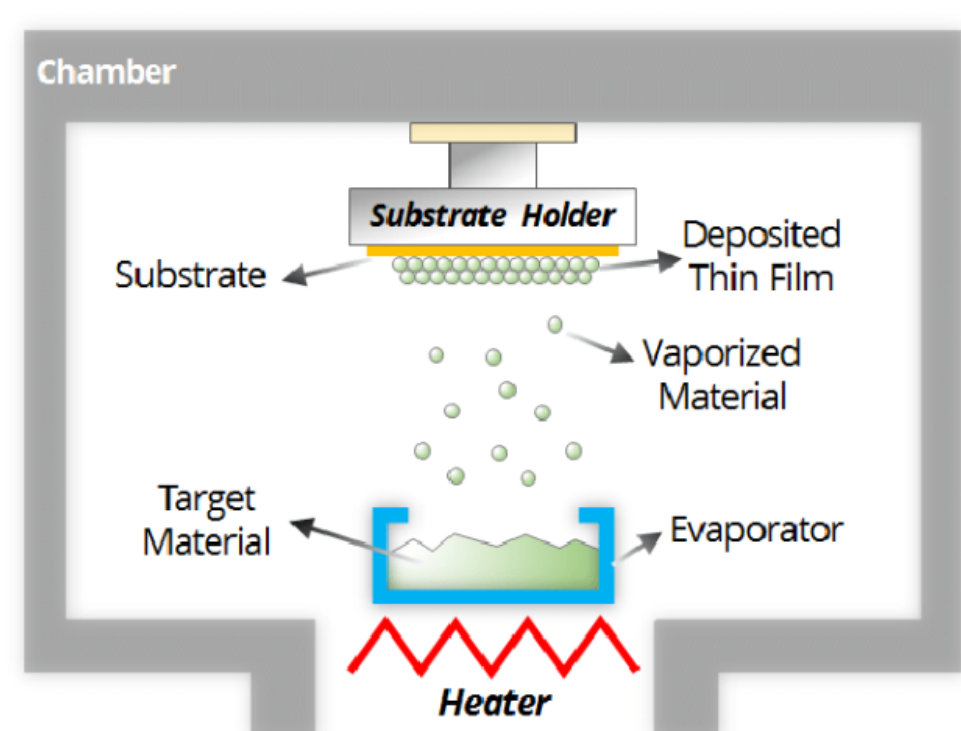


- Granular layer
- Particle size : 101 ± 10 nm
- Roughness : 21 nm
- Localized/propagative? surface plasmon resonance (LSPR) located at 565 nm
- Limit Methylene blue detection : 10<sup>-8</sup> mol/L

### AFM image

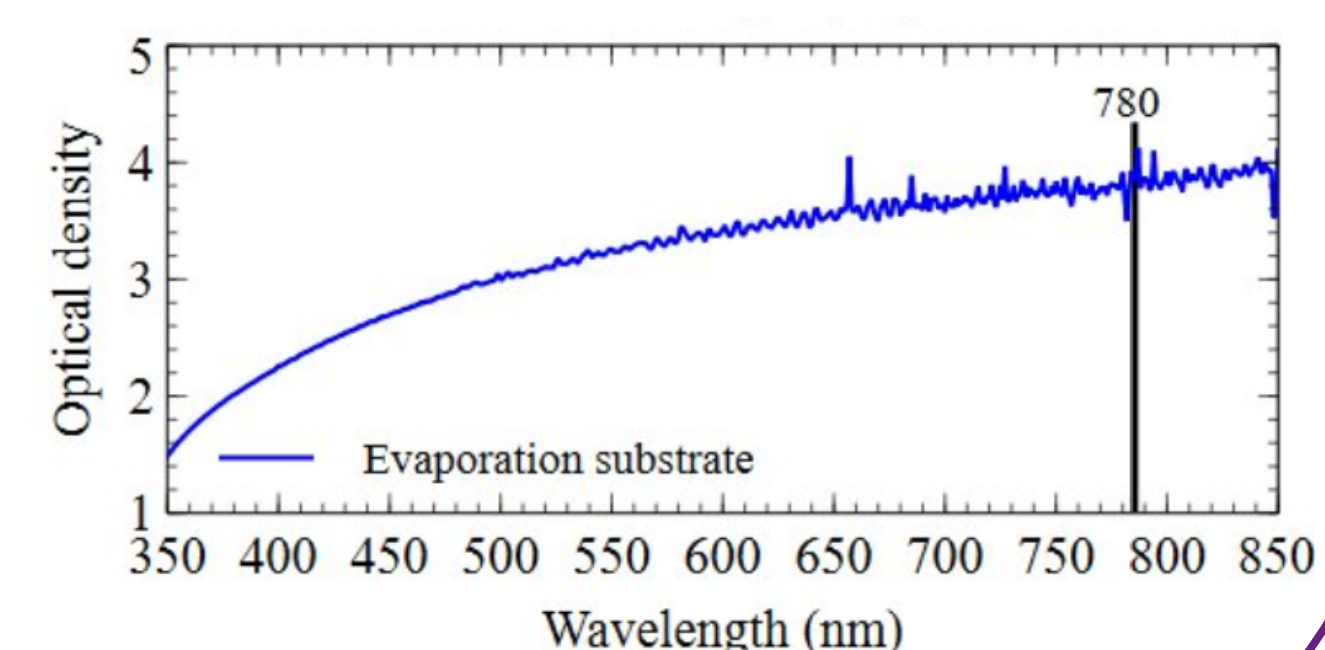
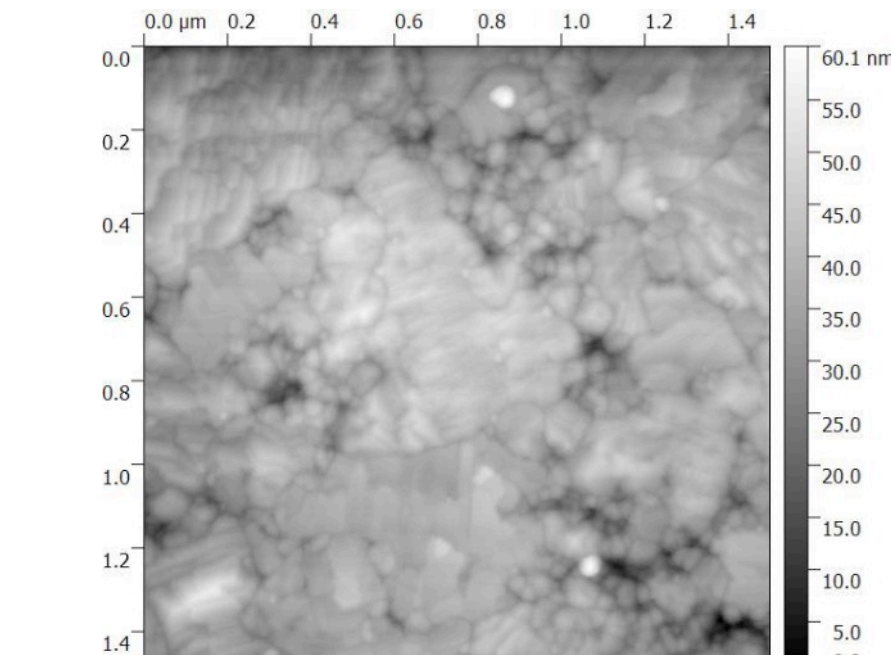


### 2. Evaporation substrate:



- Continuous layer
- Particle size : 101 ± 10 nm
- Roughness : 3 nm
- No LSPR → Propagative plasmon (SPP) ?
- Limit Methylene blue detection : 10<sup>-5</sup> mol/L

### AFM image



Methylene blue is a probe SERS molecule

## Surface-Enhanced Raman Scattering (SERS)

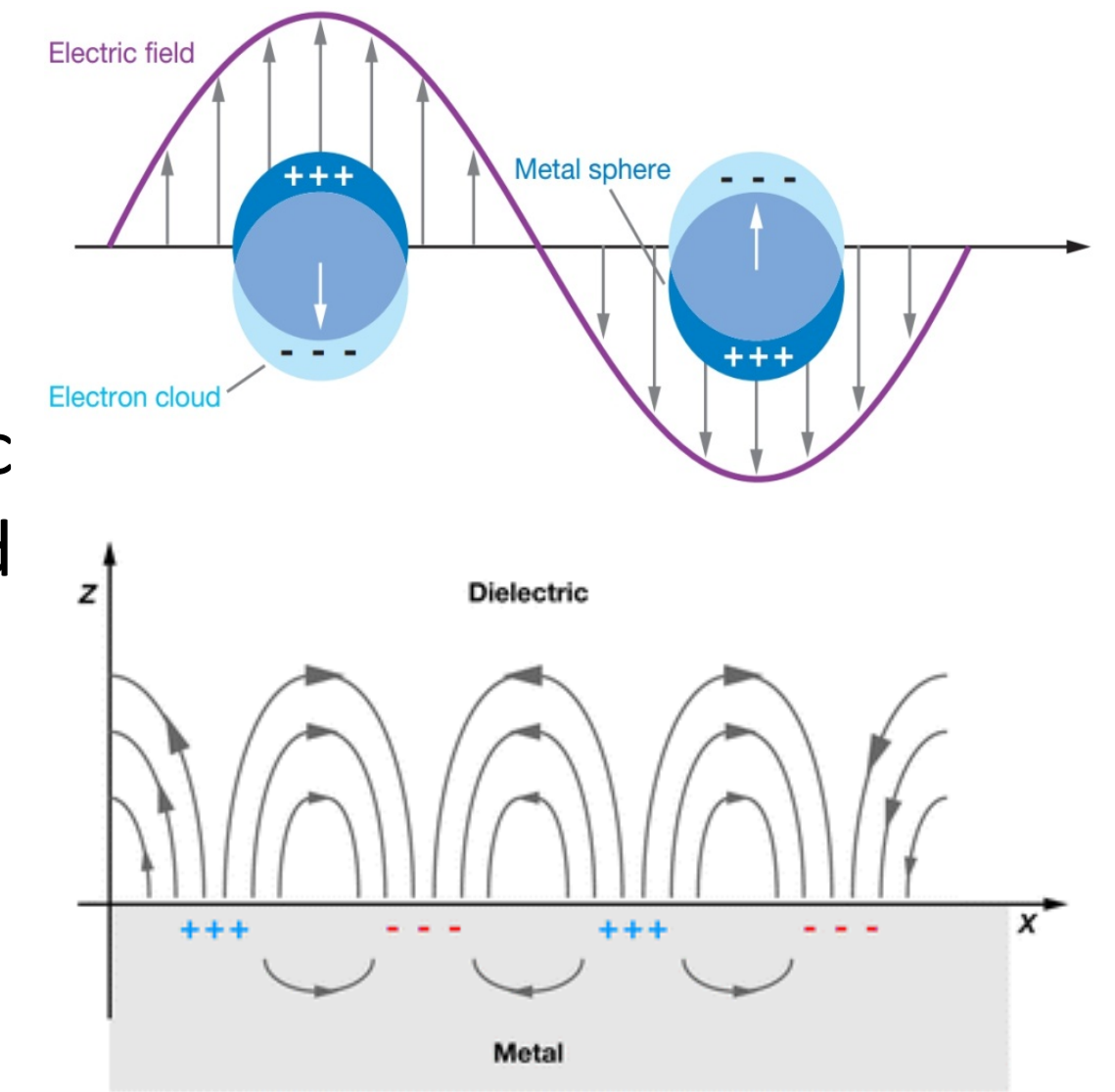
- SERS at the interface between Raman probed materials and a noble metal with a negative real part dielectric constant  $\epsilon(\omega) < 0$  (Au, Ag ...)
- Two mechanisms are responsible for SERS :

$$I_{Raman} \propto \alpha^2 E_{loc}^2$$

### 1. Electromagnetic effect :

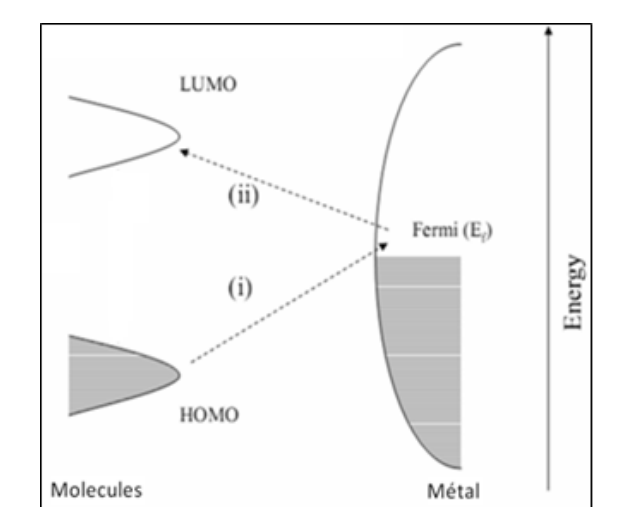
Surface plasmon resonance increases local electric field  $E_{loc}$  intensity experienced by Raman probed materials.

- LSPR in metal nanoparticles.
- SPP in continuous metal film.



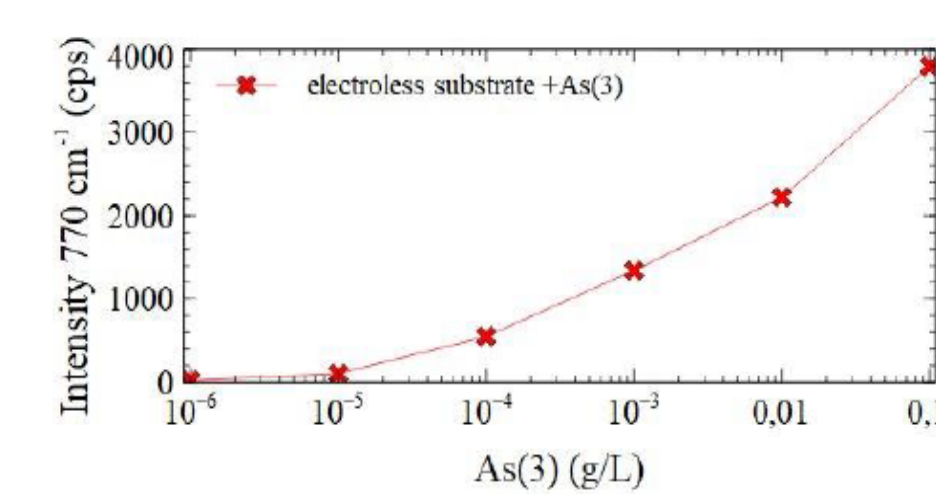
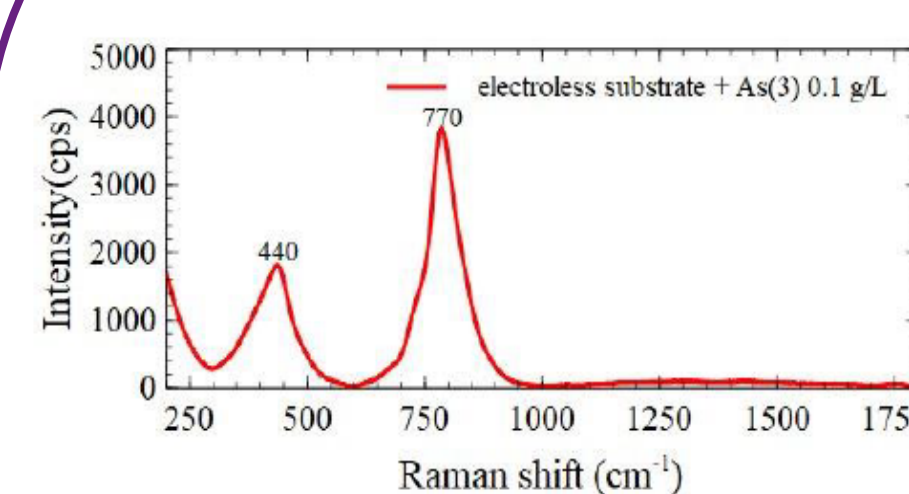
### 2. Chemical effect :

Charge transfer can take place between metal and adsorbed molecules inducing an increase of dielectric polarizability  $\alpha$ .



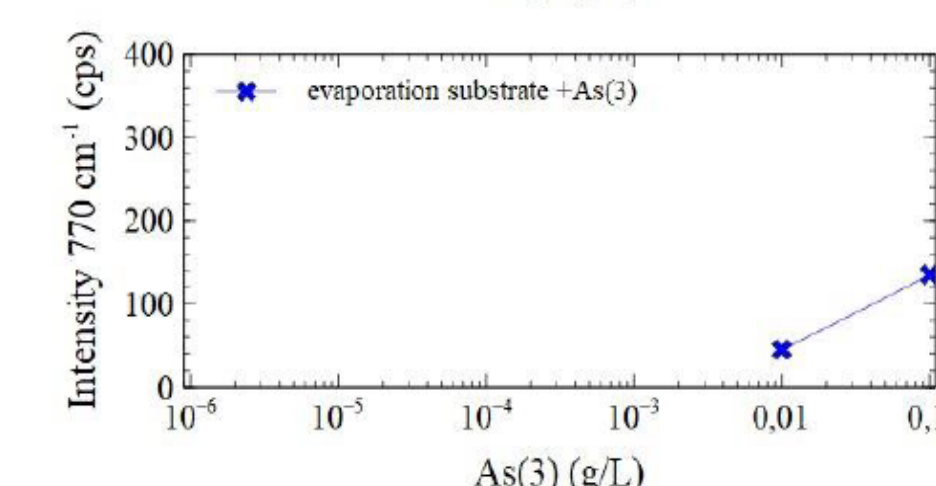
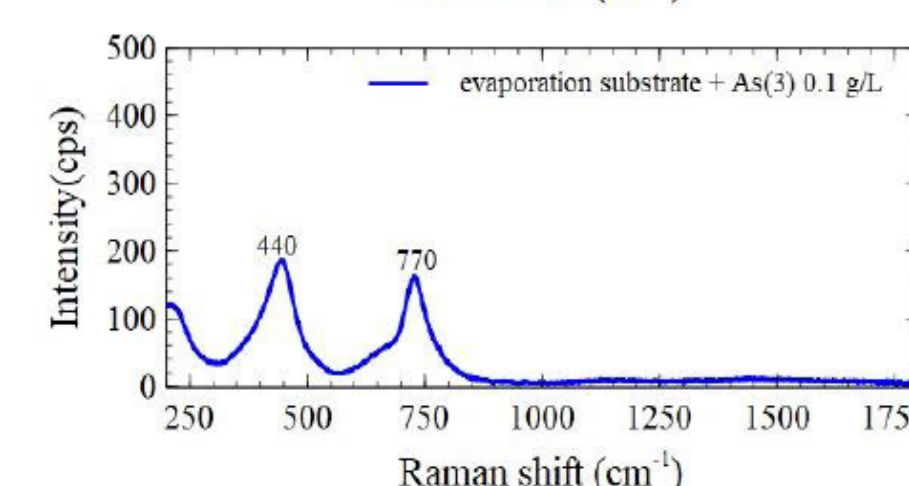
## Arsenic detection

Measurement settings:  
 $\lambda = 780$  nm  
 $P = 60$  W/cm<sup>2</sup>  
Sample exposure: 20\*3(s)

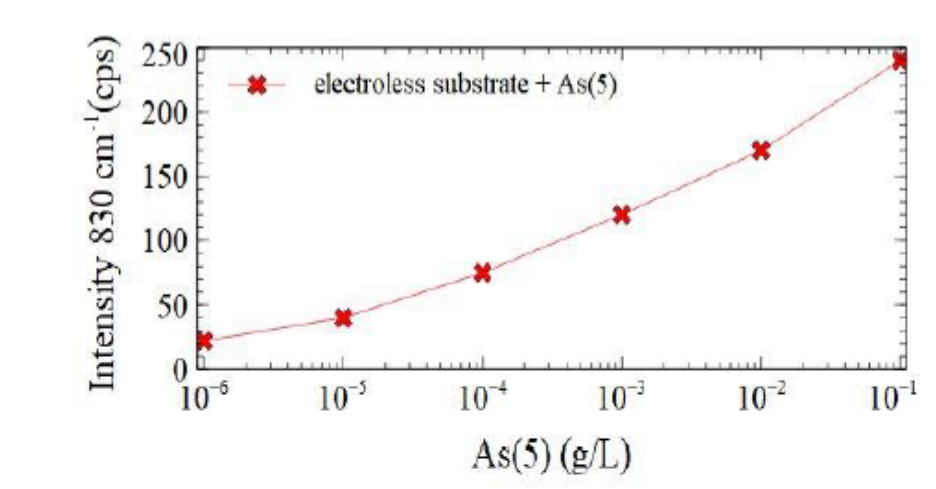
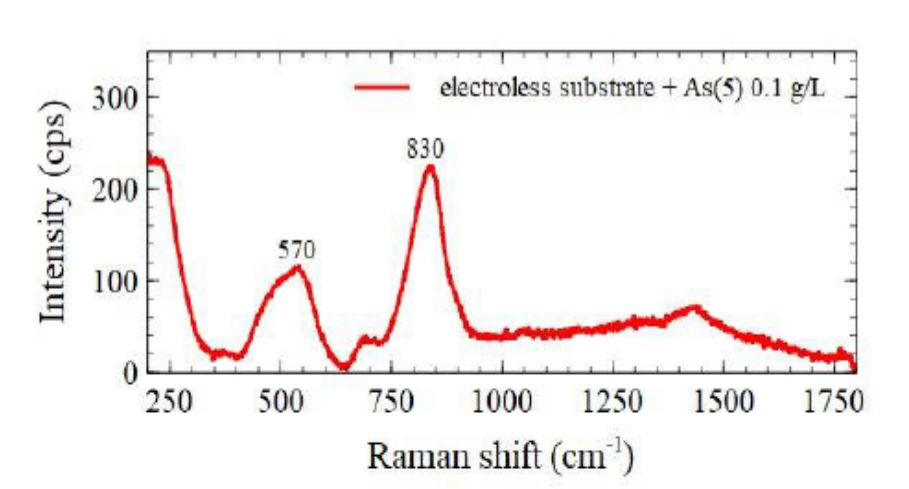


### 1. As(3)

Raman shift (cm <sup>-1</sup> )	Vibrations
440	As-O
770	As-OH

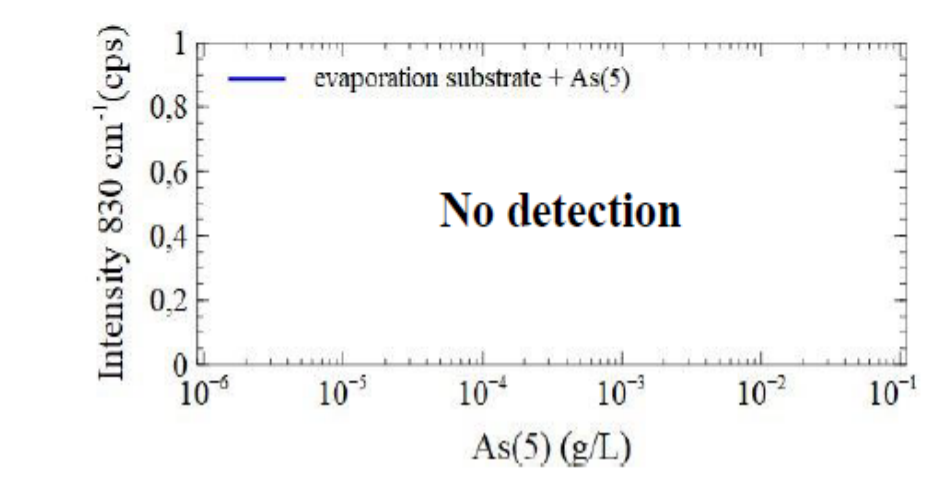
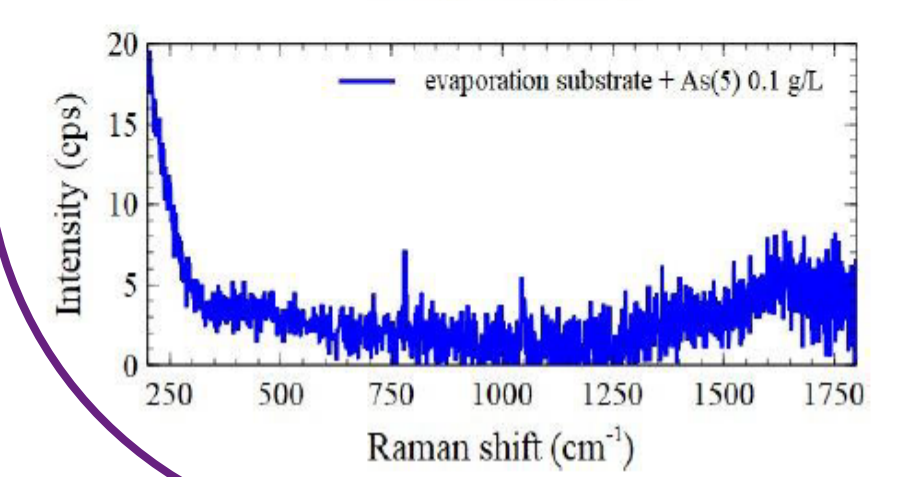


Electroless substrate: 10<sup>-6</sup> g/L (1ppb)  
Evaporation substrate: 10<sup>-2</sup> g/L (10<sup>4</sup>ppb)



### 2. As(5)

Raman shift (cm <sup>-1</sup> )	Vibrations
570	As-O
830	As-OH



Electroless substrate: 10<sup>-6</sup> g/L (1ppb)  
Evaporation substrate: No detection at 10<sup>-1</sup> g/L

## Conclusion

### Substrates characterization :

- Evaporation substrate : continuous film → no LSPR (SPP?)
- Electroless substrate : granular layer → LSPR at 565 nm

### SERS effect:

Electroless substrate presents much better SERS effect than evaporation substrate

### Detection limit of Arsenic

	As(3)	As(5)
Evaporation substrate	10 <sup>-2</sup> g/L (10 000 ppb) <b>Standard WHO : NO</b>	No detection <b>Standard WHO : NO</b>
Electroless substrate	1 µg/L (1ppb) <b>Standard WHO : OK</b>	1 µg/L (1ppb) <b>Standard WHO : OK</b>