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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
Advantages	Reference technique As speciation	Rapid measurement Low cost	Instantaneous measurement Turnkey device As Speciation
Inconveniences	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

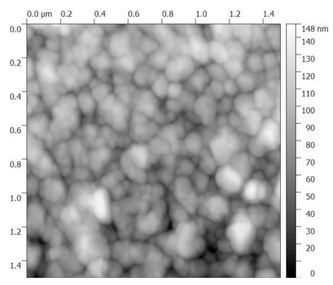
1. Electroless substrate:

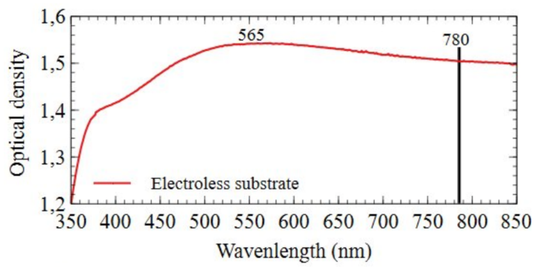
Redox reaction without generator
Aldehyde oxidation → carboxylic acid
Ag^+ reduction → mirror coating

$R\text{-}CHO + 2Ag^+(aq) + 3HO^- \rightarrow RCOO^- + 2Ag(s) + 2H_2O$

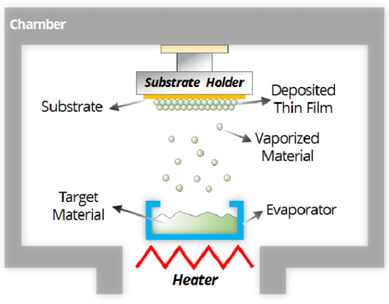
- Granular layer
- Particle size : 101 ± 10 nm
- Roughness : 21 nm
- Localized/propagative? surface plasmon resonance (LSPR) located at 565 nm
- Limit Methylene blue detection : **10^{-8} mol/L**

AFM image



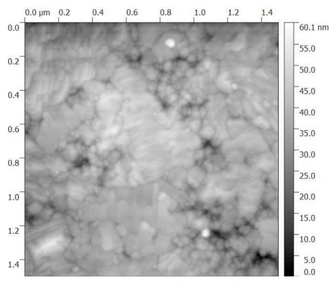


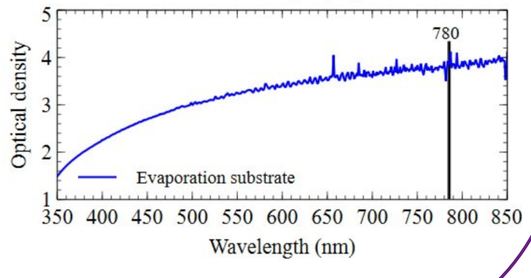
2. Evaporation substrate:



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

AFM image



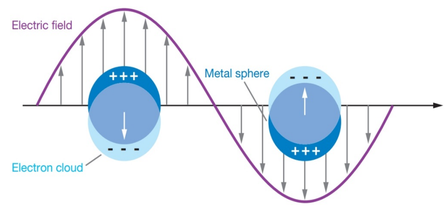


Methylene blue is a probe SERS molecule

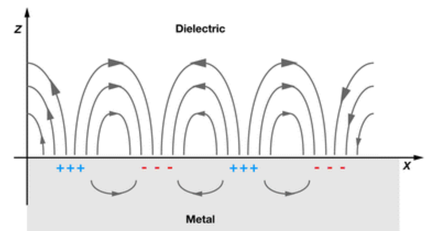
Surface-Enhanced Raman Scattering (SERS)

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

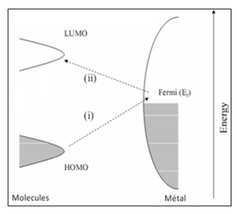
$$I_{Raman} \propto \alpha^2 E_{loc}^2$$



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.

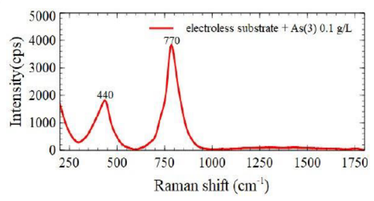


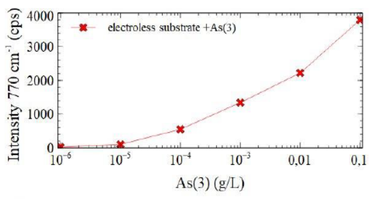
2. Chemical effect :
Charge transfer can take place between metal and adsorbed molecules inducing an increase of dielectric polarizability **α**.

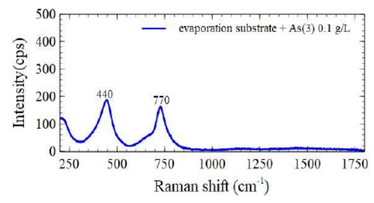


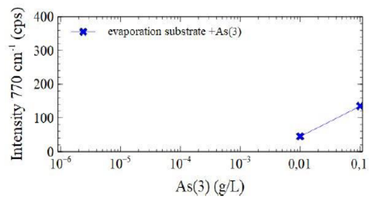
Arsenic detection

Measurement settings:
λ=780 nm
P=60 W/cm²
*Sample exposure:20*3(s)*





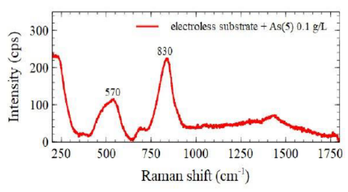


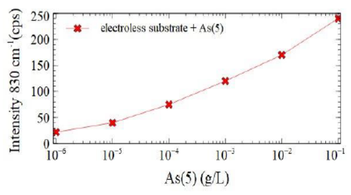


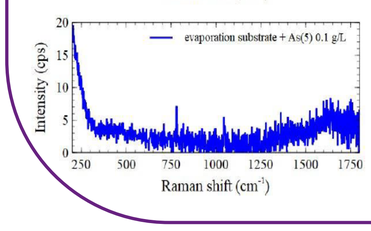
1. As(3)

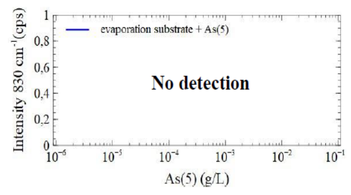
Raman shift (cm^{-1})	Vibrations
440	As-O
770	As-OH

Electroless substrate: 10^{-6} g/L (1ppb)
Evaporation substrate: 10^{-2} g/L (10^4ppb)









2. As(5)

Raman shift (cm^{-1})	Vibrations
570	As-O
830	As-OH

Electroless substrate: 10^{-6} g/L (1ppb)
Evaporation substrate:
No detection at 10^{-1} 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^{-2} g/L (10 000 ppb) **Standard WHO : NO**	No detection **Standard WHO : NO**
Electroless substrate	1 µg/L (1ppb) **Standard WHO : OK**	1 µg/L (1ppb) **Standard WHO : OK**