

New Methods of Separating and Detecting
Metal Ion Levels in Various Waters:
Electroactive Ion Exchanger and Raman
Spectroscopy

by

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BACKGROUND

Background



- Heavy metals constitute a major proportion of the contaminants in chemical effluents and they cannot be degraded or destroyed
- In water bodies, metals accumulate in sediment and organisms from where they may be transferred into the food chain
- Recommendations for chemical industries to limit the concentrations of heavy metals (Helcom; Cd 0.2 mg/l; Zn 2.0 mg/l)

Background



- In circulated water of different processes, metals may cause different kinds of problems e.g. for process operation, and they may also deteriorate the product quality as well.

Membrane processes provide a viable alternative for heavy metal recovery. For example micellar-enhanced and polymer-enhanced ultra filtration technologies have already shown their feasibility and are potential alternatives for further development.

Heavy metal complexes may be removed from water by adsorption

- It is important to notice, that membranes & adsorption are energy efficient ways of treating different kinds of water, they can be very selective and deal with a variety of water quality conditions; in addition metals can be recovered from the materials, if needed
- These separation technologies may also be used in the development of continuous concentration methods.



Background

- The measurement of small concentrations of metallic species in a water matrix is very demanding. Traditionally the measurements have been carried out with sophisticated laboratory analysis.
- EU-directives 2003/40/EC and 2002/178/EC set limits for **food safety**: they list maximum limit values for potable water and give performance characteristics for measurement methodologies.

Antimony	0.0050 mg/l
Arsenic	0.010
Barium	1.0
Boron	
Cadmium	0.003
Chromium	0.050
Copper	1.0
Cyanide	0.070
Fluorides	5.0
Lead	0.010
Manganese	0.5
Mercury	0.0010
Nickel	0.020
Nitrates	050
Nitrites	0.1
Selenium	0.010

Background

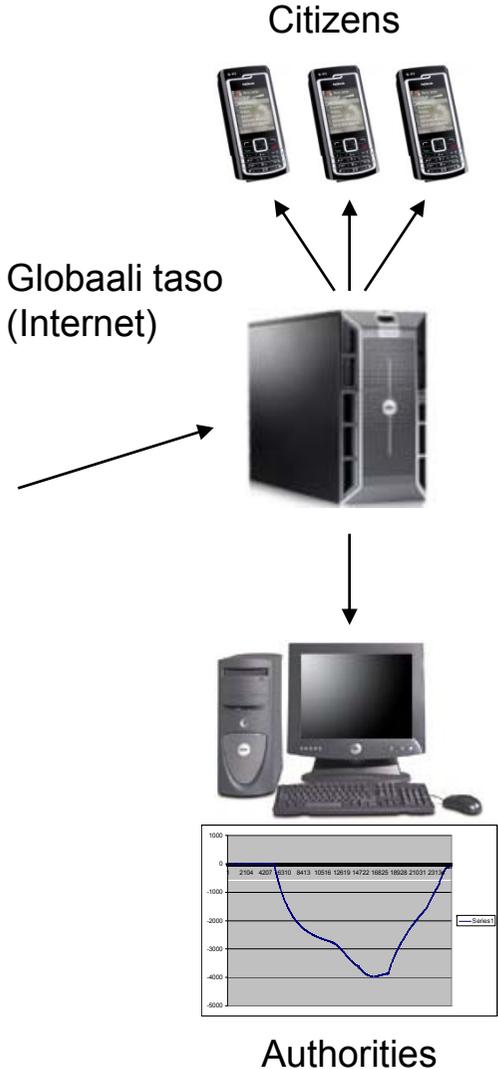
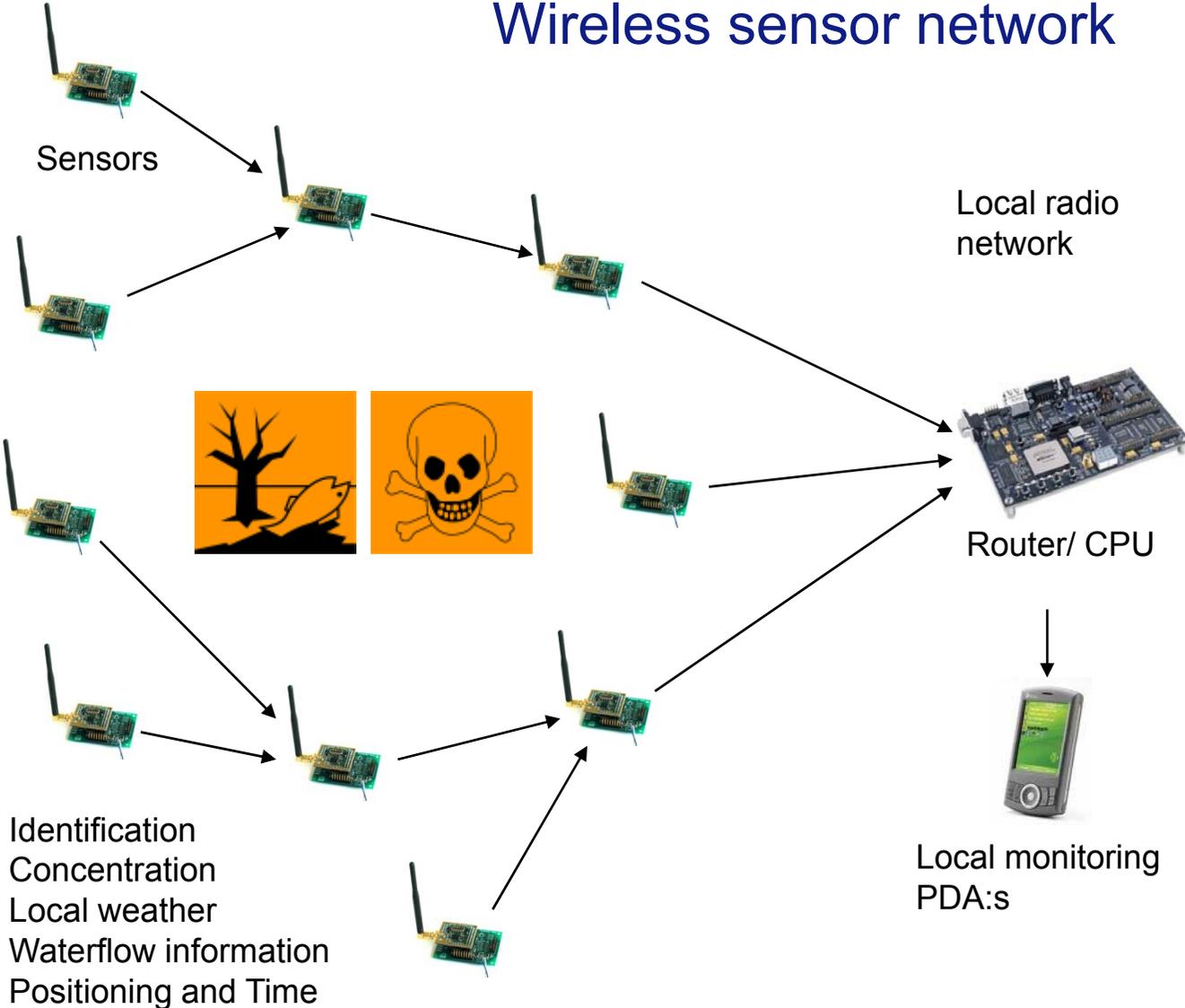
- The public awareness of the environmental impacts of mining industry have grown lately – the possibility of the contamination of e.g. river near the mine is not likely, but still possible and important issue especially for neighbouring area
- The continuous monitoring of metal content in the waterways near mining areas would satisfy the need for the information for both the mining industry and the citizens



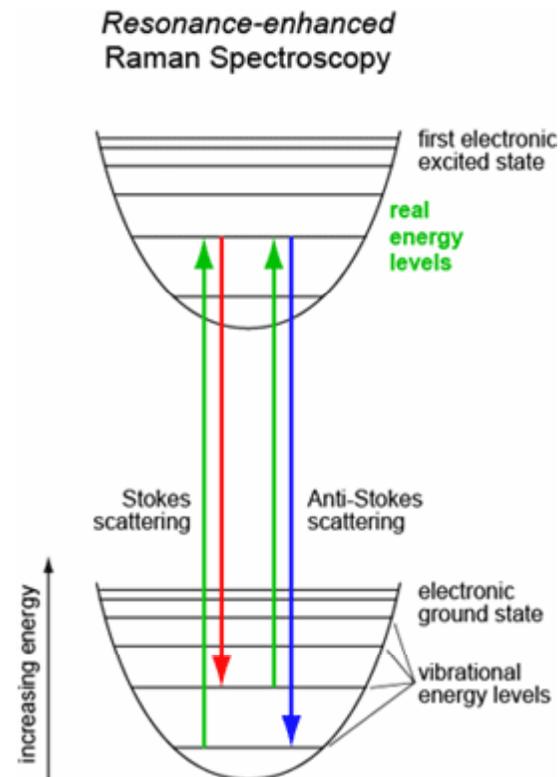
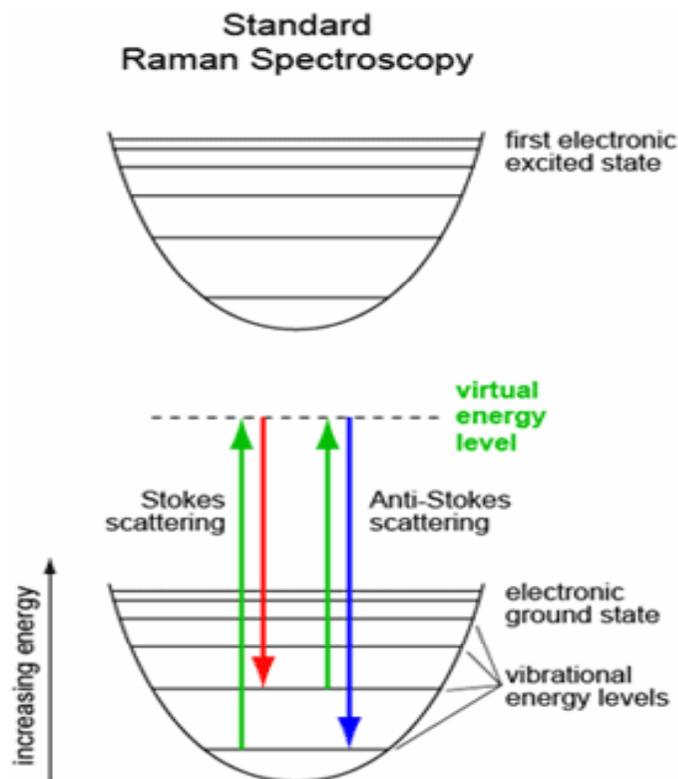
Online monitoring of environmental impacts

- Online monitoring of concentrations on production site when the area is relatively large and does not have infrastructure (power supply, hard wired network)
- Monitoring in unexpected situations when the existing measurements do not provide adequate status information (Ad-Hoc measurements)
- Periodical measurements on demand to verify the changes in long-term (mobile instrumentation) to reduce the costs

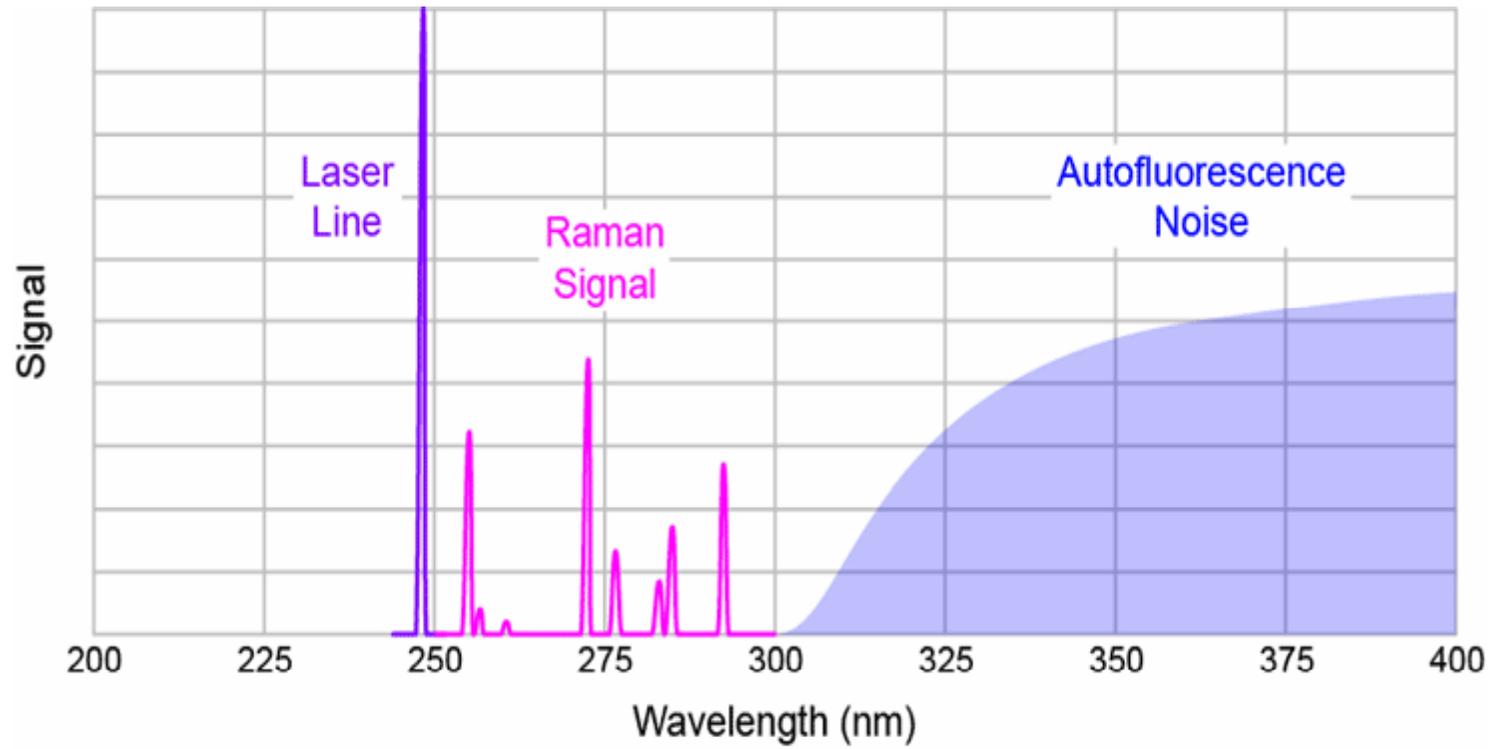
Wireless sensor network



Standard vs. Resonance Raman



UV Raman Advantage



Development of In-Situ Sensors for the Detection of Groundwater Contamination

- High sensitivity is achieved through a variation of Raman spectroscopy known as Surface Enhanced Raman Spectroscopy (SERS). A million fold enhancement of Raman light scattering can be achieved with specially roughened silver surfaces.
- Furthermore, silver coated SERS probes overcome a major problem of our approach to remote sensing with optical fibers by filtering out unwanted laser light prior to its entrance into the collection fiber. These sensors can be placed several hundred meters (e.g., down a well) from measurement instruments providing a new method for in-situ analysis of groundwater.
- **Investigators:** Keith T. Carron, Ken I. Mullen, Laura Peitersen, L. Gayle Hurley, and DaoXin Wang, Department of Chemistry, University of Wyoming.

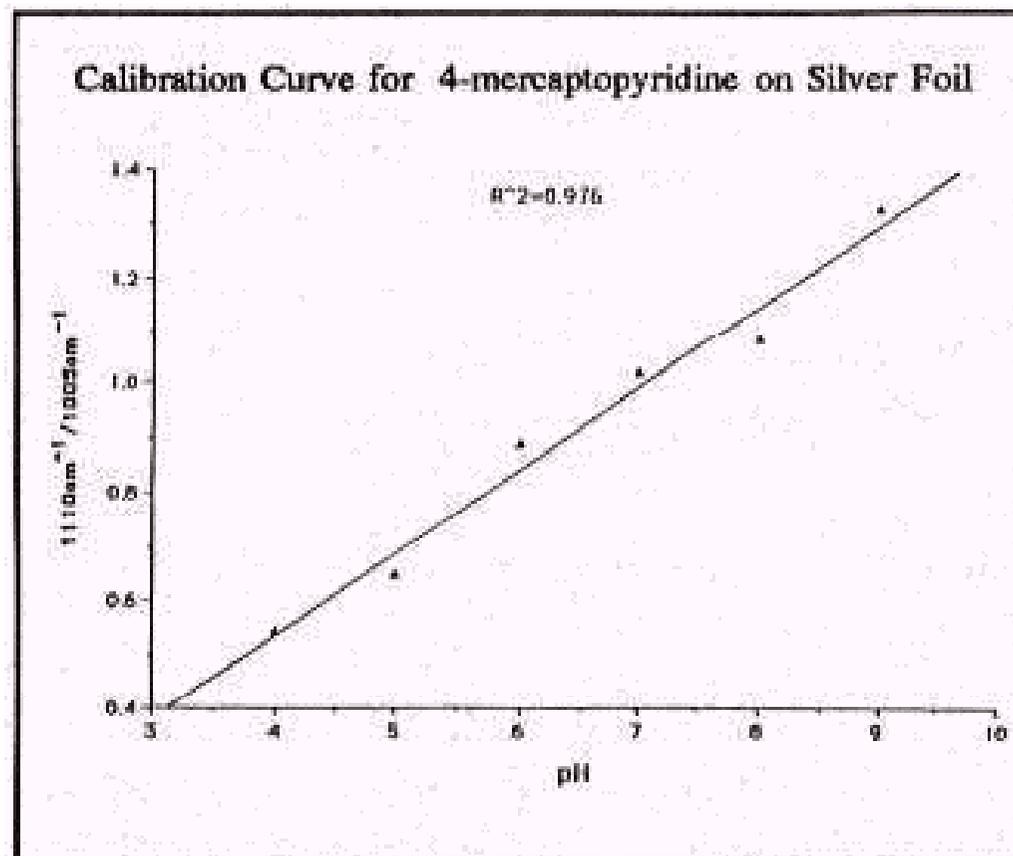
Development of In-Situ Sensors for the Detection of Groundwater Contamination

- **Results:** Metal ions, pH and aromatic organics have been successfully detected and concentrations determined in laboratory tests using SERS. Metal ions were detected by analyzing the Raman spectrum of metal ion indicators bound to the silver substrate on probes. Most metal ion indicators contain groups that combine with metal ions, thus changing the Raman spectrum of the indicator.
- One advantage of metal ion indicators is that they often contain a carboxylic acid or sulfonic group which increases the water solubility of the indicator. Laboratory test results indicate detection limits for copper (Cu^{2+}) to be in the low parts per billion range and lead (Pb^{2+}) has been detected at the parts per trillion level.

Development of In-Situ Sensors for the Detection of Groundwater Contamination

- Probes to monitor pH were developed for two reasons. The first is to monitor the pH of groundwater. SERS sensors for pH produced excellent test results. A calibration curve was analyzed for variations in pH and relative Raman intensity for peaks associated with a protonated and with a deprotonated form of the pH indicator.
- Regression analysis of the calibration curve indicates a very close fit of the test data (a correlation coefficient of 0.98) using a probe with 4-mercaptopyridine on silver foil.
- The second reason for looking at pH at surfaces is to develop ways to buffer the surface pH such that large variations in the groundwater pH will not affect the probes. Furthermore, variation in surface pH is an excellent method for controlling the selectivity of the metal ion indicators. It should be possible to use a single metal ion indicator coupled with pH modified surfaces to fine tune the selectivity toward specific metal ions.

Development of In-Situ Sensors for the Detection of Groundwater Contamination



Calibration curve corresponding to the intensity ratio of two Raman peaks and variation with pH.

Selective-Ultratrace Detection of Metal Ions with SERS

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APPLIED SPECTROSCOPY

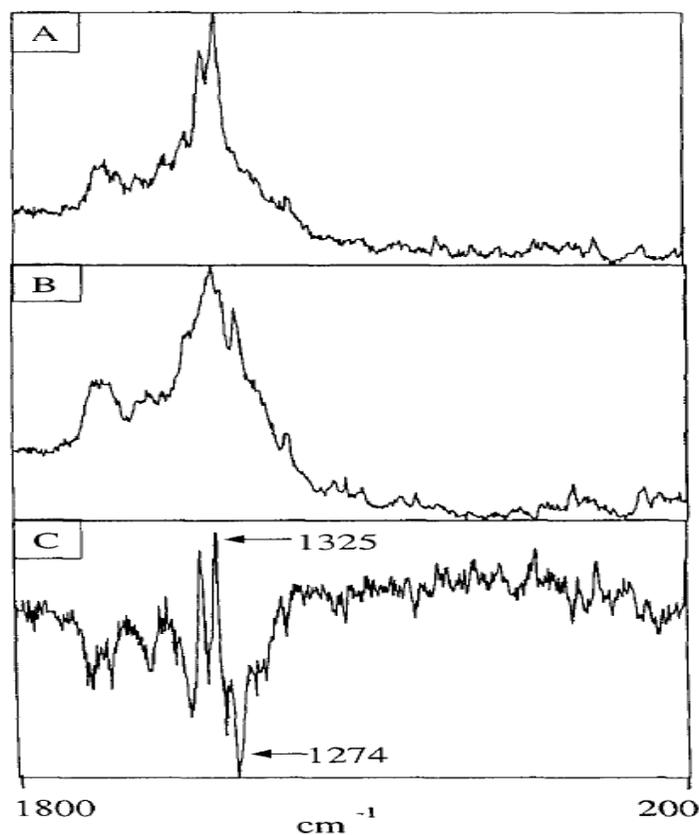


FIG. 3. SERS spectra of (A) 2.7×10^{-4} M EBT and 2.7×10^{-4} M Pb^{2+} , and (B) 2.7×10^{-4} M EBT; C is the difference spectra of A minus B. The intensity difference between the 1325-cm^{-1} and 1274-cm^{-1} bands was found to produce good quantitative results for Pb determinations.

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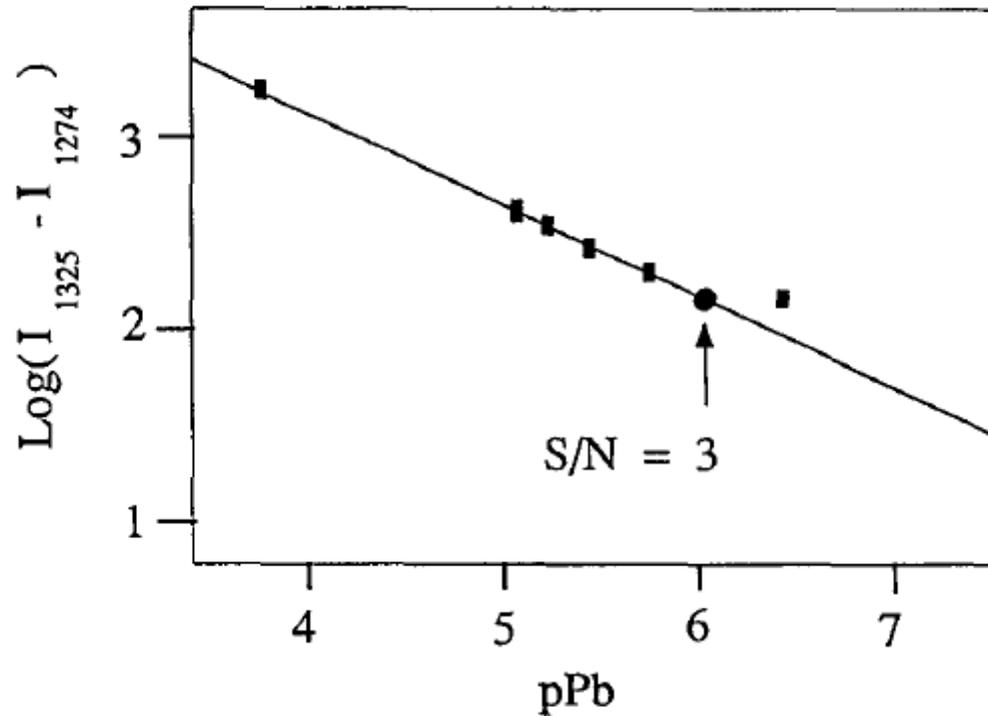


FIG. 4. The SERRS concentration profile for Pb^{2+} . The detection limit is 270 ppb as determined by the point at which the $S/N = 3$. Data below the detection limit were not used in the linear regression. The error bars represent the relative error.

Preliminary Research Done in Oulu

Experimental

- **Synthesis and modification of gold nanoparticles**
- To prepare the aqueous gold nanoparticles, 0.6 ml of 10 mg/ml trisodium citrate was added to 100 ml of 0.1 mg/l boiling tetrachloroauric acid aqueous solution while stirring. The mixture was kept boiling for about 15 minutes until a deep wine red color was observed, indicating the formation of gold nanoparticles, and then cooled down to room temperature.
- The gold nanoparticles were preconcentrated before modification. (Transmission electron microscopy (TEM) measurements showed that the mean diameter of the prepared gold nanoparticles was about 50 nm).
- For the preparation of MBA (p-mercaptobenzoic acid) modified gold nanoparticles, 1 μ l of 1 mmol/l MBA ethanol solution was added to 1 ml preconcentrated gold nanoparticles solution to full cover nanoparticles with a MBA monolayer.

Experimental

- **Self-Assembled Monolayer (SAM) Formation of MBA on gold surface**
- Thin gold film evaporated on a glass slide with an ultrathin chromium layer was used as the substrate. The film was first rinsed by ethanol twice and dried by nitrogen.
- After that, it was annealed by gas light for about 1 minute to form a large terrace with an atomic scale flat, and cooled down to room temperature in the nitrogen environment.
- The formation of the self-assembled monolayer (SAM) of MBA was accomplished by immersing the gold substrates into 1 mmol/l MBA solution for about 4 h, and rinsed by ethanol twice and Mill-Q water to remove the physically adsorbed MBA molecules.

Experimental

- **Immobilization of metal ions and MBA capped gold nanoparticles onto gold substrate**
- The MBA modified gold substrate was immersed into copper nitrate solution for about half an hour for capturing the copper ion by the terminal carboxyl group on the surface, and cleaned by three distilled water three times.
- At last, the MBA modified gold substrate linked with copper ion was exposed to MBA capped gold nanoparticles basic solution for about half an hour to attach the gold nanoparticles on to the substrates.
- After being taken out the gold nanoparticles solution, the substrate was rinsed by Mill-Q water several times to remove any nanoparticles, which were not bonded to the gold surface.

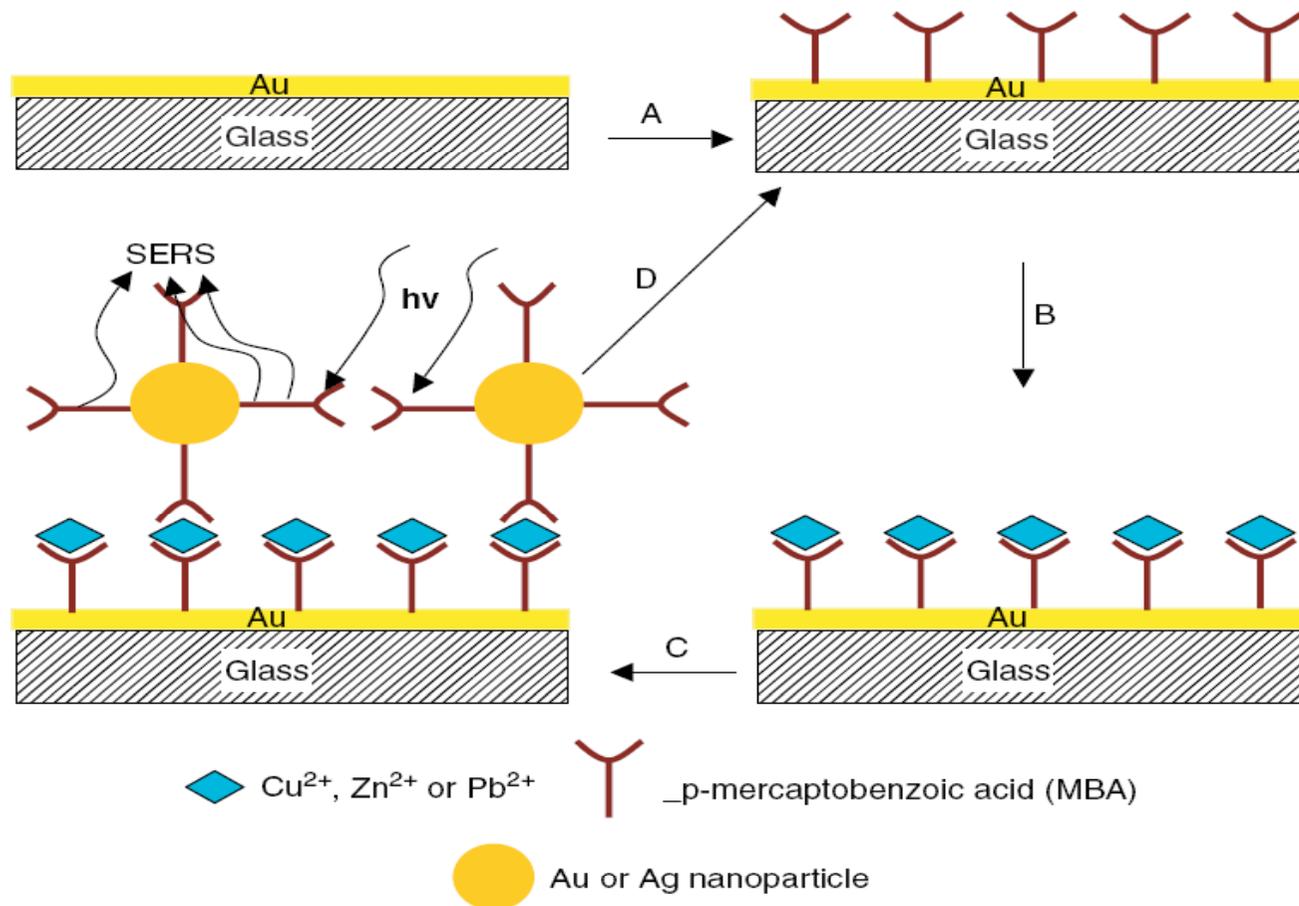
Experimental

- SERS (performed on a LabRam HR800 confocal micro Raman system with the excitation line of 632.8 nm, Dilor, France).
- The solutions were prepared by fresh Mill-Q water for avoiding the influence the trace metal contamination.

Experimental

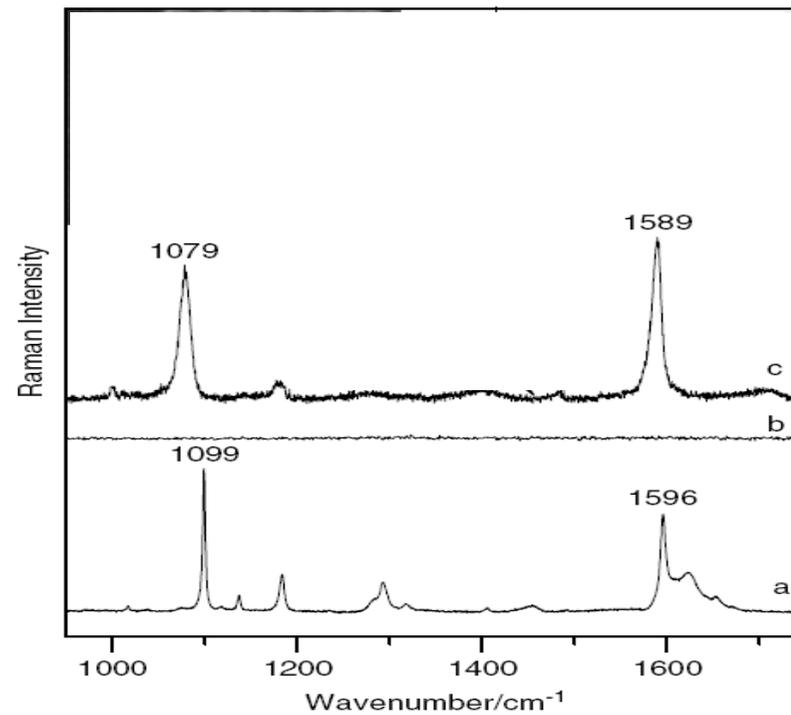
- Four steps involved in the construction of the sandwich structure as:
- (i) the formation of MBA SAM onto an atomic flat gold film (non-SERS active) on glass surface (step A in the figure below),
- (ii) capturing copper ions onto the MBA modified substrate from the analytical medium (step B),
- (iii) immobilizing MBA capped gold nanoparticles through the copper ions carboxylate linkage (step C),
- (iv) recycling the sensor by removing copper ions by strong chelator (in this case an EDTA solution) (step D).

Schematic diagram



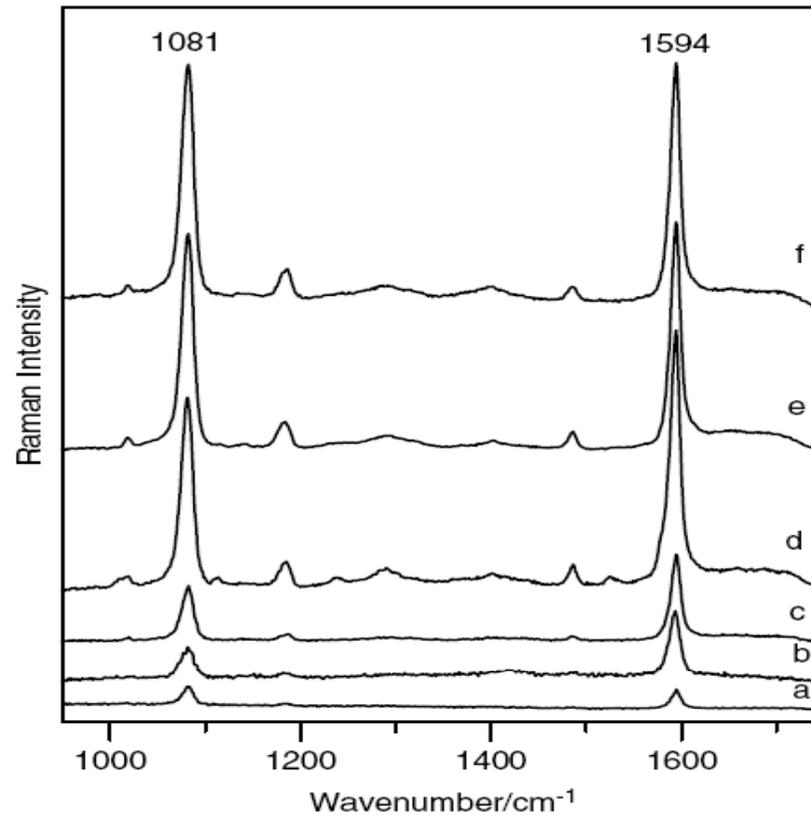
. Schematic diagram of surface enhanced Raman spectroscopy based detection on heavy metal ion.

Raman Spectrum of MBA



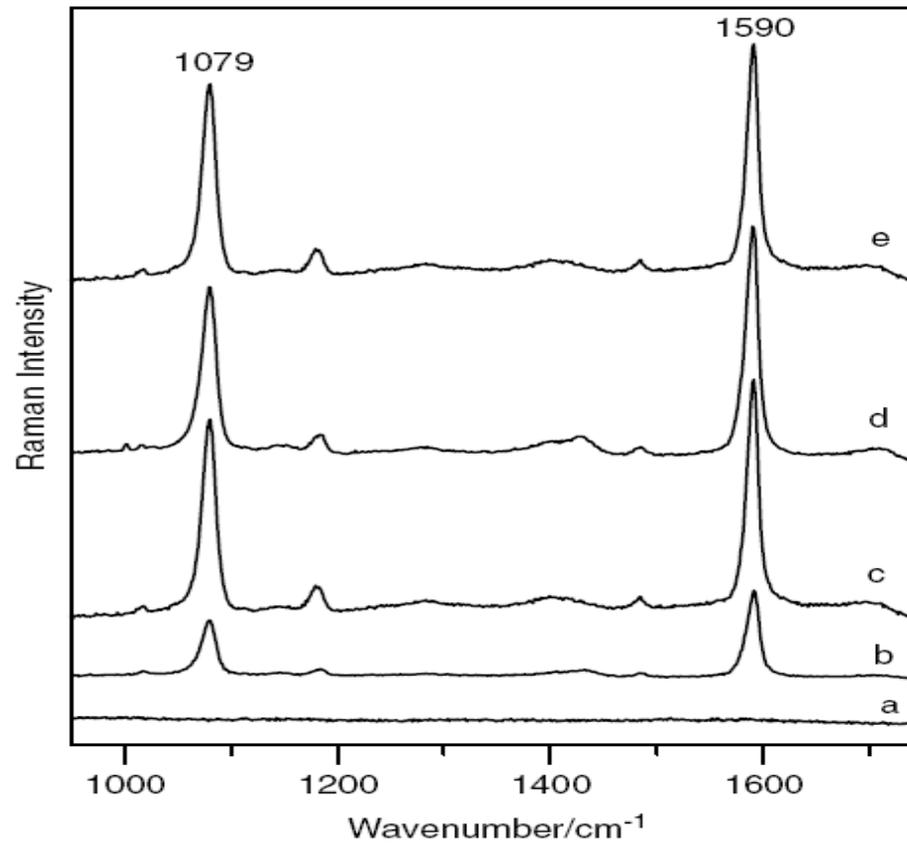
Normal Raman spectrum of MBA solid (a), Raman spectrum from the gold substrate without copper ions linkage underwent the immersion in the MBA capped gold nanoparticles solution (b), SERS spectrum of MBA from the gold substrate underwent two steps of copper ions linkage (c),

Lead ion detection via SERS



SERS spectra from the gold substrate with the carboxyl linkage of Pb^{2+} of 10^{-12} mol/dm³ (a), 10^{-8} mol/dm³ (b), 10^{-7} mol/dm³ (c), 10^{-6} mol/dm³ (d), 10^{-5} mol/dm³ (e) and 10^{-4} mol/dm³ (f).

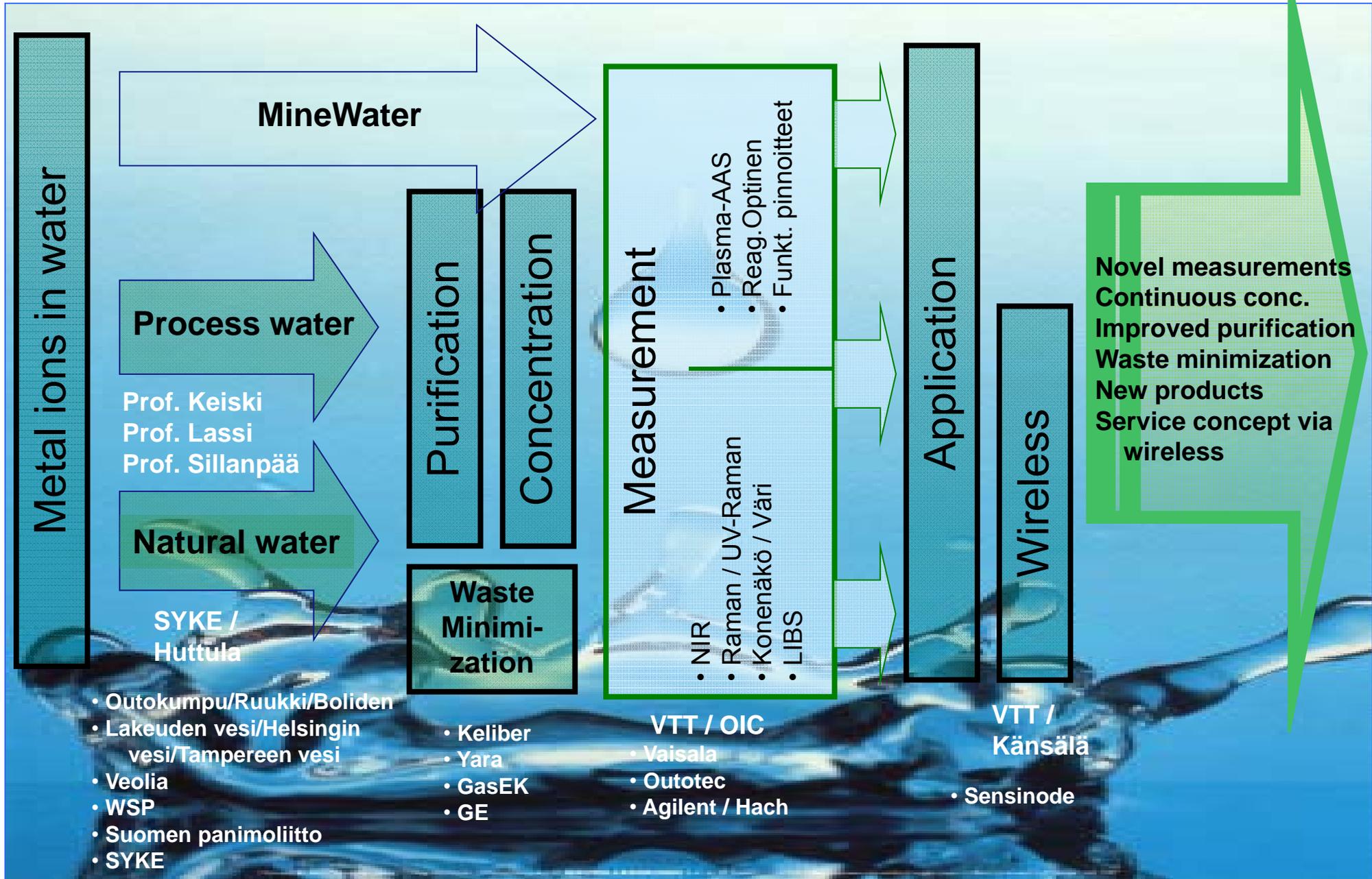
Zinc ion detection via SERS

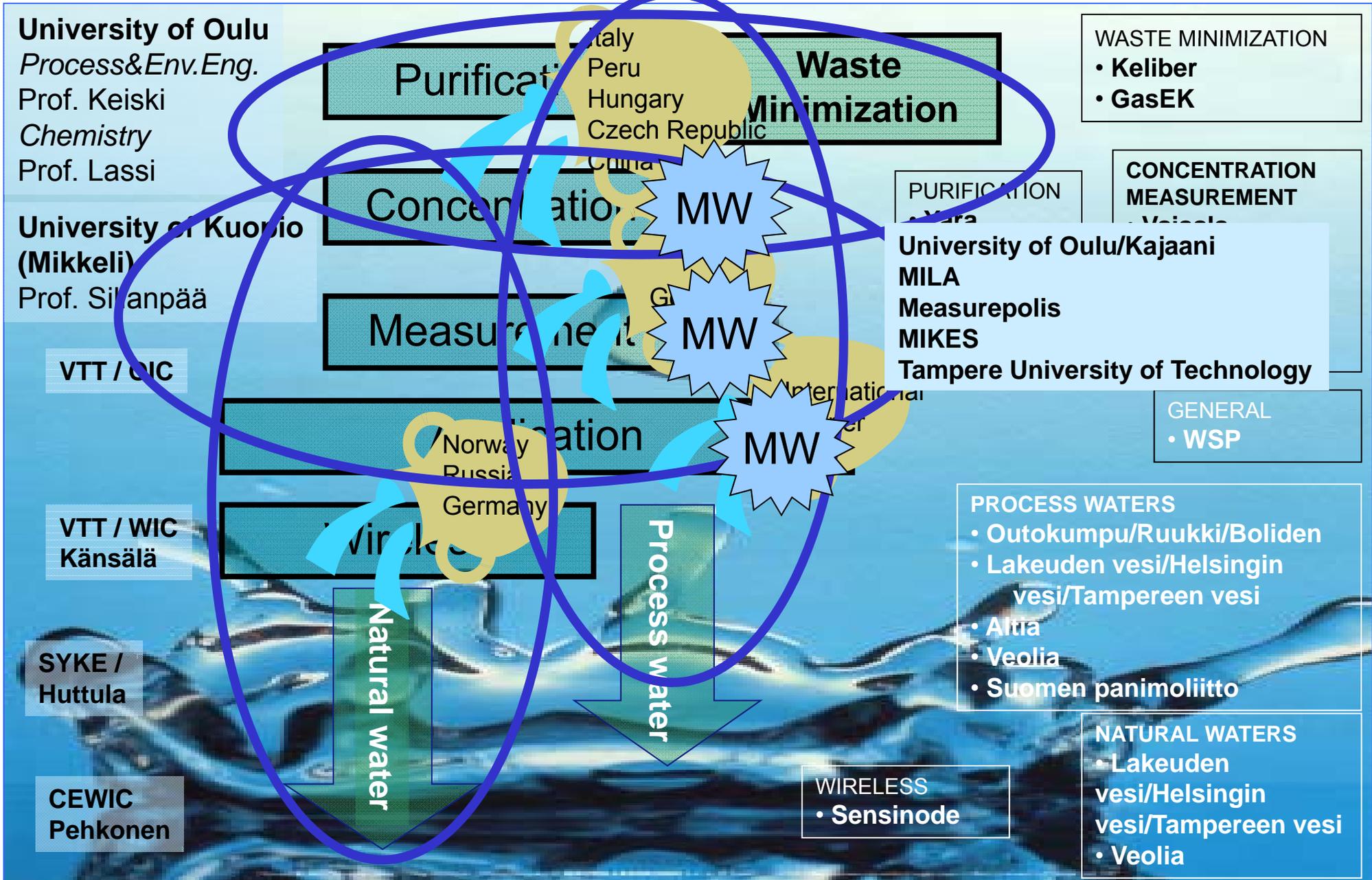


SERS spectra from the gold substrate without metal ions linkage (a), with Zn²⁺ of 10⁻⁶ mol/dm³ (b), 10⁻⁵ mol/dm³ (c), 10⁻⁴ mol/dm³ (d) and 10⁻³ mol/dm³ (e).

Challenges and Future Work

- For the Ion Exchange:
- Membrane fouling, naturally occurring organic chelators (i.e., competition with the immobile anion), time of separation, matrix effects, not yet attempted with the ISM layer.
- For Raman:
- In real water streams, the spectra perhaps too complex, unless pre concentration and/or purification is carried out.
- A combination of ELECTROACTIVE ION EXCHANGER/RAMAN for relatively low level metal ion detection (at least in industrial effluents where the number of species is better known and more limited) !!!





Objectives of Moniwater

1. To make a **comprehensive survey** on the existing continuous measurement methods for small concentrations of metals in water, concentration methods as well as markets
2. To **test** new measurement methods in the laboratory and in real applications
3. To develop **continuous concentration/sampling** systems for measurement needs
4. To construct a **wireless-pilot** for monitoring of metal ions
5. To develop **purification** technologies for metal ions removal
6. To test industrial by-products in metal ions removal: **waste minimization**



Q & A

- Thank you for your attention