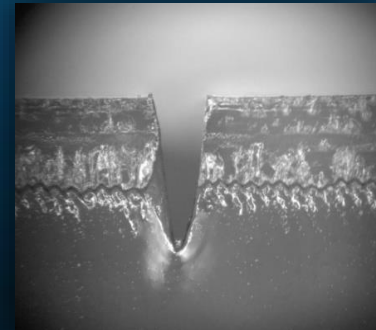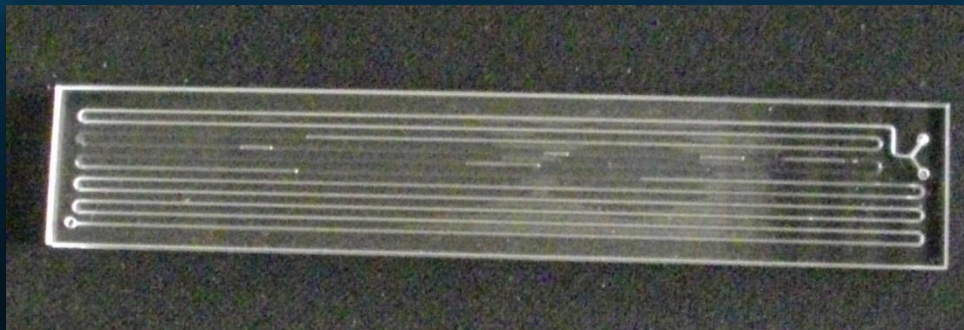# On-Line Chip-Based Devices Coupling with ICP-MS for Determination of Trace Elements and Their Species

# What are "The worst of the worst" to Analytical Chemistry

Complex matrix

Low content

In vivo

Speciation

Miniaturization

On-line system

fast response time    low sample consumption    on-site monitoring    high stability

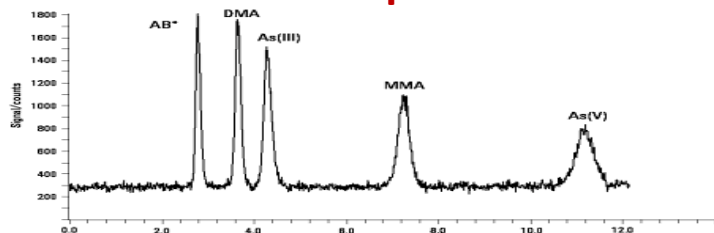# Mutual problems to be solved: micro-trace analysis

**Speciation**
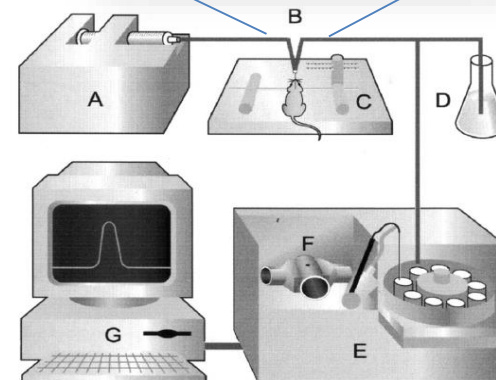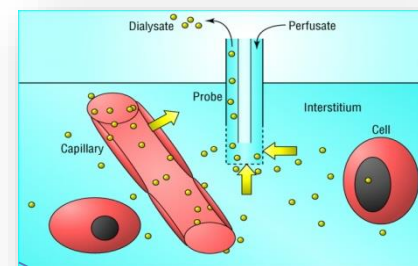
**In-vivo monitoring**

**High salt content eluent**

**High salt content perfusate**

**Low analyte concentration**

**Limited sample volume**

# Micro-trace analysis and Chip-based analytical techniques

## Problems of Micro-trace analysis

- Interferences
- Detectability
- Contamination
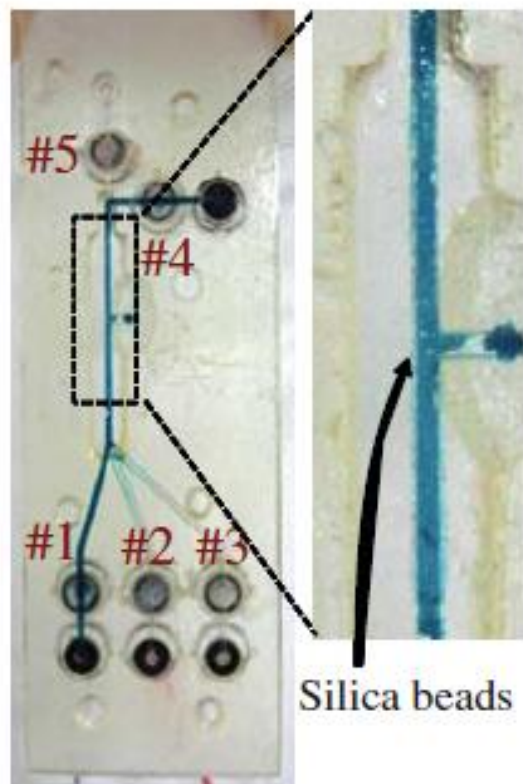- Manipulation
- Temporal resolution
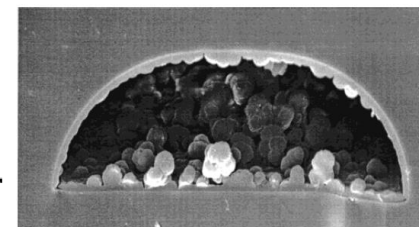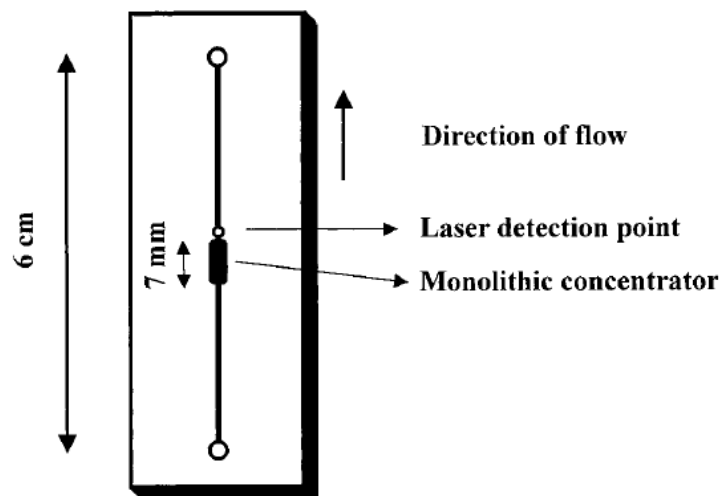
## Why miniaturized channels

- High surface to volume ratio
- Shorter diffusion length
- Reduce amount of used reagents
- Reduce cost of manufacture
- Minimize dead volume
- Easy atomization

Pure& Appl. Chem., 60, 1417-1424,1988.

Angew. Chem. Int. Ed. 2007, 46, 4913 –4916.
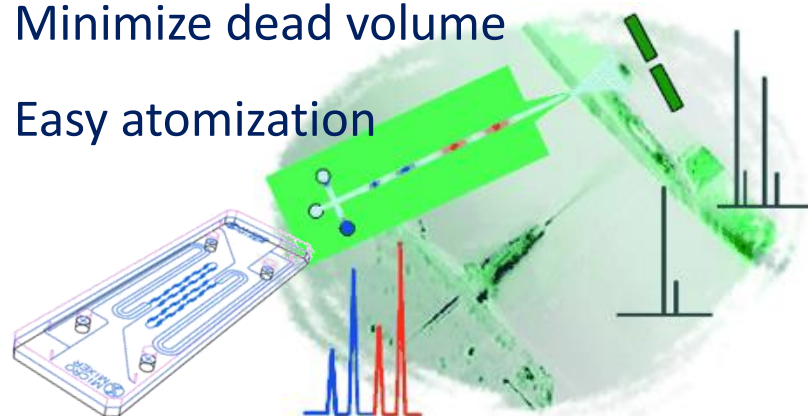
# High fluidic back pressure makes a separation in micro-channel difficult
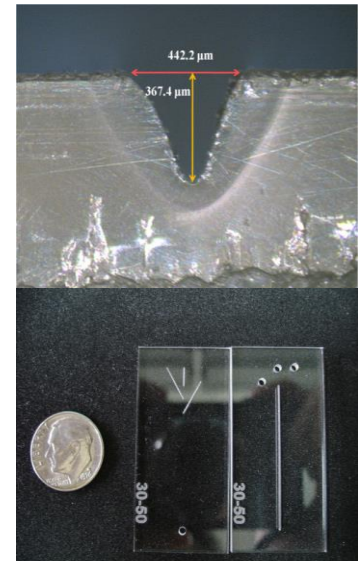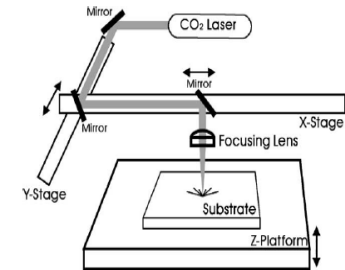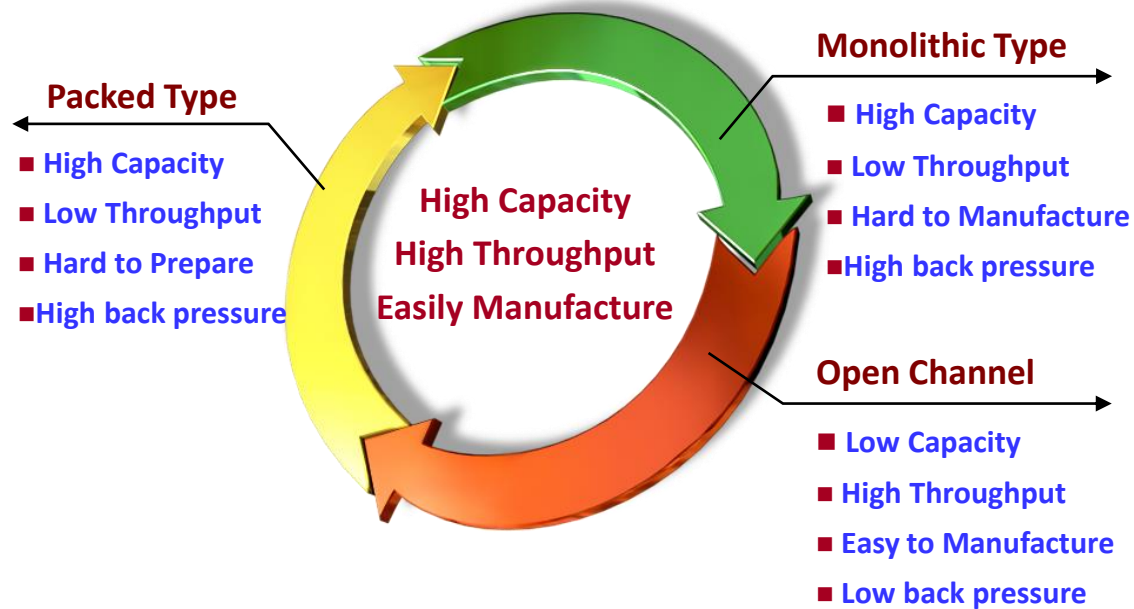


Silica beads

During the SPE process, a high fluidic back pressure of >200 kPa is generated when fluids are flowed through a microchannel packed with a solid support such as silica beads, sol-gel, or a monolithic column.



6 cm

7 mm

**Direction of flow**

**Laser detection point**

**Monolithic concentrator**

# New Technique Brings New Benefits!

## —Chip-Based Solid Phase Extraction



**Packed Type**

- High Capacity
- Low Throughput
- Hard to Prepare
- High back pressure

**Monolithic Type**

- High Capacity
- Low Throughput
- Hard to Manufacture
- High back pressure

**Open Channel**

- Low Capacity
- High Throughput
- Easy to Manufacture
- Low back pressure

High Capacity
High Throughput
Easily Manufacture

# New Material Brings New Possibility!



Native PMMA → (NaOH) → Functionalized PMMA → (HNO₃) → Acidified f-PMMA
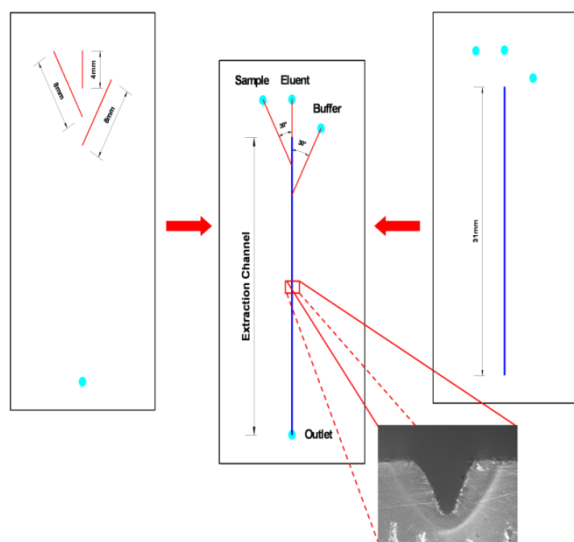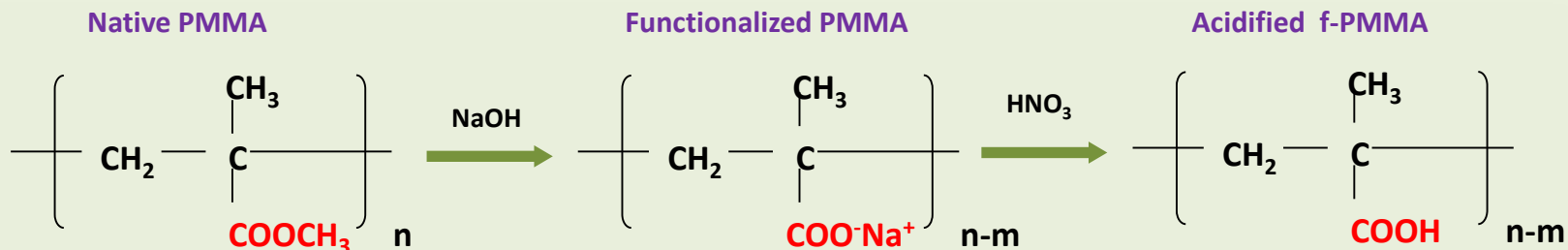
ATR-FTIR spectra
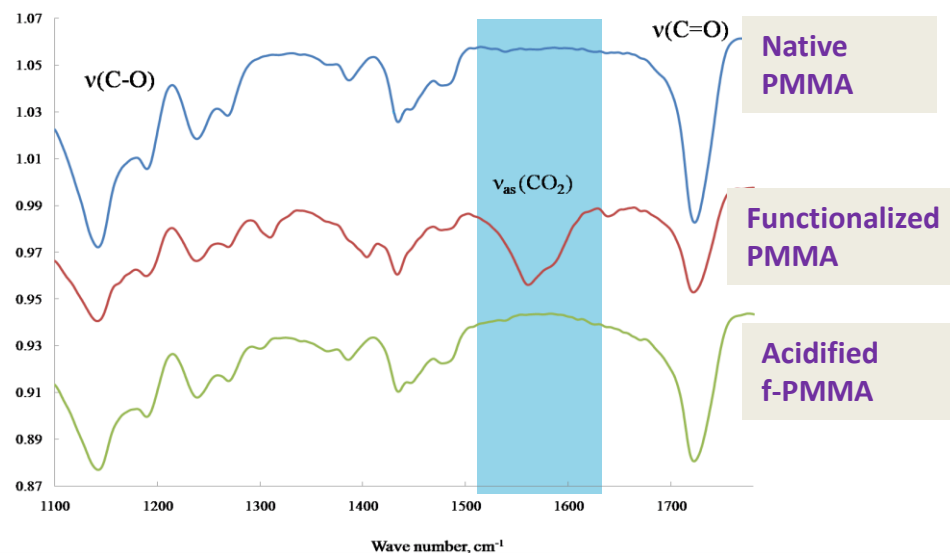
# Chip-Based Open-Channel SPE-ICP-MS



**On-Line Sample Pretreatment System**

**Sampling Configurations**

Agilent 7500a

ICP-MS Detection

Buffer

Air

Air

NH₃

0.5% HNO₃/Rh

0.5% HNO₃

CBSPED

*Direct Syringe-Injection Mode*

*Microdialysis Sampling Mode*
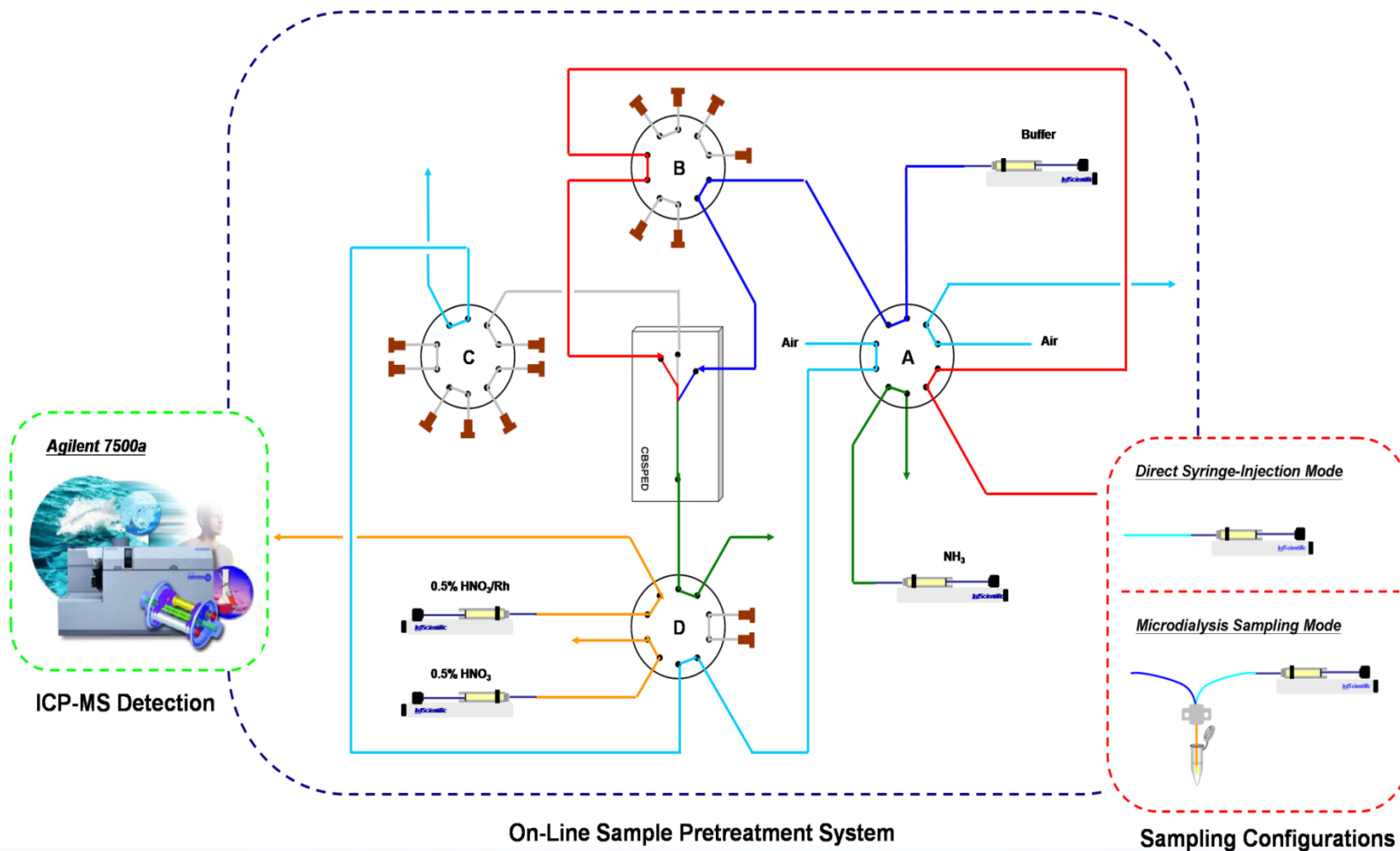
# Analytical Performance

| Element | R | MDL ng L$^{-1}$ | 2670 (urine) | | 1643e (water) | |
|---|---|---|---|---|---|---|
| | | | Certified value, μg L$^{-1}$ | Measured value, μg L$^{-1}$ | Certified value, μg L$^{-1}$ | Measured value, μg L$^{-1}$ |
| Mn | 0.995 | 64.7 | (330)[b] | 319 $\pm$ 5 | 39.0 $\pm$ 0.5 | 42 $\pm$ 0.4 |
| Co | 0.999 | 23.6 | -- | -- | 27.1 $\pm$ 0.3 | 27 $\pm$ 0.1 |
| Ni | 0.997 | 76.9 | (300)[b] | 278 $\pm$ 12 | 62.4 $\pm$ 0.7 | 60 $\pm$ 2.3 |
| Cu | 0.996 | 51.3 | 370 $\pm$ 30 | 344 $\pm$ 10 | 22.8 $\pm$ 0.3 | 22 $\pm$ 0.6 |
| Pb | 0.998 | 5.9 | 109 $\pm$ 4 | 100 $\pm$ 2 | 19.6 $\pm$ 0.2 | 22 $\pm$ 0.2 |

[a]Sample volume = 15 μL.  [b]Reference value.

# Validation of Applicability: *In-vitro* dynamic monitoring
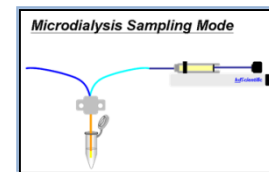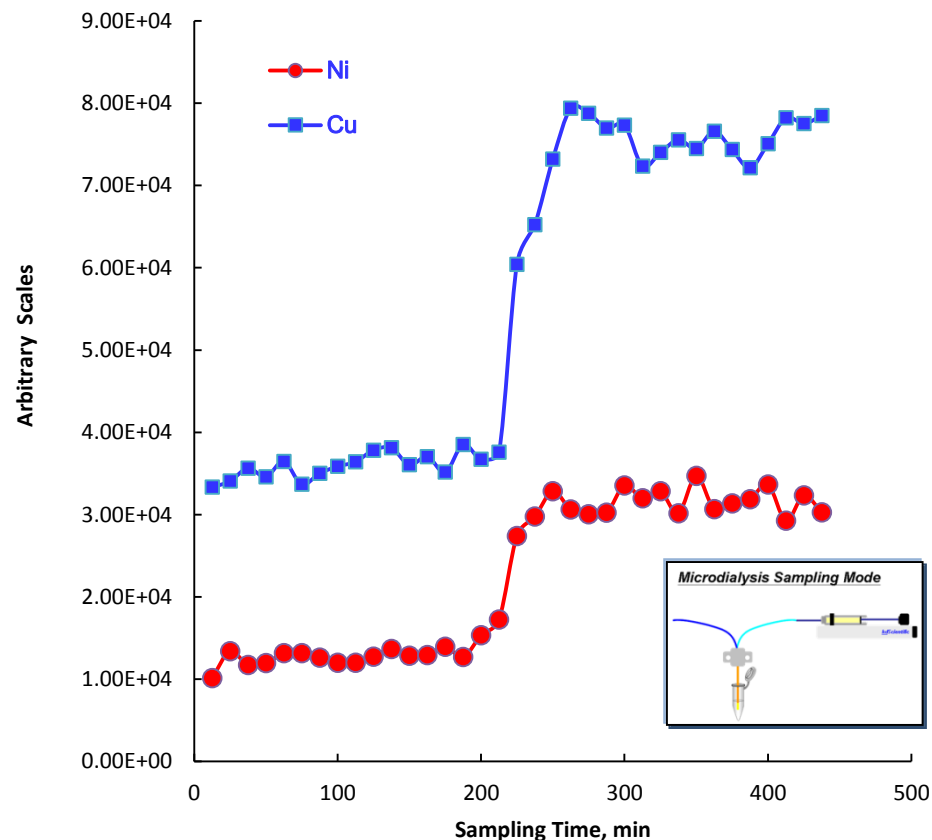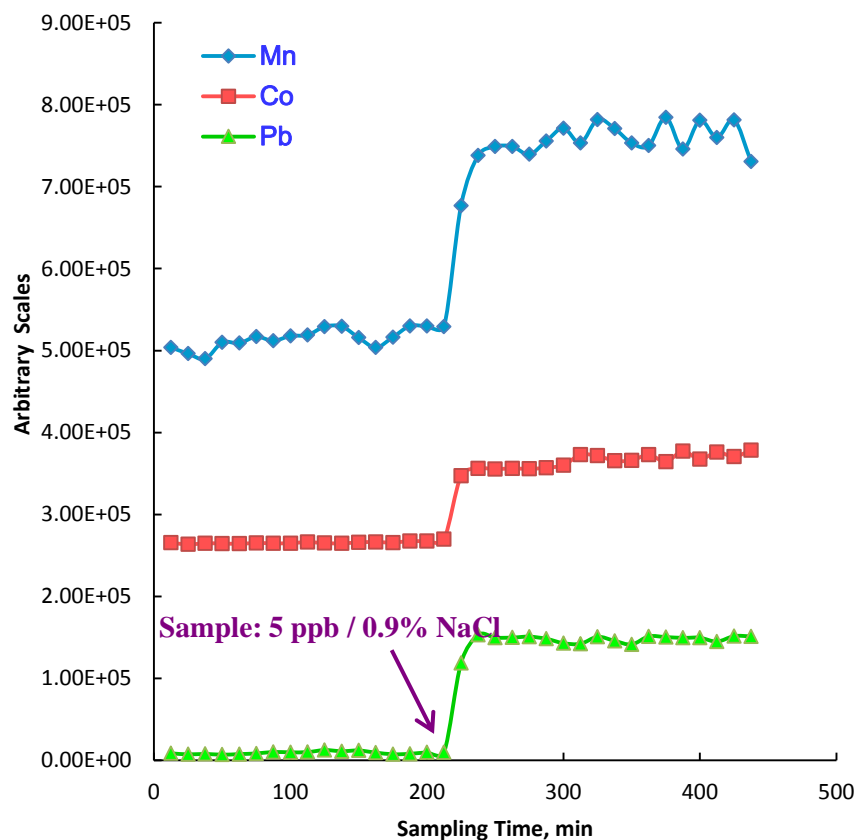


NH$_4$OH: 0.2% (w/v) (10sec) , Flow rate of absorption: 20 μL/min, Buffer: 40 mM  (pH= 9), Sample loading: 10 μL