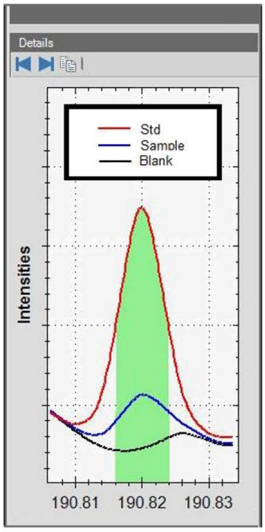
Environmental Chemical Analysis

Inorganic Environmental Analysis

Ricardo Bettencourt da Silva

2025/10/10



Environmental Chemical Analysis - Inorganic analysis

Content

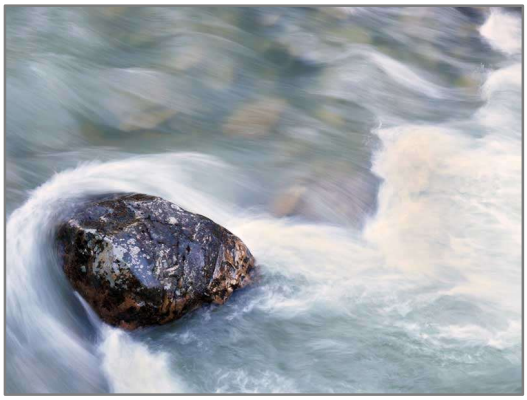
- Introduction to Inorganic Environmental Analysis
  What we measure, where we find it, and why it's regulated
- Sampling and Sample Preparation
  The critical first steps: Ensuring data integrity starts in the field
- Analytical Techniques for Inorganic Parameters
  From simple probes to high-tech spectrometers
- The Standard Addition Method
  A clever technique to overcome complex sample matrices
- Calculating and Reporting Results on a Dried Basis
  Why "dry weight" is the gold standard for solid samples
- Quality Assurance & Data Validation [Summary]
  How do we know our numbers are correct and defensible

Environmental Chemical Analysis – Inorganic analysis

Introduction to Inorganic Environmental Analysis

Defining the Scope:

The branch of analytical chemistry focused on the quantitative determination of elements and inorganic compounds *(typically excluding carbon-based molecules)* in environmental matrices.



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Introduction to Inorganic Environmental Analysis

Core Purpose:

- Pollution Assessment: Identify and quantify contaminants like heavy metals and nutrients that can harm ecosystems and human health.

- Regulatory Compliance: Provide data to enforce laws which set legal limits for contaminants.

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Introduction to Inorganic Environmental Analysis

Core Purpose:
(…)
- Fate and Transport Studies: Track how pollutants move through water, soil, and air.

- Baseline Monitoring: Establish natural background levels to distinguish from human-caused pollution.

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Key Inorganic Parameters

General "Master Variables":
- pH: Controls solubility, toxicity, and biological availability of many substances. A change in pH can mobilise otherwise stable metals.

- Conductivity: A rapid, non-specific measure of the total dissolved ionic content. High conductivity can indicate salinity pollution or geological influence.

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Key Inorganic Parameters

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Major Ions:

The "bulk" ions that define the fundamental chemical character of water.

- Cations: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}
  (often related to hardness and salinity)
- Anions: Cl^{-}, SO_4^{2-}, HCO_3^{-}/CO_3^{2-}
  (from weathering, industrial discharge, or seawater intrusion).

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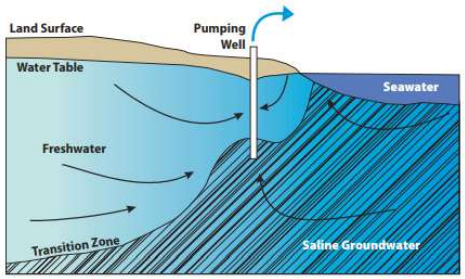

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Key Inorganic Parameters

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Nutrients:

Essential for life, but problematic in excess.

- Nitrogen species (NO_3^{-}, NO_2^{-}, NH_3) and Phosphorus (PO_4^{3-}) are key drivers of eutrophication, leading to algal blooms and oxygen depletion.

Trace Metals:

Often the primary concern for toxicity.

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Key Inorganic Parameters

(…)

Trace Metals:

Often the primary concern for toxicity.

Priority Pollutants: Pb, As, Cd, Hg, Cr are highly regulated due to their persistence and toxicity, even at parts-per-billion (ppb) levels.

Leather Tanning and Finishing

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Sample Types and Regulatory Relevance

Connecting Matrices to Mandates:

Sample Matrix	Analysis (Environmental concern)	Regulatory Driver (Example)
Water	Metals (toxicity) and Nutrients (eutrophication)	Discharge permits & Safe drinking water (Maximum limits for As, Pb and NO_3^-).
Soil & Sediment	Metals (long-term contamination) and, Nutrients and pH (agriculture)	Site cleanup, Resource conservation and Waste management
Sludge/Biosolids	Metals (prevent food chain transfer)	Strict limits for metals if sludge is to be land-applied as fertilizer
Air Particulates	Trace metals (source assessment; e.g., Pb from aviation, As from smelting ("fundição").	Ambient Air Quality Standards for PM (risk assessment for toxic air pollutants)

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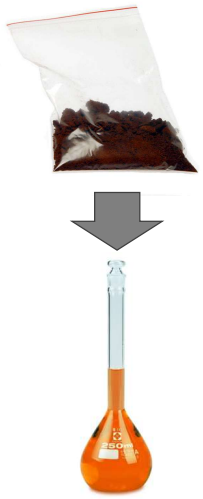
Sampling and Sample Preparation

Fundamental principle:
Reduce the risk of sample contamination. The goal is to obtain a representative sample and preserve its chemical integrity until analysis.

The Three Pillars of Sample Integrity:

- **Representative Sampling:** Correct location, depth, and technique.
- **Appropriate Preservation:** Immediate action to stop chemical/biological changes.

Proper Preparation: Converting the sample into a form the instrument can analyse.



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Sampling, Preservation & Storage

Sampling Techniques:

- **Water: Grab samples for a snapshot in time.**
- **Composite samples (automatic samplers) to average over time. The choice depends on the monitoring objective.**
- **Solids: Use core samplers to preserve stratification in sediment. Composite sampling from multiple points in a soil field to get a representative value.**

Sampling plan of a land field

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Sampling, Preservation & Storage

Preservation & Storage (The "Why"):

- Acidification (to pH <2): For metals. Prevents adsorption to container walls and precipitation as hydroxides or carbonates.

- Refrigeration (4°C): Slows microbial metabolism that can convert NH_3 to NO_3^- or reduce NO_3^- to N_2 gas.

(...)

Refrigerated chamber

rjsilva@ciencias.ulisboa.pt

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Sampling, Preservation & Storage

Refrigerated chamber

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Sampling, Preservation & Storage

Preservation & Storage (The "Why"):
(…)

- Holding Times:

Ex: Mercury in water must be analysed within 28 days if preserved with acid, but only 48 hours for nitrate without preservation.

Exceeding the holding time invalidates the data.

Refrigerated chamber

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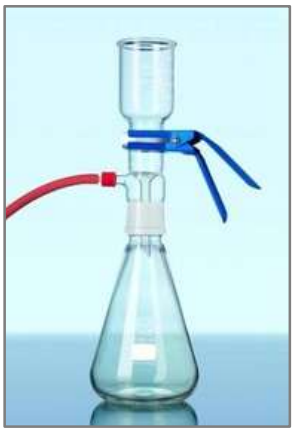
Laboratory Preparation: From raw sample to analysable item

• Filtration (0.45 µm filter):
Operationally defines "Dissolved" vs. "Suspended." This is critical because the dissolved fraction is often more bioavailable and mobile.

For example, dissolved copper is more toxic than copper bound to a sediment particle.



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Laboratory Preparation: From raw sample to analysable item

(…)

• Digestion:

Uses strong acids (HNO_3, HCl, HF) and heat (hotplate or microwave) to destroy the organic matrix and dissolve target metals from soils, sludges, and particulates. The result is a clear liquid solution suitable for AAS or ICP.

Less stringent acid digestion can be used (*aqua regia* extractable) to determine the more available metals from a soil (…)

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Laboratory Preparation: From raw sample to analysable item

(…)

• Digestion by HNO_3:

Oxidation of Organic Matter: Nitric acid's primary role is to act as a strong oxidizing agent. It breaks down carbon-hydrogen bonds in organic materials, converting them into carbon dioxide and water. The generalized reaction is:

$$(CH_2)_n + 2n\ HNO_3 \rightarrow nCO_2\uparrow + 2n\ NO\uparrow + 2n\ H_2O$$

Metals (M) are also oxidized to M^{n+}

Environmental Chemical Analysis – Inorganic analysis

Laboratory Preparation: From raw sample to analysable item

(…)

• Digestion by aqua regia:

Aqua regia digests solid samples by using a mixture of hydrochloric acid (HCl) and nitric acid (HNO_3) to both oxidize and complex metal ions, releasing them from the solid matrix for analysis. The nitric acid acts as an oxidizing agent to break down organic matter and oxidize metal sulfides, while the hydrochloric acid supplies chloride ions (Cl^-) that form highly soluble chloro-complexes with the now-oxidized metal ions.

(…)

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Laboratory Preparation: From raw sample to analysable item

(…)

• Digestion by aqua regia:

(…) This dual action allows aqua regia to extract a "pseudo-total" measure of many elements, especially more mobile and bioavailable trace metals, although it is not sufficient for dissolving some highly refractory materials like certain silicates.

Not the best practice,… but a nice video:
https://www.youtube.com/shorts/sraL5PrlY60?app=desktop

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Laboratory Preparation: From raw sample to analysable item

(...)
- Digestion:

Hotplate digestion:
https://www.youtube.com/watch?v=T_SHDoaPTTY

Microwave digestion:
https://www.youtube.com/watch?v=aqoowILFPCw

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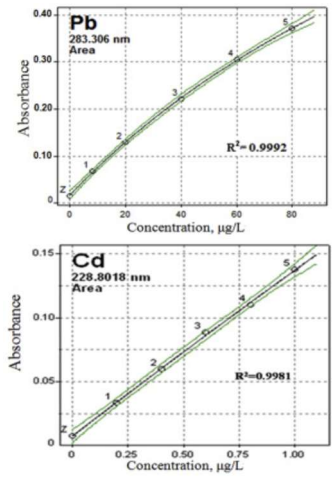
Laboratory Preparation: From raw sample to analysable item

(...)
- Dilution:

Essential to bring the analyte concentration within the linear range of the instrument's calibration curve. A concentrated sample can saturate the detector, leading to inaccurate results.



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Laboratory Preparation: From raw sample to analysable item

(…)

• Moisture Determination:

A subsample of the wet solid is weighed, dried at 105°C to constant weight, and re-weighed. The weight loss is the % Moisture. This is required to report results on a dry weight basis, which eliminates the variable of water content and allows for valid comparison against dry-weight-based regulatory standards.

Oven

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Analytical Techniques: An Overview

The choice of technique is a balance of:

• Required Detection Limit (How low do you need to go?)

• Number of analytes needed (Single vs. Multi-element)

• Sample Throughput (How many samples per day?)

• Cost (Capital and operational)

• Matrix Complexity (Does it cause interference?)

Electrothermal atomic absorption spectrometer

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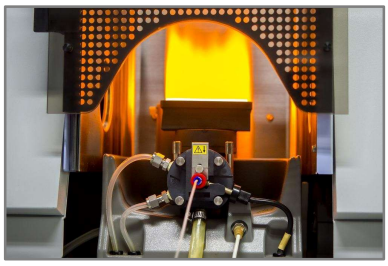
Spectroscopic Methods

Atomic Absorption Spectroscopy (AAS):
• How it works: A liquid sample is aspirated into a flame or graphite furnace to create free ground-state atoms. A lamp emitting light specific to the element (e.g., a Pb lamp for lead) is shone through the atoms. The amount of light absorbed is measured.
• Best for: Labs with a focused, recurring need for a specific metal. Not efficient for broad-scale screening.



Flame atomic absorption spectrometer

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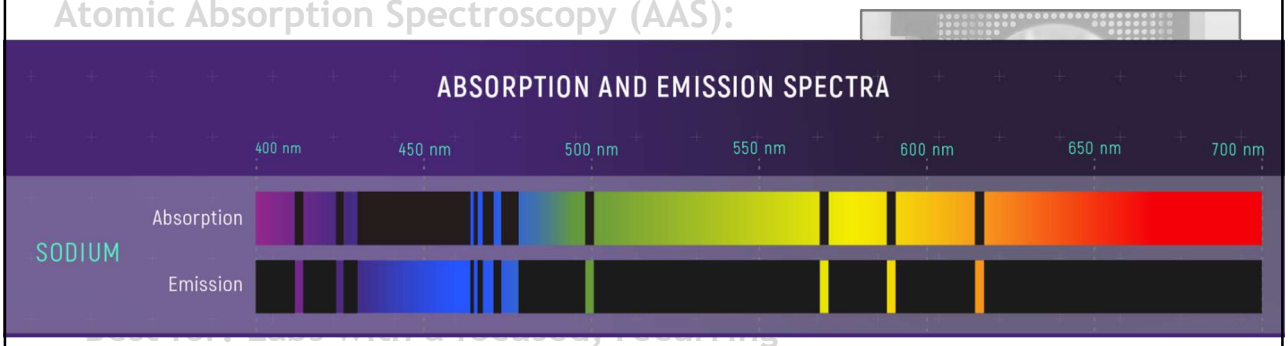
Spectroscopic Methods

Atomic Absorption Spectroscopy (AAS):



need for a specific metal. Not efficient for broad-scale screening.

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Spectroscopic Methods

Inductively Coupled Plasma – OES / MS (ICP-OES / ICP-MS):

- How it works: A ~10,000 K argon plasma vaporizes, atomizes, and ionizes the sample.
- ICP-OES: Measures the characteristic light emitted as excited electrons fall back to lower energy levels.

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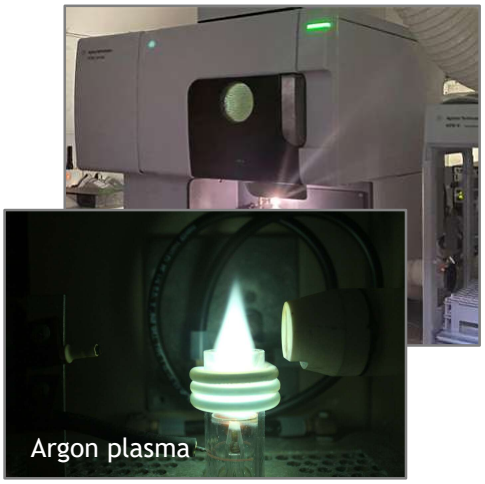

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Spectroscopic Methods

Inductively Coupled Plasma – OES / MS (ICP-OES / ICP-MS):

(…)

- ICP-MS: Uses a mass spectrometer to separate and count the ions themselves.

- ICP-MS is the "Gold Standard": It offers the lowest detection limits (parts-per-trillion), wide dynamic range, and fast multi-element capability. It is the preferred method for regulated metals analysis.

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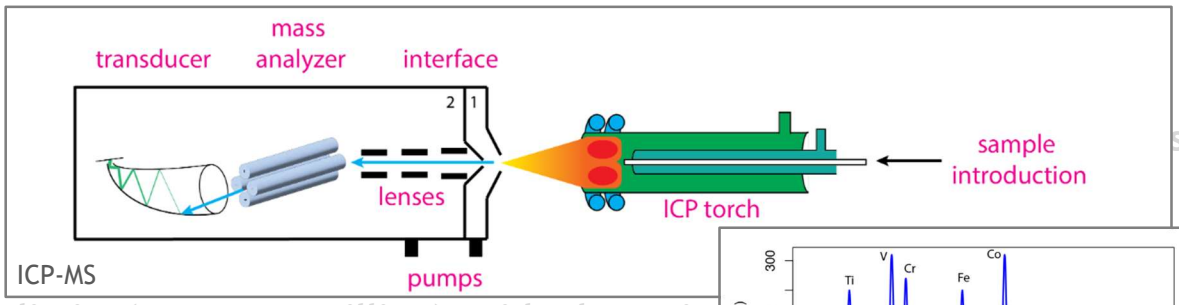
Spectroscopic Methods



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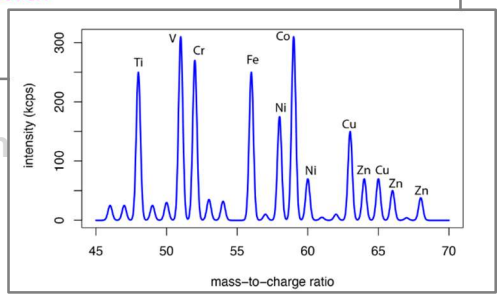

ICP-MS spectra

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Spectroscopic Methods

(…)
UV-Vis Spectrophotometry:
How it works: Not for metals directly.

The analyte (e.g., phosphate) is reacted with specific reagents to form a coloured complex. The intensity of the colour, measured by its absorption of light, is proportional to concentration.

Best for: Nutrient analysis (NO_3^-, PO_4^{3-}, NH_3) and specific anions.

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Spectroscopic Methods

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UV-Vis Sp
How it w

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Best for: nions.

Testing a drinking water sample for Nitrite by UV/Vis spectroscopy

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Chromatography

Ion chromatography:
Analytical technique that separates and quantifies ions and polar molecules based on their electrical charge and interaction with an ion-exchange stationary phase. An eluent (mobile phase) carries the sample through a column containing charged resin particles, allowing for separation of ions by selectively binding and eluting them at different rates. IC is a sensitive and accurate method used across various industries to analyse water, food, pharmaceuticals, and environmental samples for inorganic and organic ions.

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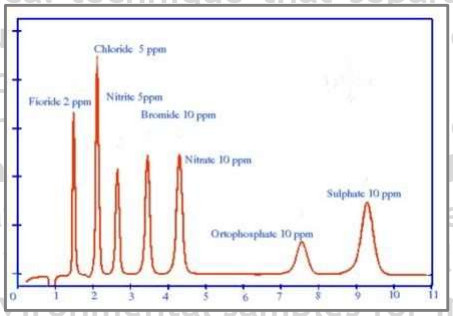
Chromatography

Ion chromatography:

Analytical technique that separates and quantifies ions and polar molecu… ca… with an ion-exc… A… carries the sar… or… ticles, allowin… by… eluting them a… en… d used across … ys… iticals, and environmental samples for inorganic and organic ions.



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Chromatography

Ion chromatography:
(…)
How it Works
Sample Preparation: Liquid samples are often filtered to remove particulate matter and prevent column clogging.
Injection: The prepared sample is introduced into the ion chromatograph.
Elution: A liquid eluent (mobile phase) carries the sample through the chromatography column.
(…)

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Chromatography

Ion chromatography:
(…) Separation: The column contains an ion-exchange resin, which has charged functional groups. Ions in the sample with opposite charges bind to the resin, while those with the same charge pass through more quickly.
Elution of Separated Ions: A different eluent is used to displace the bound ions, allowing them to separate and move down the column at different speeds.
Detection: As ions elute from the column, they are detected, often by a conductivity detector or a spectrophotometric detector.

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Chromatography

Ion chromatography:
(…)
Chromatogram: The results are displayed as a chromatogram, a graph showing the time it takes for each ion to pass through the column (retention time) and the amount of the ion (peak area/height).
Applications
Environmental Analysis: Determining inorganic ions like chloride, fluoride, sulfate, and nitrate in drinking water and wastewater.
Advantages
High Sensitivity and Selectivity

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Electrophoresis

Capillary electrophoresis:
Analytical separation technique that uses an electric field to move charged molecules through a narrow, submillimeter-diameter capillary filled with a buffer. Analytes separate based on their charge-to-size ratio and electrophoretic mobility, a process influenced by the buffer's pH and ionic strength. CE offers high efficiency, rapid analysis, and requires minimal sample and reagent volumes, making it a versatile method for analyzing biomolecules, DNA, and other water-soluble components, often used in conjunction with mass spectrometry (MS).

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Electrophoresis

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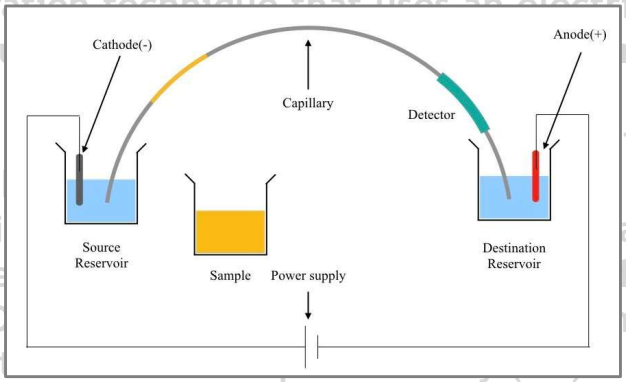

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Electrochemical Methods

- pH Electrode:

A potential develops across a thin glass membrane sensitive to H^+ ions. This potential is measured against a stable reference electrode and converted to a pH value. Calibration with buffers (pH 4, 7, 10) is critical.

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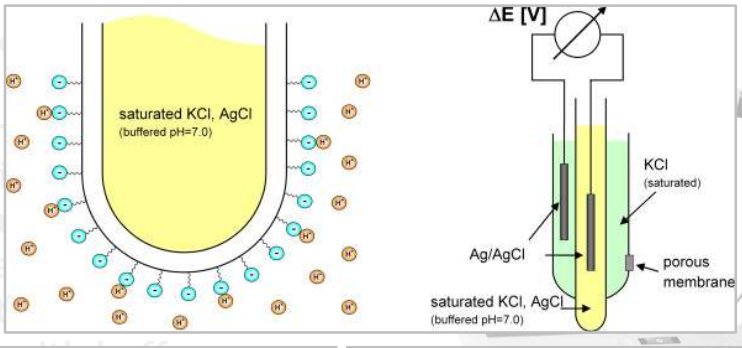
Electrochemical Methods



SiOH surface groups of the glass dissociate in an aqueous test solution in SiO^- and H^+. The equilibrium and the surface potential will depend on the H^+ concentration of the test solution, i.e., the pH.

Schematic of a pH-measuring electrode. The glass electrode from the upper panel filled with a buffer solution is connected with an Ag/AgCl electrode. A surrounding reference electrode electrically connected to the test solution by a diaphragm is used as return electrode.

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Electrochemical Methods

- Conductivity Probe:

•• Applies an AC voltage between two electrodes. Ions in solution carry the current. The easier the current flows, the higher the conductivity.
Reports in µS/cm.

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Electrochemical Methods

- Ion-Selective Electrodes (ISEs):

•• How it works: Similar to a pH probe, but with a membrane specific to a particular ion (e.g., a crystal of LaF_3 for F^-). The potential change is proportional to the log of the ion's activity.
•• Pros & Cons: Excellent for field screening and continuous monitoring. However, other ions can interfere (e.g., OH^- interferes with the F^- ISE), so the matrix must be considered.

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Exercise

A 1.145 g of a soil sample (S35/25) was acid digested by microwave and its volume transferred to a 50 mL volumetric flask. After diluting from 5 mL to 10 mL, the solution was analysed by FAAS. Below are sample solution and calibrators signals:

Pb (µg L^{-1})	Absorbance Rep 1	Absorbance Rep 2
0.0 (Blank)	0.002	0.001
10	0.045	0.047
25	0.112	0.109
50	0.218	0.221

	Absorbance
Sample solution	0.177

Estimate the mass fraction of Pb in the sample in mg kg^{-1}.

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Quality Control in Analysis

- Calibration Curve:

The foundation of all quantitative analysis. A series of standards of known concentration are run to create a model (Signal = Slope * Concentration + Intercept). The sample concentration is calculated from its signal using this model. The correlation coefficient (*r*) should be >0.995.

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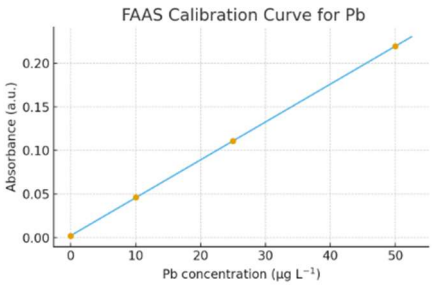

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Quality Control in Analysis

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• Method Detection Limit (MDL):
The minimum concentration that can be measured with 99% confidence that it is greater than zero. Determined by analysing multiple low-level spikes and calculating the standard deviation.

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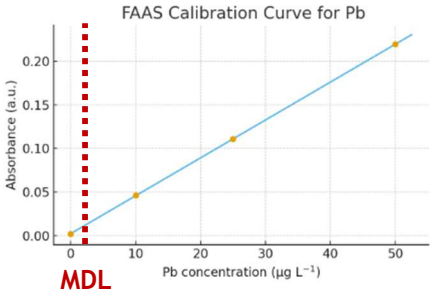

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Quality Control in Analysis

(…)

• Blanks:
  •• Method Blank: Exposes contamination from lab reagents, glassware, and the lab environment. Any significant detection in the blank questions the validity of all samples in the batch.
  •• Trip Blank: (For VOCs) Travels with samples to check for cross-contamination during transport. (…)

Trip Blank

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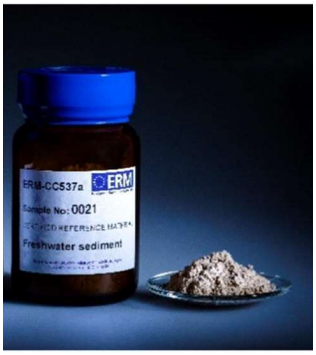
Quality Control in Analysis

(…)

- QC Samples:
  Continuing Calibration Verification (CCV): A standard run after every 10-20 samples. Verifies the calibration hasn't drifted.
  Laboratory Control Sample (LCS): A "known" sample (often a Certified Reference Material) taken through the entire preparation and analysis process. It is the primary check on accuracy.



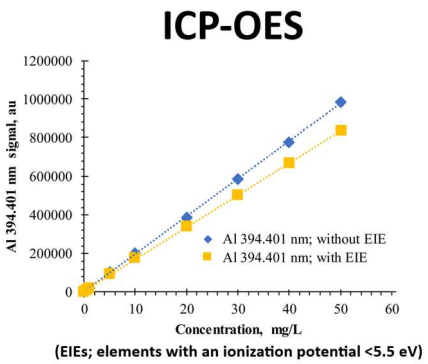
Certified reference material

Environmental Chemical Analysis – Inorganic analysis

The Standard Addition Method

(…)

- The Problem with External Calibration: It assumes the standard and sample matrices are identical. In complex environmental samples (e.g., seawater, wastewater, soil digests), the matrix can cause a matrix effect:
  Suppression: Matrix components lower the analyte signal.
  Enhancement: Matrix components increase the analyte signal. (…)



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The Standard Addition Method

(…)
•• The Solution:
» Matrix matched standards (MMS)
or, if MMS are not possible:
» Standard Addition
Since you can't easily remove the matrix, you add the calibration standards directly to the sample. This way, the matrix is identical for all calibration points and the unknown, so any suppression/enhancement affects them all equally and is effectively cancelled out.

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The Standard Addition Method

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or, if not M
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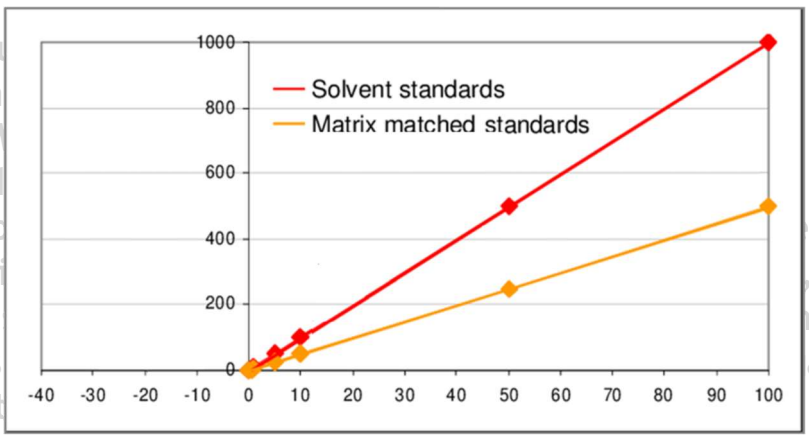

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The Standard Addition Method

(…)
Step-by-Step Process Explained:
Aliquot: Take several identical volumes of the sample *(the sample must be diluted)*.

Spike: Add increasing, known amounts of the analyte standard to all but one aliquot. One aliquot is left unspiked (the "0" addition).

Measure: Analyse all aliquots and record the signals.
(…)

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The Standard Addition Method

(…)
Plot & Extrapolate:
- Plot Signal (y-axis) vs. Concentration of Added Standard (x-axis).
- Fit a straight line through the data points.
- Extrapolate the line backwards (to the left) until it crosses the x-axis.
- The absolute value of this x-intercept is the original concentration of the analyte in the sample.

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The Standard Addition Method

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Plot & Extr

Plot Sig rd

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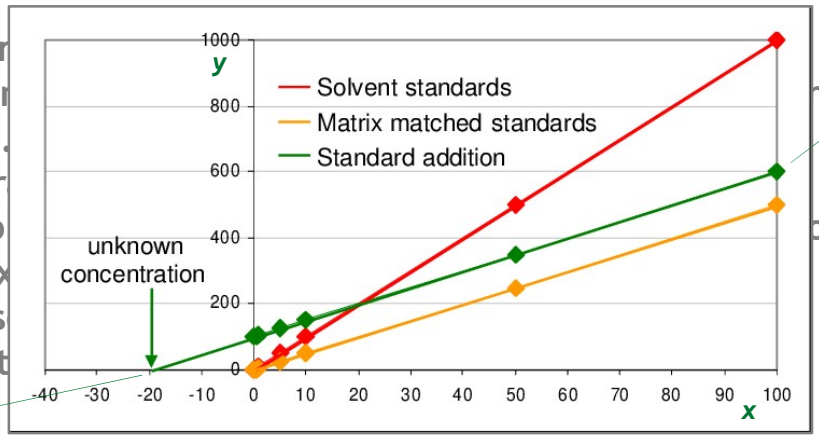

Environmental Chemical Analysis - Inorganic analysis

Exercise (1/2)

A 1.145 g of a soil sample (S35/25) was acid digested by microwave and its volume transferred to a 50 mL volumetric flask. After diluting from 5 mL to 10 mL, the solution was analysed by FAAS using the standard addition method, whose signals are below:

Added Pb (µg L^{-1})	Absorbance Rep 1	Absorbance Rep 2
0	0.178	0.178
10	0.235	0.237
25	0.315	0.314
50	0.459	0.469

Estimate the mass fraction of Pb in the sample in mg kg^{-1}.

Exercise (2/2)

Knowing the parallel moisture content determination of sample S35/25 described below, estimate the mass fraction expressed in dried mass basis:

Initial mass: 5.625 g

Mass after drying at (103 °C to 105 °C): 3.994 g