Analytical methods for determination of metals in environmental samples

G. de Gennaro, B.E. Daresta, P. Ielpo, M. Placentino
LEnviroS, Laboratory of Environmental Sustainability
Department of Chemistry - University of Bari
An analytical method for the determination of the heavy metals is composed of 3 steps:

- **Sampling**
  - seawaters
  - riverwaters
  - groundwaters
  - rainwaters
  - sediments
  - sludges
  - particulate

- **Pretreatment of the sample:** it depends on analyte of interest and consists in acidification (e.g. Fe$^{3+}$ in waters), acid digestion (e.g. Zn$^{2+}$ in sediments), filtration (in order to remove coarse particles to preserve the analytical instrumentation), preconcentration, etc.

- **Analysis**
  - AAS
  - ICP-MS
  - ICP-AES
  - IC
  - XRF
Analytical technique choose

- Cost
- Sensitivity (Limit Of Detection)
- Physical state of matrix
- Availability of instrumentation !!!
Main analytical techniques used to determine heavy metals in environmental matrices are:

- Atomic Absorption Spectrometry (AAS)
- Inductively Coupled Plasma Atomic Emission Spectrometry (ICP/AES)
- Inductively Coupled Plasma Mass Spectrometry (ICP/MS)
- Neutron Activation Analysis (NAA)
- X-ray fluorescence (XRF)
- Ion Chromatography (IC)
Atomic Absorption Spectrometry
Atomic Absorption Spectrometry (AAS) is an analytical technique that measures the concentrations of elements. Atomic absorption spectroscopy can be used to analyze the concentration of over 62 different metals in a solution and is so sensitive that it can measure down to parts per billion of a gram (ug/dm$^{-3}$) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level.

\[ E = h\nu = \frac{hc}{\lambda} \]
Atoms of different elements absorb characteristic wavelengths of light. Analysing a sample to see if it contains a particular element means using light from that element. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample.

In AAS, the sample is atomised — *ie converted into ground state free atoms in the vapour state* — and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporised sample. Some of the radiation is absorbed by the lead atoms in the sample.
An atomic absorption spectrophotometer consists of a light source, a sample compartment and a detector. In this method, light from a source is directed through the sample to a detector. The source of light is a lamp whose cathode is composed of the element being measured. Each element requires a different lamp.
An HCL usually consists of a glass tube containing a cathode made of the material of interest, an anode, and a buffer gas (usually a noble gas). A large voltage across the anode and cathode will cause the buffer gas to ionize, creating a plasma. These ions will then be accelerated into the cathode, sputtering off atoms from the cathode. These atoms will in turn be excited by collisions with other atoms/particles in the plasma. As these excited atoms decay to lower states, they will emit photons, which can then be detected and a spectrum can be determined.

The shape of the cathode concentrates the radiation into a beam which passes through a quartz window, and the shape of the lamp is such that most of the sputtered atoms are redeposited on the cathode.
Atomisation of the sample

Two systems are commonly used to produce atoms from the sample. Aspiration involves sucking a solution of the sample into a flame; and electrothermal atomisation is where a drop of sample is placed into a graphite tube that is then heated electrically. Some instruments have both atomisation systems but share one set of lamps. Once the appropriate lamp has been selected, it is pointed towards one or other atomisation system.

Ethyne/air (giving a flame with a temperature of 2200–2400 °C) or ethyne/dinitrogen oxide (2600–2800 °C) are often used. A flexible capillary tube connects the solution to the nebuliser. At the tip of the capillary, the solution is ‘nebulised’ – ie broken into small drops. The larger drops fall out and drain off while smaller ones vaporise in the flame. Only ca 1% of the sample is nebulised.
Electrothermal atomisation

The figure shows a hollow graphite tube with a platform. 20 µl of sample (ca 1/100th of a raindrop) is placed through the sample hole and onto the platform from an automated micropipette and sample changer. The tube is heated electrically by passing a current through it in a pre-programmed series of steps. The details will vary with the sample but typically they might be 30–40 seconds at 150 °C to evaporate the solvent, 30 seconds at 600 °C to drive off any volatile organic material and char the sample to ash, and with a very fast heating rate (ca 1500 °C s-1) to 2000–2500 °C for 5–10 seconds to vaporise and atomise elements (including the element being analysed). Finally heating the tube to a still higher temperature – ca 2700 °C – cleans it ready for the next sample. During this heating cycle the graphite tube is flushed with argon gas to prevent the tube burning away. In electrothermal atomisation almost 100% of the sample is atomised. This makes the technique much more sensitive than flame AAS.
The Beer-Lambert Law

The diagram shows a beam of monochromatic radiation of radiant power \( I_0 \), directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power \( I \).

\[
A = \varepsilon bc
\]

Where

- \( A \) is absorbance (no units, since \( A = \log_{10} \frac{I_0}{I} \))
- \( \varepsilon \) is the molar absorbtivity with units of \( \text{L mol}^{-1} \text{cm}^{-1} \)
- \( b \) is the path length of the sample - that is, the optical pathlength.
- \( c \) is the concentration of the compound in solution, expressed in \( \text{mol L}^{-1} \)
Quantitative analysis can be achieved by measuring the absorbance of a series of solutions of known concentration. A calibration curve and the equation for the line can be used to determine an unknown concentration based on its absorbance.
Hydride (generation) atomic absorption spectrometry

The method of hydride atomic absorption spectrometry is used for the analysis (especially traces) of arsenic, antimony, tin, selenium, bismuth and mercury. It is used to separate and preconcentrate analytes from sample matrices by a reaction that turns them into their hydride vapors. Sodium borohydride is the common reagent of choice for the reduction.

Hydride generation atomic absorption spectrometry (HG-AAS) facilitates the reaction of sodium borohydride with these elements to produce volatile hydrides which are purged from solution and detected spectrophotometrically. This method can produce very low detection limits (20-500 ng/L), but it is prone to severe matrix interferences. The major issue with hydride generation methods is that they are operationally limited to the quantification of elements in solution.

The time from reagent mixing and when the volatile hydride is separated from the liquid and sent to the optical cell is also important. The timing of that process is controlled by flowing reagents together using a peristaltic pump and tubing of specific lengths. After being mixed together the liquid mixture flows through a tube of a specific length (read this as a controlled reaction time) and is ultimately flowed into a gas/liquid separator where the hydride and some gaseous hydrogen (produced by the NaBH4 + H2 reaction) bubble out and are purged (via a high purity inert gas) into the optical cell via a gas transfer line.
• **ICP-AES** Inductively Coupled Plasma – Atomic Emission Spectrometry)

• **ICP-MS** (Inductively Coupled Plasma – Mass Spectrometry)
• ICP-AES Inductively Coupled Plasma – Atomic Emission Spectrometry

The radio frequency-generated and maintained Ar plasma, portions of which are as hot as 10,000 K, excites the electrons. The plasma is used to atomize and ionize the elements in a sample.

When the electrons return to ground state at a certain spatial position in the plasma, they emit energy at the specific wavelengths peculiar to the sample's elemental composition. Light emitted from the plasma is focused through a lens and passed through an entrance slit into the spectrometer. There are two types of spectrometers used in ICP-AES analysis: sequential (monochromator) and simultaneous (polychromator).
Steps of ICP-AES analysis

Step 1: **sample preparation**

Step 2: **nebulization** (liquid becomes aerosol)

Step 3: **desolvation/volatilization**

Step 4: **atomization**

Step 5: **excitation/emission** (atoms gain energy by collisions and emit light with characteristic $\lambda$)

Step 6: **separation/detection** (light emitted is scattered and measured)
• **Inductively Coupled Plasma Mass Spectrometry (ICP-MS)** is a very powerful tool for *trace* (ppb-ppm) and *ultra-trace* (ppq-ppb) elemental analysis.

The resulting ions are then passed through a series of apertures (cones) into the high vacuum mass analyzer.

The isotopes of the elements are identified by their mass-to-charge ratio (*m/e*) and the intensity of a specific peak in the mass spectrum is proportional to the amount of that isotope (element) in the original sample.
ICP - AES

ICP - MS
X-ray Fluorescence
X-ray Fluorescence: how does it work?

Fluorescence involves emission of an X-ray photon after ionization of the atom by a primary beam X-ray.
An X-ray from the tube is impacting in the sample where it will interact with an electron from one of the inner shell of the A atom. It knocks the electron out of its orbital. This leaves a void which will be promptly filled by an electron from an outer shell. This electron has a higher energy than the electron it is replacing. The excess energy is expelled in the form of an X-ray with a wavelength specific for the atom of A.
XRF techniques

- **Energy Dispersive X-ray fluorescence** – **EDXRF** uses a detector to process directly the complete spectrum into an energy dispersive scale.

- **Wavelength Dispersive X-ray fluorescence** - **WDXRF** uses appropriate crystals to separate the emission spectrum into discrete wavelengths before detecting them.

  - **Micro x-ray fluorescence** (μXRF) gets its name because these instruments are designed to analyze very small spot sizes.
  
  - In **Total Reflection X-Ray Fluorescence** (TRXRF) the excitation beam is totally reflected by the substrate and only particles on the surface are excited giving rise to x-ray fluorescence emissions. In this way the background normally associated with XRF measurements is much reduced, leading to higher sensitivity and lower detection limits.
Energy Dispersive X-ray Spectrometer

X-ray Generator

Sample

Secondary target

Detector

X-ray Source (X-ray Tube or Radioactive Isotope)

Electronics

Micro Processor / Computer

Read-Out

Sample

Fluoresced and Scattered X-rays

Incident X-rays

Filter

Tube Source

Detector
Energy Dispersive XRF

- EDXRF spectrometers include a high-tech detector using a Silicon Lithium drifted crystal cooled at low temperature (-90°C).
- This crystal is able to discriminate between X-ray photons of different energies, thus the name of the technique: energy dispersion.
- Detector picks up all the photons emitted by the sample and total detector countrate is about 50 kcps - often saturated
  - Specific filters are used to filter out part of the spectrum, e.g. the major elements.
  - Secondary targets are used to better excite only a part of the elements of the periodic table.
**Principle of the Si(Li) detector**

- Si(Li) crystal of the detector absorbs an incoming X-ray photon which ionizes atoms and produces electron (-) and hole (+) pairs.
- Amount of electron/hole pairs is proportional to the energy of the X-ray photon.
- Detector output pulses are amplified, digitized and sorted depending on their magnitude.
- Detector must be cooled at –90°C.
EDXRF cannot measure Na – U simultaneously !!
Advantages:

- Element coverage: Sodium to Uranium
- Various sample types:
  - Solids or liquids samples
  - Bulk sample or thin films
- Wide dynamic range ppm-%
- Minimal sample preparation
- Non-destructive
- Multi-element
- Transportable for field analyses
- Low maintenance and operating costs
In general, analysis of Na – U requires at least 3 spectra
Detection limits and dynamic range

Solids
Liquids

ICP-MS
ICP-AES
GFAAS
AAS

XRF

TRACE
BULK

1 ppq 1 ppt 1 ppb 1 ppm 1,000 ppm 100%

Liquids
Solids
Applications

**Industries**
- Laboratory – R&D
- Environmental
- Petrochemical
- Plastics
- Chemicals
- Forensics
- Electronics
- Academics - Education
- Food industry

**SAMPLE TYPES**
- Metals
  - Alloy composition
  - Plating thickness
- Geological
- Environmental
  - Soil/hazardous waste
  - Aerosol filters
- Petrochemicals
- Polymers
- Catalysts
- Copy toner/paint pigments
- Small parts or pieces
- Thin-film samples
- Data storage
- Nutritional products
Materials Analysis with XRF

- Oils
- Polymers
- Ores and raw materials
- Chemicals
- Metals, Slags
- Glass
- Ceramics
- Food products
2004 EDXRF Applications
“Distribution”
Air filters

- No sample preparation
- 50 elements
- Loadings range from a few nanograms to hundreds of micrograms
- Thin-film fundamental parameters algorithms to analyze any air filter
• Using the AAS, ICP-MS, ICP-AES it’s necessary to remove sample matrix interferences and/or preconcentrate metals of interest.

• ...moreover in a tipycal laboratory a cheap instrumentation is available:

  Ion Chromatography

In letterature several papers and reviews are available about the metals determination by Ion chromatography in different matrices.
Ion Chromatography

<table>
<thead>
<tr>
<th>Metals</th>
<th>Sample</th>
<th>Sample preparation</th>
<th>Separation</th>
<th>Detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(III)</td>
<td>Seawater</td>
<td>Preconcentration</td>
<td>CIC Self-made chrome azucre S polymer, potassium nitrate, pH gradient</td>
<td>UV-Vis 580 nm PCR with pyrocatechol violet</td>
</tr>
<tr>
<td>Al(III), inorganic species</td>
<td>Rainwater</td>
<td>Filtration</td>
<td>IC Mitsubishi-Kagaku MCI-gel SC-01 calcium nitrate, pH 4</td>
<td>Fluorescence, 500 nm, 590 nm PCR with lumogallion</td>
</tr>
<tr>
<td>U(VI)</td>
<td>Saline lake water</td>
<td>Spiking</td>
<td>CIC Self-made methylthymol blue polymer, potassium nitrate, pH gradient</td>
<td>UV-Vis 600 nm PCR with Arsenazo III</td>
</tr>
<tr>
<td>U(VI) and other actinides</td>
<td>Soil</td>
<td>Microwave acid leaching</td>
<td>CIC FDCA coating on polymer, nitric acid</td>
<td>ICP-MS</td>
</tr>
<tr>
<td>Cu(II), Pb(II), Co(II), Ni(II), Mn(II), Cd(II)</td>
<td>Seawater, Oyster tissue</td>
<td>Acid digestion, preconcentration</td>
<td>CIC y-aminoethylhydroxyamine resin, potassium nitrate, acetate pH 5.5</td>
<td>UV-Vis 495 nm PCR with PAR</td>
</tr>
<tr>
<td>Mn(II), Cd(II), Zn(II)</td>
<td>Freshwater</td>
<td>Spiking</td>
<td>CIC BioChemMack IDA, potassium chloride/nitrate, pH 2.5</td>
<td>UV-Vis 495 nm PCR with PAR</td>
</tr>
<tr>
<td>Co(II), Ni(II), Mn(II), Cu(II), Cd(II), EDTA</td>
<td>River water</td>
<td>Flow injection preconcentration</td>
<td>IPC LiChrospher C18 silica, sodium dodecylsulfate, tartrate pH 3.5</td>
<td>UV-Vis 510 nm PCR with PAR</td>
</tr>
<tr>
<td>Cd(II), Co(II), Pb(II), Zn(II), Cu(II), Cu(II) complexes</td>
<td>Wastewater, surface water</td>
<td>Filtration</td>
<td>IPC Supelco Discovery C18 silica, cetyltrimethylammonium bromide, sodium sulfate, Hepes pH 7</td>
<td>UV 258 nm PCR with iron nitrate</td>
</tr>
<tr>
<td>Cu(II), U(VI), Zn(IV), Th(IV), Fe(III), Sn(IV), Ba(II), lanthanides</td>
<td>Waste sludge</td>
<td>Dissolution</td>
<td>IC Dionex CS-3, acid gradient</td>
<td>UV-Vis 620 nm PCR with Arsenazo III</td>
</tr>
<tr>
<td>Cu(II), Ni(II), Zn(II), Co(II), Pb(II), Fe(II)</td>
<td>Air particulate</td>
<td>Microwave acid digestion</td>
<td>IC Dionex CS-2, oxalate, citrate, pH 3.6</td>
<td>UV-Vis 520 nm PCR with PAR</td>
</tr>
<tr>
<td>Fe(III), Fe(II), Ni(II), Zn(II), Co(II), Cu(II), Cd(II), Mn(II), Pb(II)</td>
<td>Marine sediment</td>
<td>Ammonium acetate extraction, pH 5</td>
<td>IC Dionex CS-5A: oxalate gradient</td>
<td>UV-Vis 530 nm PCR with 5-Bz-PADAP</td>
</tr>
<tr>
<td>Pb(II), Cd(II), Cu(II)</td>
<td>Drinking water</td>
<td>Preconcentration</td>
<td>IC Dionex CS-5A, MetPac CC-1 IDA oxalate gradient</td>
<td>UV-Vis 560 nm PCR with 5-Bz-PADAP</td>
</tr>
<tr>
<td>Pb(II), Cd(II), Zn(II), Ni(II)</td>
<td>Air particulate</td>
<td>Microwave acid digestion</td>
<td>IC Dionex CS-5A: oxalate gradient</td>
<td>UV-Vis 520 nm PCR with PAR</td>
</tr>
<tr>
<td>Fe(III), Fe(II), Ni(II), Zn(II), Cu(II), Cd(II), Mn(II), Pb(II)</td>
<td>Sewage waste water</td>
<td>Acidification, filtration</td>
<td>IC Dionex CS-5A PDCA eluent</td>
<td>UV-Vis 530 nm PCR with PAR</td>
</tr>
<tr>
<td>Cu(II), Cd(II), Ni(II), Zn(II), Co(II), C(II), Cd(II), Mn(II)</td>
<td>Fertiliser solution</td>
<td>Dilution</td>
<td>IC Dionex CS-5A: oxalate gradient</td>
<td>UV-Vis 520 nm PCR with PAR</td>
</tr>
<tr>
<td>Co(II), Cd(II), Ni(II), Zn(II), Pb(II), Mn(II), Ph(II)</td>
<td>Groundwater</td>
<td>Acidification, filtration</td>
<td>IC Dionex CS-5A: oxalate gradient</td>
<td>UV-Vis 520 nm PCR with PAR</td>
</tr>
</tbody>
</table>
Ion Chromatography: how does it work?

Step 1: the sample solution is injected into loop by the injection port

Step 2: the pump pushes the solvent through the loop taking the sample and carrying it into the analytical column (preceded by an guard column).

Step 3: the analytes separated by the analytical column reach the detector (UV spectrophotometer, conductivity detector, amperometric detector…) in different times

Step 4: an interface links the IC instrumentation to the pc: a chromatogram is displayed on the pc screen.
Dionex applications to determine metals:

Dionex Application note 108: Determination of transition metals in serum and whole blood by IC.

Dionex Application note 131: Determination of transition metals at PPT levels in high purity water and SC2 (D clean) Baths.

Dionex Application note 158: Determination of trace sodium and transition metals in power industry samples by ion chromatography with nonsuppressed conductivity detection.


---

### Table 1. Conditions for Two Analytical Systems

<table>
<thead>
<tr>
<th>Columns</th>
<th>IonPac CSSA analytical and IonPac CGSA guard</th>
</tr>
</thead>
</table>
| Eluents          | A) MedPac PDCA Eluent (Alternatively, 0.0 mM PDCA, 66 mM potassium hydroxide, 74 mM formic acid, and 5.6 mM potassium sulfate may be used.)
|                  | B) MedPac Oxalic Acid Eluent (Alternatively, 8 mM oxalic acid, 50 mM potassium hydroxide, and 100 mM tetramethylylammonium hydroxide may be used.) |
| Flow Rate        | 1.2 mL/min |
| Detection        | Absorbance, 530 nm |
| Postcolumn Reagent | 0.5 mM PAR, dissolved in MedPac Postcolumn Diluent. (Alternatively, 1.0 M 2-dimethylaminomemethanol, 0.50 M ammonium hydroxide, and 0.30 M sodium bicarbonate may be used.) |
| Postcolumn Reagent Flow Rate | 0.7 mL/min |

---

### Analytical Columns

- IonPac CSSA, CGSA (2 mm)

### Concentration

- Time: 15 min
- Sample Volume: 30 mL
- Total Run Time: 30 min
- Detection: Vis, 530 nm

### Peaks

1. Iron 1 µg/L
2. Copper 1
3. Nickel 1
4. Zinc 1
5. Cobalt 1
6. Cadmium 1
7. Manganese 1
During these last years our research group has developed some methods for metals determinations by IC

Ref. 1 Analysis of heavy metals in atmospheric particulate by ion chromatography
P. Bruno, M. Caselli, G. de Gennaro, P. Ielpo, A. Traini

Experimental conditions:

- Injection volume: 200 µl
- Guard column: IonPac CG5A Guard Column
- Analytical column: IonPac CS5A Analytical Column
- Eluent: 28 mM oxalic acid, 250 mM sodium nitrate
- Eluent flow: 1.2 ml/min
- Detection: \( \lambda = 530 \text{ nm} \)
- Post-column reagent: 0.12 mg/l di PAR, 3 M di NH\(_4\)OH.
- Reaction coil: 375 µl
- Post-column reagent flow: 0.6 ml/min

Limit of detection (LOD) and limit of quantification (LOQ) for chromatographic method

<table>
<thead>
<tr>
<th>Elements</th>
<th>LOD (ppb)</th>
<th>LOQ (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>60</td>
<td>200</td>
</tr>
<tr>
<td>Fe</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>Cu</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Co</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Cd</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>Ni</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Mn</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
<td>30</td>
</tr>
</tbody>
</table>
In order to reduce the detection limits a preconcentration procedure has been developed:

The ion chromatograph (Dionex-600) is fitted with a piston pump and a six port valve connected to the sample loop. The loop is filled with the sample which is then delivered to the concentrator column using water as the carrier and the analytes of interest were retained on the concentrator column. Finally by switching the injection valve, the eluent flowed through the concentrator and the analytes reached the analytical column.

Ref. 2 Ion Chromatography Determination of Metals in Airborne Particulate with Preconcentration and Large Volume Direct Injection
P. Bruno · M. Caselli · G. Gennaro · P. Ielpo · T. Ladisa · C.M. Placentino, Chromatographia 2006, 64, November (N° 9/10), 537-542.
Table 1. Limit of detection (LOD) and limit of quantification (LOQ) for column switching and large volume direct injection procedures

<table>
<thead>
<tr>
<th>Elements</th>
<th>LOD (ppb)</th>
<th>LOQ (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Fe</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Co</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Cd</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Ni</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Mn</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Zn</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

In the chromatogram the red line is obtained by method of Ref. 1, while the black line is obtained by Ref. 2.
Investigation on post column reagent in order to determine Cu(II), Ni(II), Co(II), Fe(II), and Pd(II) at ppb/subppb levels

Ref. 3 A method for the determination of Cu (II), Ni(II), Co(II), Fe(II) and Pd(II) at ppb/subppb levels by ion chromatography. P. Bruno, M. Caselli, G. de Gennaro, P. Ielpo, V. de Pinto, B.E. Daresta and C.M. Placentino, *Journal of Liquid Chromatography & Related Technologies*, 2007

**Experimental conditions:**
DX 600 (Dionex, Sunnyvale, CA, USA), equipped with a spectrophotometric variable wavelength.
Loop volume: 5 mL;
Eluent: oxalic acid (28 mM) and sodium nitrate (250 mM);
Guard column: IonPac CG5A; Analytical column: IonPac CS5A;
Reaction coil: 375 mL;
Eluent flow: 1.2 mL/min; PCR: PAR, 0.39 mM, in acetate buffer at pH 6 and of hexadecylpyridinium chloride, 6.6 mM (a stock hexadecylpyridinium chloride solution was prepared by dissolving the salt in ethanol, 10% w/w solution);
PCR flow: 0.6 mL/min;
Detection wavelength: 540 nm.

After solvent investigation a study on post column reagent has been performed

*Figure 2.* Chromatogram of a heavy metals standard solution. Peaks: Cu(II) (2 ppb), Ni(II) (1 ppb), Zn(II) (100 ppb), Co(II) (1 ppb), Fe(II) (5 ppb), Pd(II) (10 ppb). Loop volume: 5 mL.
Table 2. Limit of detection (LOD) for Cu(II), Ni(II), Zn(II), Co(II), Fe(II), and Pd(II) in method 1 (proposed method), in method 2 (method of Bruno et al.\textsuperscript{[26]}) and in method 3 (method of Bruno et al.\textsuperscript{[25]}).

<table>
<thead>
<tr>
<th>Element</th>
<th>Method 1 LOD (ppb)</th>
<th>Method 2 LOD (ppb)</th>
<th>Method 3 LOD (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>1.1</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>0.5</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>39</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Co(II)</td>
<td>0.18</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>4</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>1.7</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Ref.3       Ref.2       Ref.1
A comparison between AAS and IC data:

Determination of Fe, Mn, Cu, Zn, Ni and Co by AAS and IC

<table>
<thead>
<tr>
<th>Campioni</th>
<th>Fe µg/m³</th>
<th>Mn µg/m³</th>
<th>Cu µg/m³</th>
<th>Zn µg/m³</th>
<th>Ni µg/m³</th>
<th>Co µg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PTS</td>
<td>AAS</td>
<td>IC</td>
<td>AAS</td>
<td>IC</td>
<td>AAS</td>
</tr>
<tr>
<td>T 20/07/2006</td>
<td>2.3</td>
<td>2.2</td>
<td>0.043</td>
<td>0.044</td>
<td>0.010</td>
<td>0.026</td>
</tr>
<tr>
<td>T 22/07/2006</td>
<td>7.5</td>
<td>7.2</td>
<td>0.101</td>
<td>0.101</td>
<td>0.034</td>
<td>0.034</td>
</tr>
<tr>
<td>T 23/07/2006</td>
<td>1.7</td>
<td>2.0</td>
<td>0.050</td>
<td>0.042</td>
<td>0.248</td>
<td>0.032</td>
</tr>
<tr>
<td>T 24/07/2006</td>
<td>6.7</td>
<td>6.0</td>
<td>0.127</td>
<td>0.113</td>
<td>0.094</td>
<td>0.185</td>
</tr>
<tr>
<td>T 29/07/2006</td>
<td>12.7</td>
<td>12.0</td>
<td>0.208</td>
<td>0.190</td>
<td>0.023</td>
<td>0.064</td>
</tr>
<tr>
<td>T 31/07/2006</td>
<td>8.7</td>
<td>10.3</td>
<td>0.066</td>
<td>0.090</td>
<td>0.004</td>
<td>0.037</td>
</tr>
<tr>
<td>T 01/08/2006</td>
<td>13.2</td>
<td>12.8</td>
<td>0.152</td>
<td>0.153</td>
<td>0.030</td>
<td>0.109</td>
</tr>
<tr>
<td>T 02/08/2006</td>
<td>2.1</td>
<td>2.9</td>
<td>0.027</td>
<td>0.027</td>
<td>0.024</td>
<td>0.032</td>
</tr>
<tr>
<td>M 28/07/2006</td>
<td>0.5</td>
<td>0.4</td>
<td>0.013</td>
<td>0.012</td>
<td>0.063</td>
<td>0.094</td>
</tr>
<tr>
<td>M 29/07/2006</td>
<td>0.5</td>
<td>0.5</td>
<td>0.022</td>
<td>0.009</td>
<td>0.045</td>
<td>0.046</td>
</tr>
</tbody>
</table>

LOD Ni = 0.0007 µg/m³
LOD Co = 0.002 µg/m³
GRAZIE

LENVIROS
Laboratory of Environmental Sustainability
Dipartimento di Chimica – Università degli Studi di Bari

Martino Amodio, Eleonora Andriani, Magda Brattoli, Paolo Bruno, Maurizio Caselli, Barbara Daresta, Gianluigi de Gennaro, Lucrezia de Gennaro, Antonietta de Leonibus, Pierina Ielpo, Annalisa Parenza, Marcella Placentino, Vincenzo Paolillo, Livia Trizio, Giovanna Turturro, Maria Tutino