New Technique for Online Measurements of Trace Metals in Ambient Particulate Matter (PM)

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Motivation, Rationale and Objectives

- Transition elements and metals are important PM species found usually in trace concentrations
- Some are highly toxic (Fe, Cu, V, Cr, Mn, Ni etc)
- They are also important species for PM source apportionment
- Traditional PM sampling methodologies usually involve collection of particles onto substrates by filtration or inertial impaction
- Collected particles are extracted using different types of solvents and analyzed by various analytical techniques (ICP-MS, etc)

- **Drawbacks**:
    - Long turn-around time for processed results
    - Long sampling intervals for collection of sufficient mass for subsequent chemical analysis
    - Changes in chemical speciation (e.g. oxidation state shifts in redox active metals)
    - Expensive analysis (especially ICP-MS)

- Advanced on-line aerosol sampling technologies were developed in recent years to overcome these limitations (PILS etc)
- Most of these technologies are inadequate for the measurement of trace level species due to their low signal-to-noise ratio.

Aerosol-Into-Liquid Collector:

Aerosol-Into-Liquid Collector (*Wang et al., AS&T, 2013*) provides highly concentrated slurry samples of ambient PM

Advantages:

- High sampling flow rate (200 lpm)
- Provides highly concentrated $PM_{2.5}$ and $PM_{2.5\text{-}10}$ slurry samples
- Ability of continuous stable operation (at least 5 consecutive days)
- We will report on line measurement results for Cu, Fe, Cr and Mn
- Convert air pollution measurements into water pollution measurements

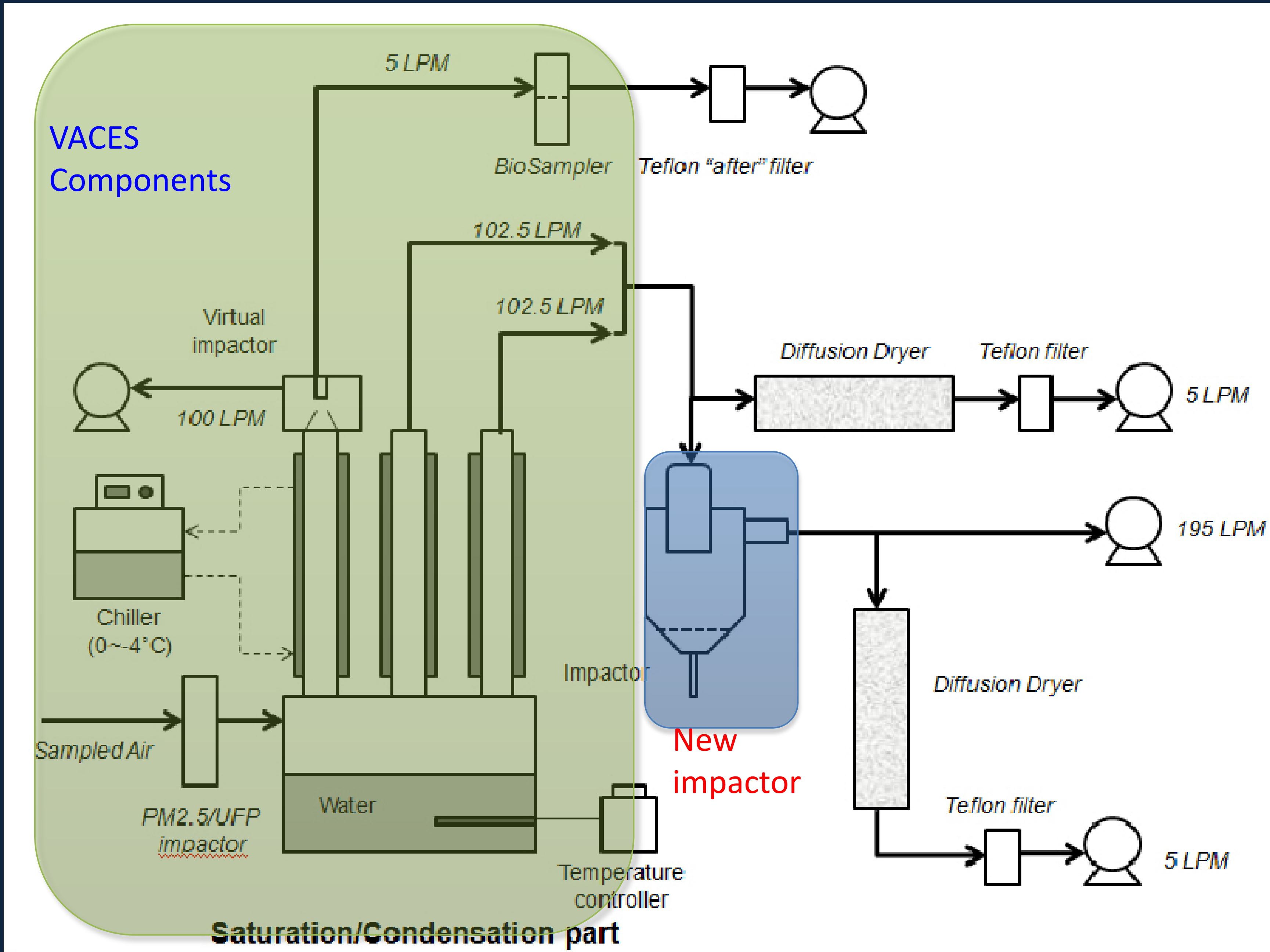


Figure 2 System schematic for collection efficiency tests

Design of the New Impactor Sampler- Sampling flow 200 lpm (Wang et al AS&T 2013)

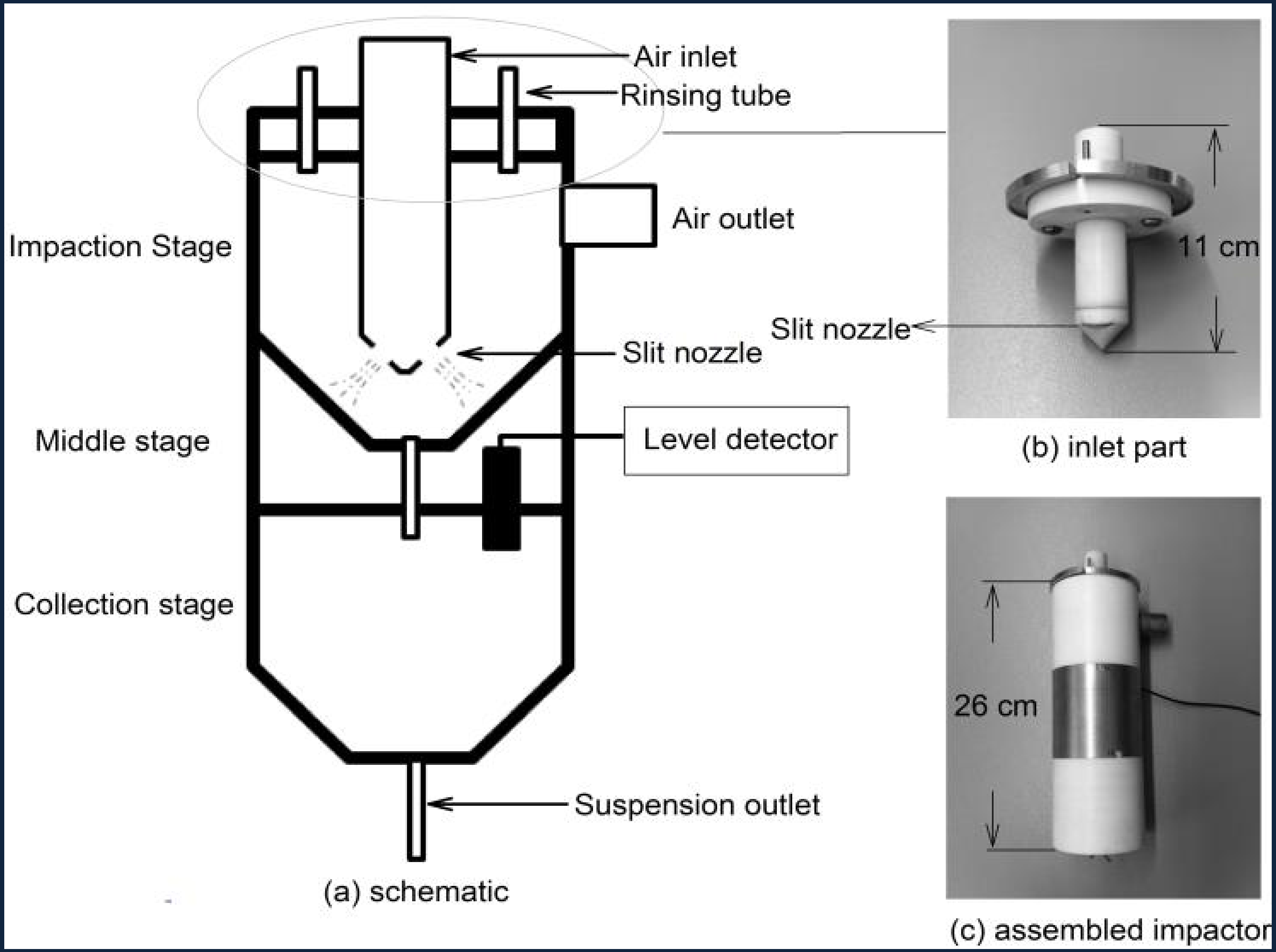


Figure 1 Schematic of impactor

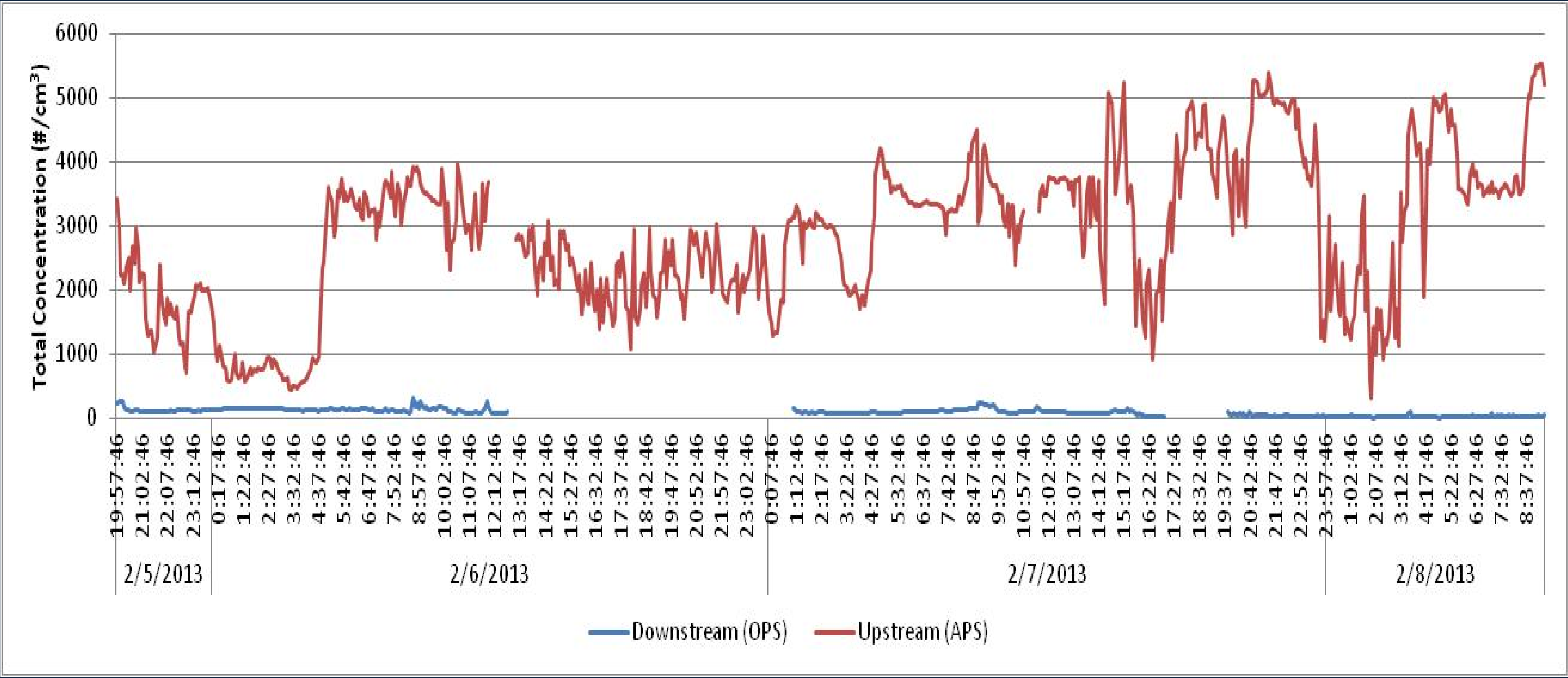
TABLE 1 Collection efficiency For Polystyrene Latex (PSL) particles and Black Carbon (BC)

Particle Size	Collection efficiency	Inlet loss	Wall loss	Fraction collected in suspension
PSL 42.5 nm	96.4%	4.5%	9.4%	82.4%
PSL 100 nm	90.3%	2.1%	7.5%	80.7%
PSL 300 nm	98.9%	1.1%	6.2%	91.4%
PSL 750 nm	95.1%	2.8%	8.1%	84.1%
PSL 1 µm	99.1%	1.7%	9.3%	88.0%
Ambient BC	94.3%	–	–	–

Field evaluation

- Continuity tests/ Unattended Sampling

  Ambient PM at USC were continuously collected over ~72 hrs period



•Number based collection efficiency = 98.8%

•*Gaps in OPS data due to software malfunction.*

On line sampler for near- continuous measurement of $PM_{2.5}$ and $PM_{2.5\text{-}10}$ Copper (Cu)

Ion Selective Electrodes (ISE)

- Ion Selective Electrodes (ISEs) are routinely used for determining the concentration (*technically the activity*) of selected ions in aqueous solutions.

- Relatively inexpensive, simple to use, and mostly function linearly over many orders of magnitude of concentration.

- Accurate measurement (within a measurement error of 2% typically) in a very short response time (several seconds to several minutes).

Source: Ion selective electrodes, www.idswater.com.

On Line PM-Bound Copper (Cu)Monitor

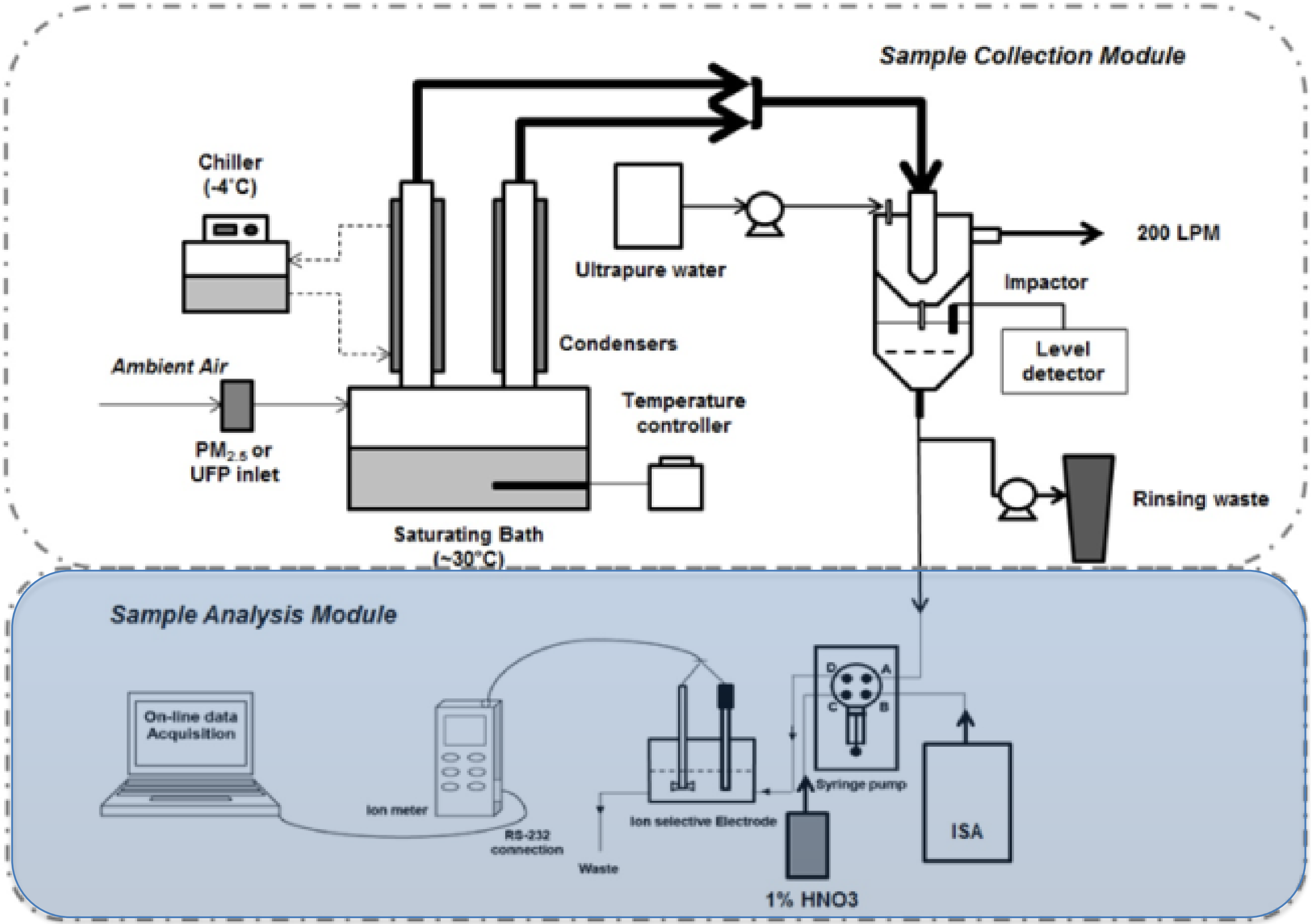
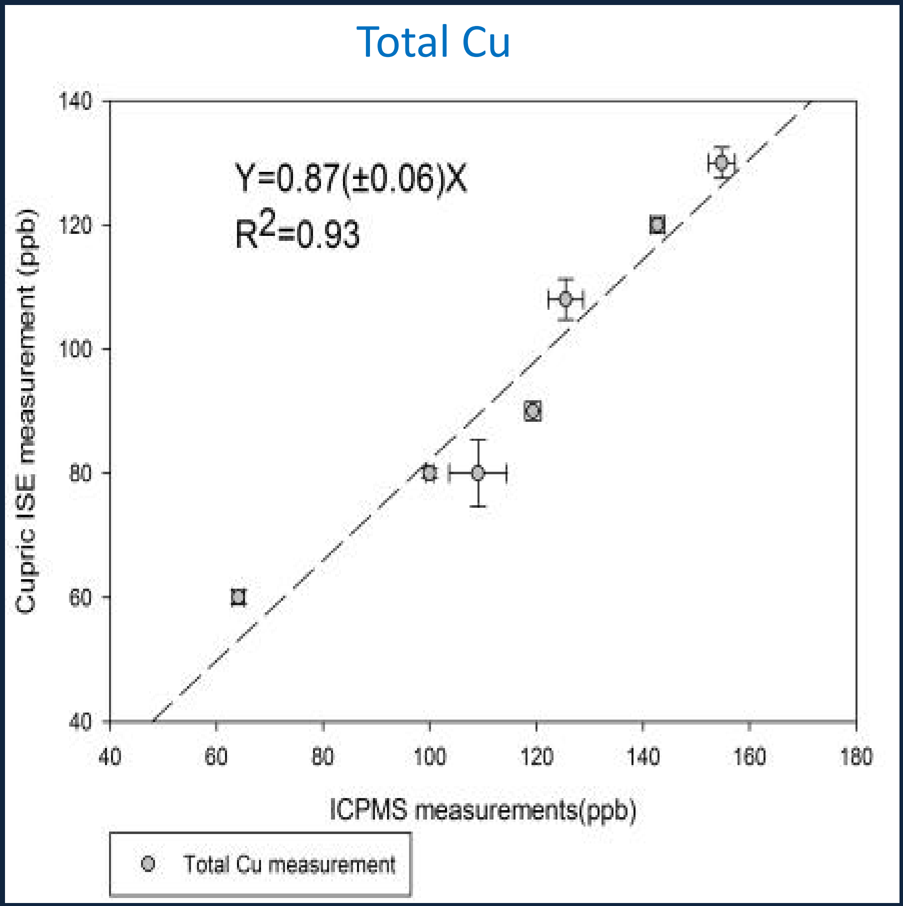
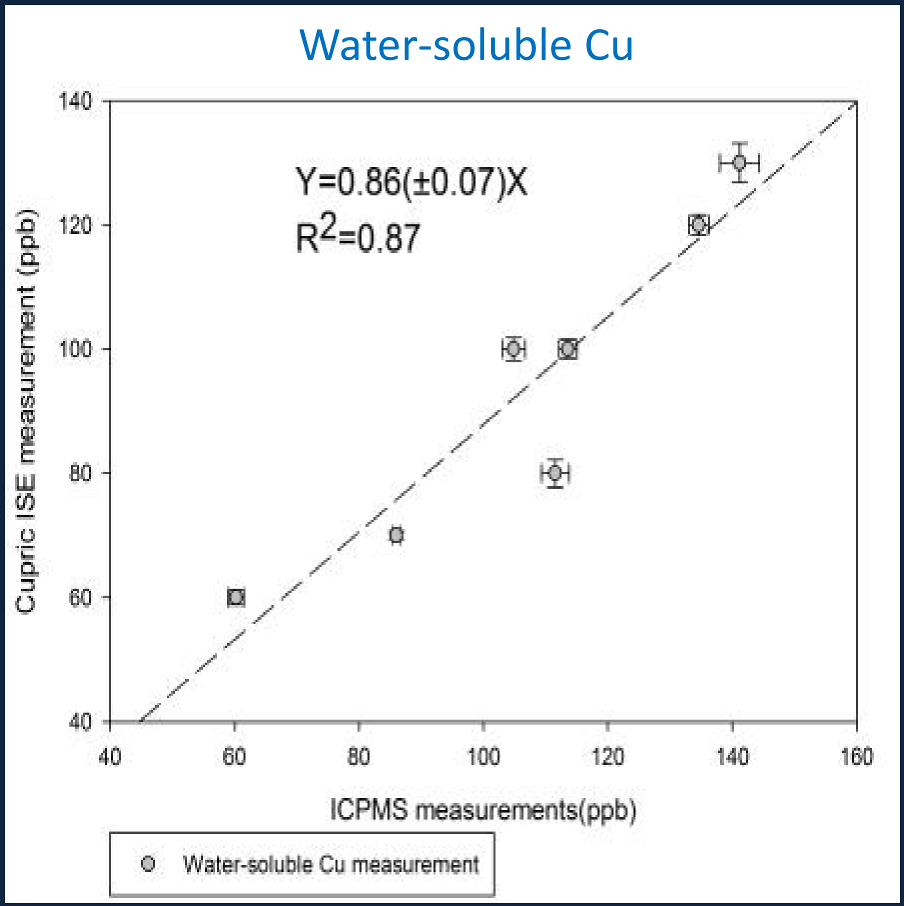


Figure 2 Schematic of Cu on line measurement system

Comparison between Cupric ISE and ICP-MS analysis of off line filter samples

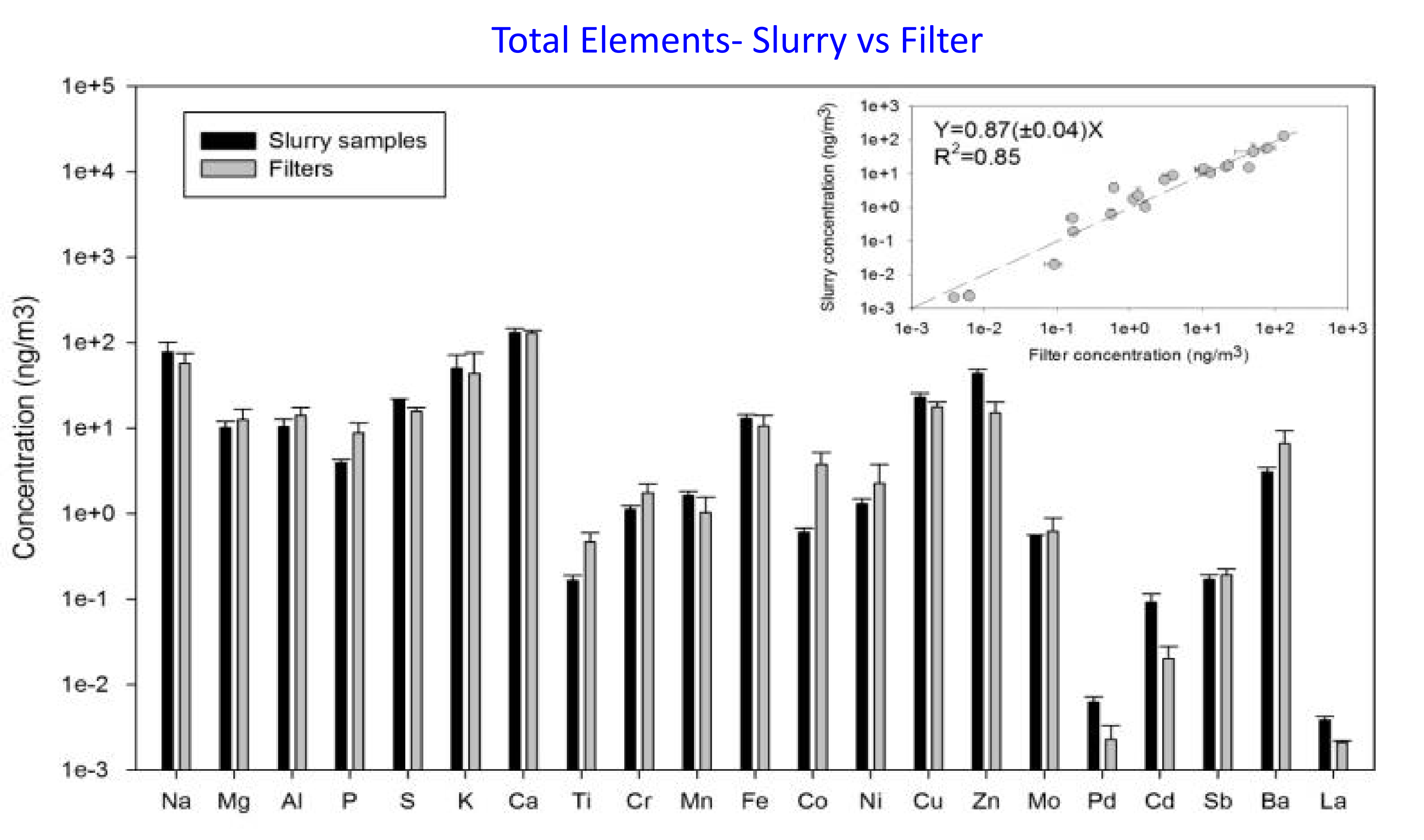




Overall very good agreement between cupric ISE and ICP-MS measurements were observed ($R^2 > 0.87$ in both comparisons).

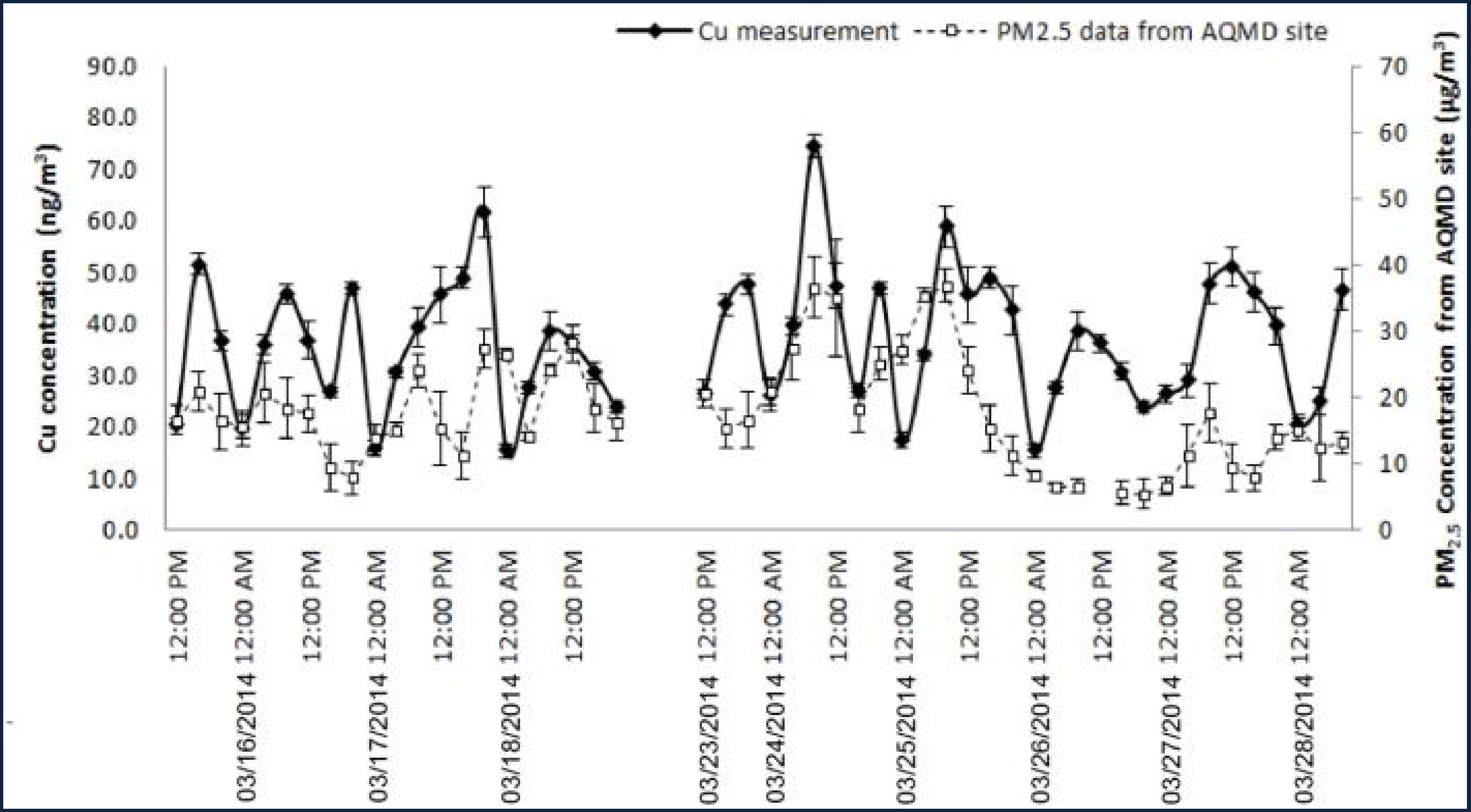
Field evaluation

- Comparison between filter and slurry samples



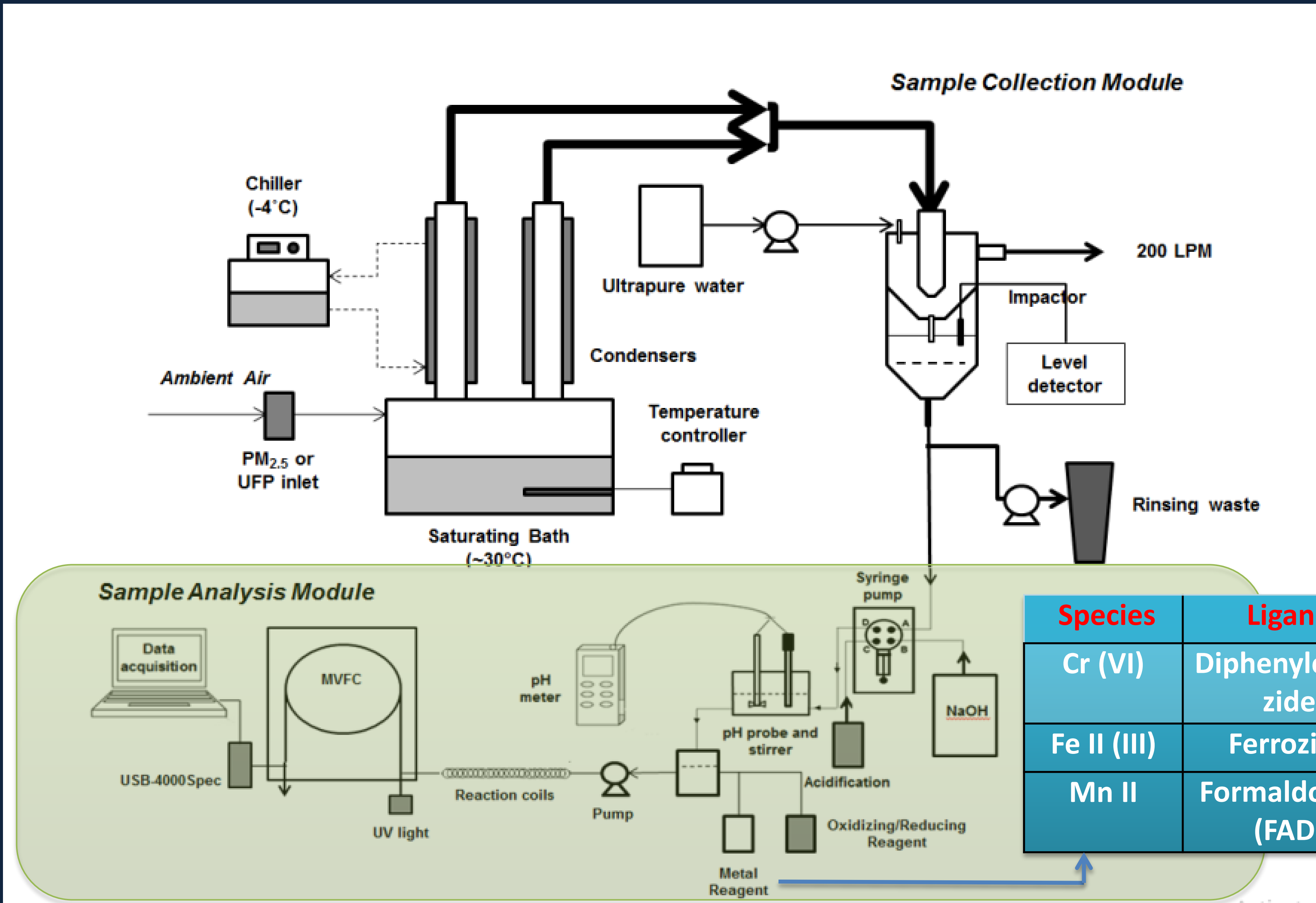
The median slurry vs filter concentration ratio : **1.02 ± 0.12**

• Continuous system operation

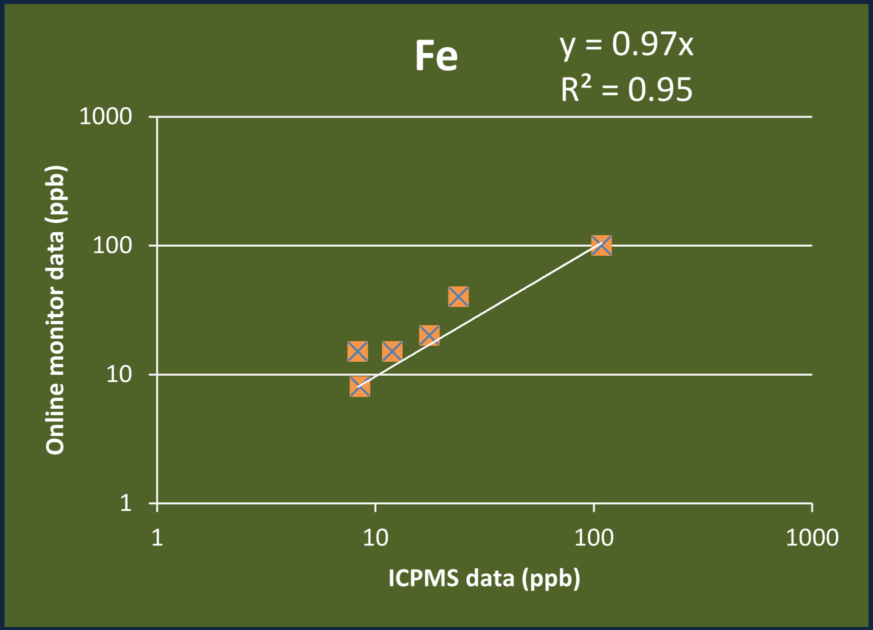


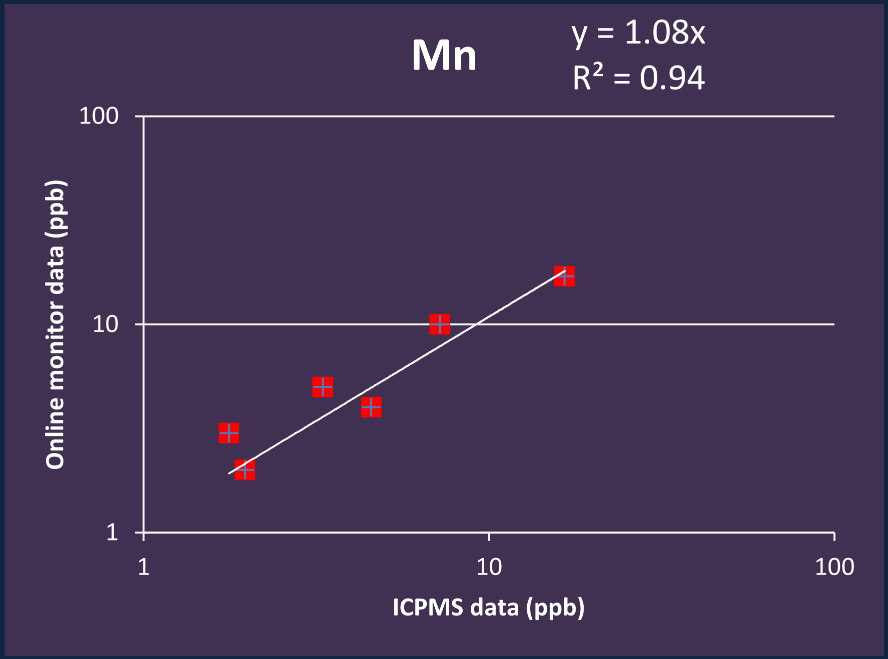
- Samples were collected/measured every 3-4 hours.
- Automated sample collection, measurement and system rinsing.
- Excellent performance for 5 consecutive days of unattended sampling.

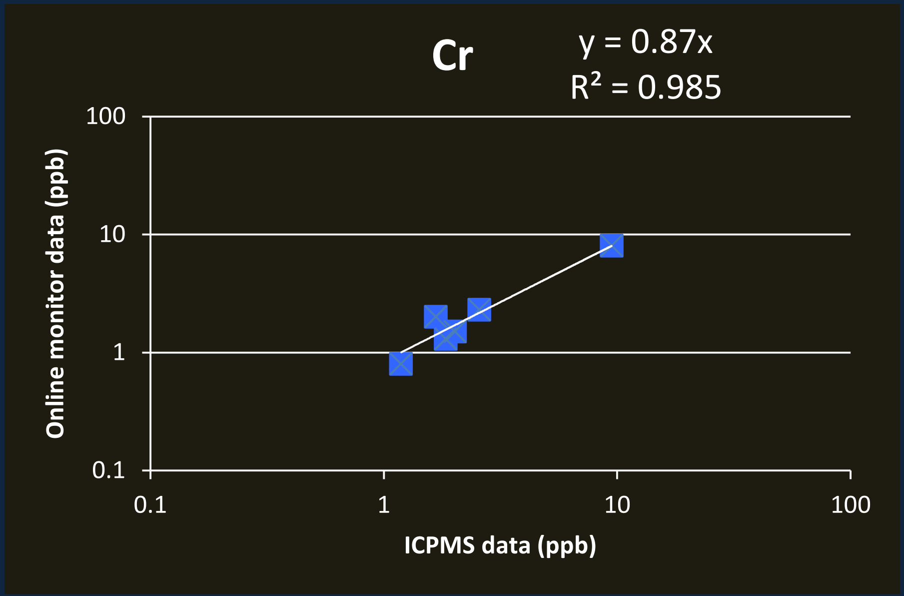
System configuration for on line measurements of Fe, Cr and Mn



Species	Ligand
Cr (VI)	Diphenylcarbazide
Fe II (III)	Ferrozine
Mn II	Formaldoxine (FAD)

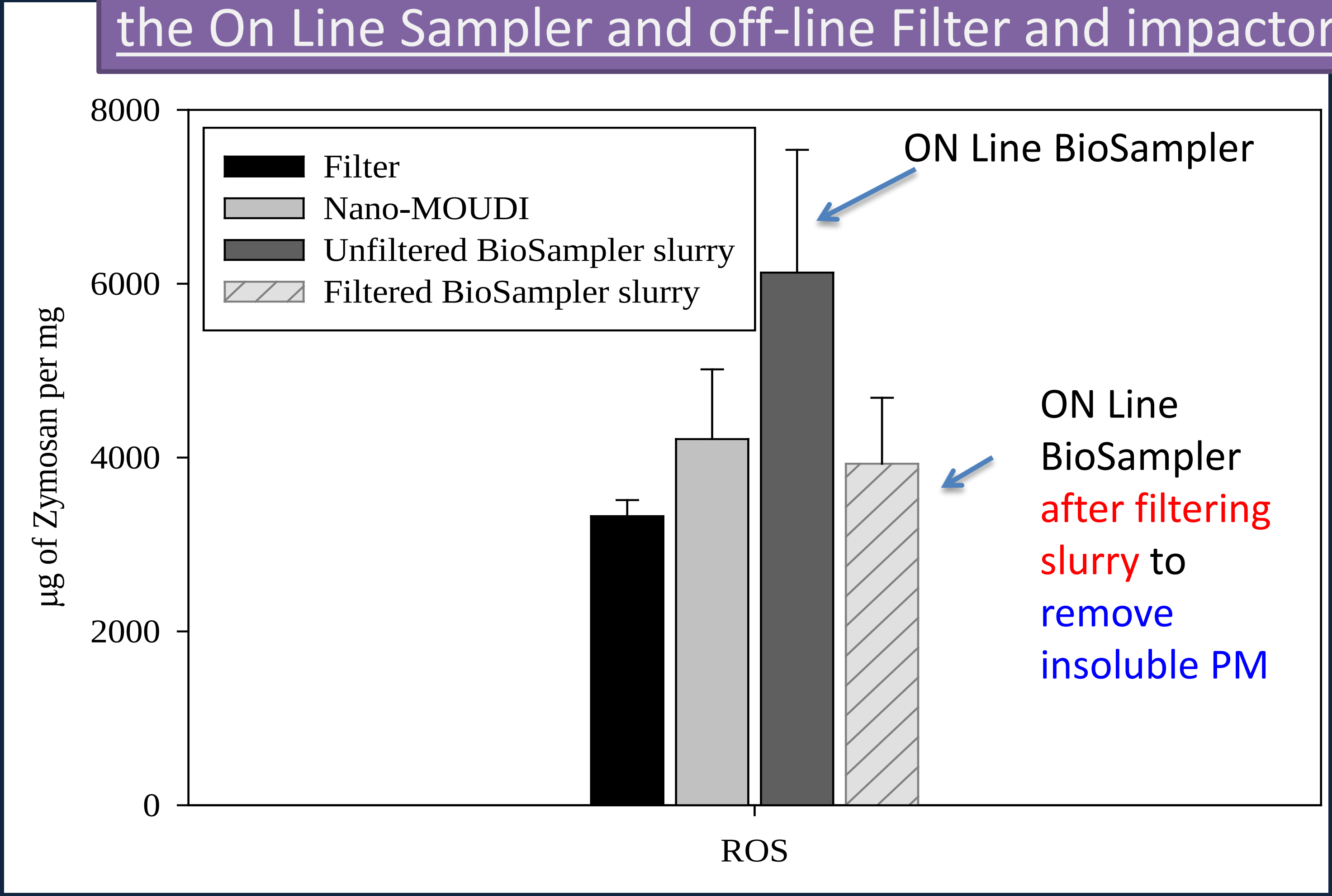






Very good agreement between off-line ICPMS and online data

Particle –Bound Reactive Oxygen Species (ROS) Measured by the On Line Sampler and off-line Filter and impactor samplers



Higher ROS with impactor/ on line sampler

Virtually identical ROS between samplers when insoluble species are removed

PUBLICATIONS

1. Wang D., Kam W., Cheung K. and Sioutas C.* "Development of a Two-Stage Virtual Impactor System for High Concentration Enrichment of Ultrafine, PM2.5 and Coarse PM". *Aerosol Science and Technology*, 47(3): 231-238, 2013

2. Wang D., Pakbin P., Shafer M.M., Schauer J.J. and Sioutas C.* "Macrophage reactive oxygen species activity of water-soluble and insoluble fractions of ambient coarse, $PM_{2.5}$ and ultrafine particulate matter (PM) in Los Angeles **".** *Atmospheric Environment*, 77:301-310, 2013

3. Wang D., Pakbin P., Saffari A., Shafer M.M, Schauer J.J and Sioutas C.* "Development and Evaluation of a High-Volume Aerosol-Into-Liquid Collector for Fine and Ultrafine Particulate Matter". *Aerosol Science and Technology*, 47(11):1226-1238, 2013

4. Wang D., Shafer M.M, Schauer J.J and Sioutas C.* "Development of a technology for online measurement of water-soluble and total copper (Cu) in $PM_{2.5}$." *Aerosol Science and Technology,* 48(8), 864-874, 2014

5. Wang D., Shafer M.M, Schauer J.J and Sioutas C.* "A new technique for online measurement of total and water-soluble copper (Cu) in coarse particulate matter (PM)" *Environmental Pollution*, 199, 227-234, 2015

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