Elemental Analysis in Soil and Fertilizer

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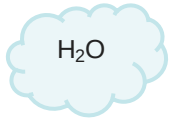
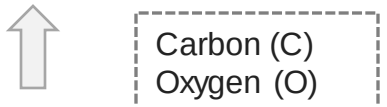
TEA Product Specialist

Introduction

O_2, CO_2



H_2O



Carbon (C)
Oxygen (O)
Hydrogen (H)

Major nutrients

Nitrogen (N)

Phosphorus (P)

Potassium (K)

Toxic

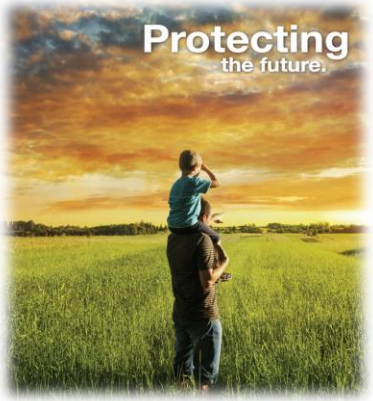
Arsenic (As)
Cadmium (Cd)
Mercury (Hg)
Lead (Pb)
Copper (Cu)
Chromium (Cr)

Secondary nutrients

Calcium (Ca)
Magnesium (Mg)
Sulfur (S)

Micronutrients

Boron (B)
Copper (Cu)
Iron (Fe)
Manganese (Mn)
Molybdenum (Mo)
Zinc (Zn)
Nickel (Ni)
Cobalt (Co)
Chromium (Cr)
Selenium (Se)
Vanadium (V)
Sodium (Na)
Silica (Si)



Introduction

O_2, CO_2

H_2O

Carbon (C)
Oxygen (O)
Hydrogen (H)

Major nutrients

Nitrogen (N)

Phosphorus (P)

Potassium (K)

Soil, plant, and fertilizers

Animal feed

Human food

Soil

- The differentiation of Total Carbon (TC) and Total Organic Carbon (TOC) → evaluates the quality of soils
- Environmental protection → agricultural land, construction sites, playgrounds, forests, and gardens, as well as wastelands

Secondary nutrients

Calcium (Ca)
Magnesium (Mg)
Sulfur (S)

Micronutrients

Boron (B)
Copper (Cu)
Iron (Fe)
Manganese (Mn)
Molybdenum (Mo)
Zinc (Zn)
Nickel (Ni)
Cobalt (Co)
Chromium (Cr)
Selenium (Se)
Vanadium (V)
Sodium (Na)
Silica (Si)

Fertilizer

In the production process, the elemental composition of fertilizers is periodically monitored for their characterization.

- Raw materials
- Finish products

Introduction

Toxic elements	Major uses and sources of soil contamination
Arsenic (As)	Pesticides, plant desiccants, animal feed additives, coal and petroleum, mine tailings and detergents
Cadmium (Cd)	Electroplating, pigments for plastics and paints, plastic stabilizers and batteries, fertilizers
Chromium (Cr)	Stainless steel, Chrome-plated metal, pigments and refractory brick manufacture
Lead (Pb)	Combustion of oil, gasoline and coal: Iron and steel production
Mercury (Hg)	Pesticides, catalysts for synthetic polymers, metallurgy, thermometers
Nickel (Ni)	Combustion of coal, gasoline, and oil; alloy manufacture, electroplating, batteries

Soil: Regulation in Thailand

Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
As	6	Hg	22
Cd	67	Ni	436.5
Cr	17.5	Mn	1710
Cu	2920	Se	365
Pb	400		

ประกาศคณะกรรมการสิ่งแวดล้อมแห่งชาติ เรื่องกำหนดมาตรฐานคุณภาพดิน

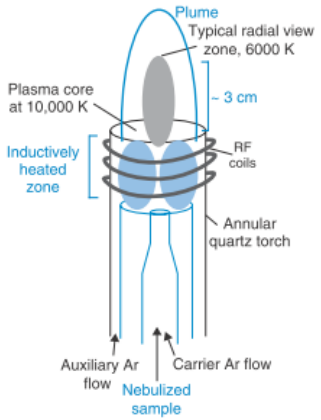
Fertilizers: Regulation in Thailand

Element	Concentration (mg/kg)
As	50
Cd	5
Cr	300
Cu	500
Pb	500
Hg	2

ประกาศกรมวิชาการเกษตร เรื่อง กำหนดเกณฑ์ปุ๋ยอินทรีย์

Techniques routinely used for soil analysis

	Organic element analyzer	Discrete analyzer	IC	Accelerated Solvent Extraction	GC & GC-MS	X-ray Fluorescence	ICP-OES & ICP-MS
Nutrient Analysis	●	●	—	—	—	●	●
Metal Contaminants	—	—	—	—	—	●	●
Inorganic Anions	—	—	●	—	—	—	—
Organic Contaminants	—	—	—	●	●	—	—



ppb to %

100 ppm to 100 %

CHNS

Oxygen

1800°C
Flash Combustion

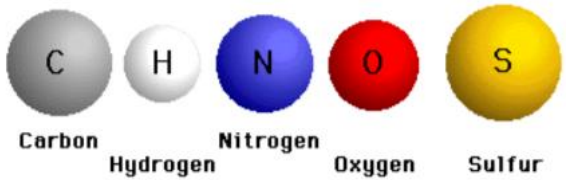
Organic Elemental Analysis (Combustion)

- The Organic Elemental Analyzer is used for Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen analysis
- The ICP-OES and ICP-MS are used to provide information of major plant nutrients (N, P, K), secondary plant nutrients (Ca, S, Mg), micronutrients such as B, Mn, Fe, Cu, Zn, Mo and Se, also the toxic elements (As, Cd, Pb and Hg)

What is Organic Elemental Analyzer?

Elemental characterization for agricultural purposes gives information useful for determining agronomy management plans. The determination of Nitrogen and carbon, Total Organic Carbon (TOC), and sulfur enables to characterization of

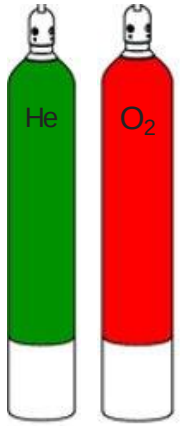
- Soils
- Leaves, Plants, Crops, and other materials
- Fertilizer



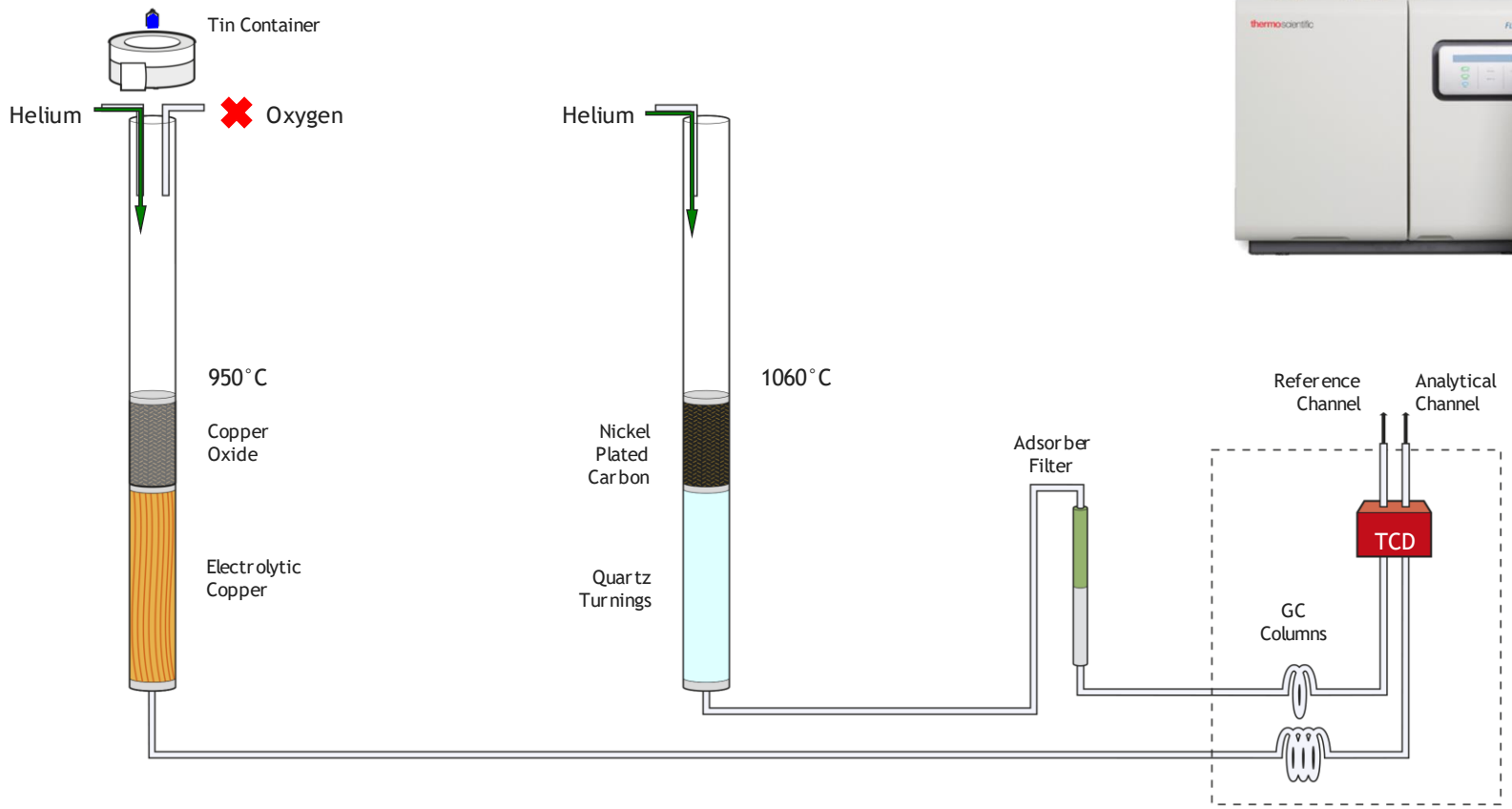
Based on the combustion of the sample. Upon combustion, the sample generates uniform compound gases of the elements C, H, N, and S. These combustion products are measured using gas chromatography and thus the ratio of the elements in the original sample is determined. C, H, N, and S can all be determined simultaneously whereas O by pyrolysis.

Quantification of the sample	Weighting
Quantitative oxidation of the sample	Combustion
Reduction of combustion gases	Reduction
Separation of the oxidation gases	Chromatography
Generation of signal	Detection

CHNS Analytical configuration

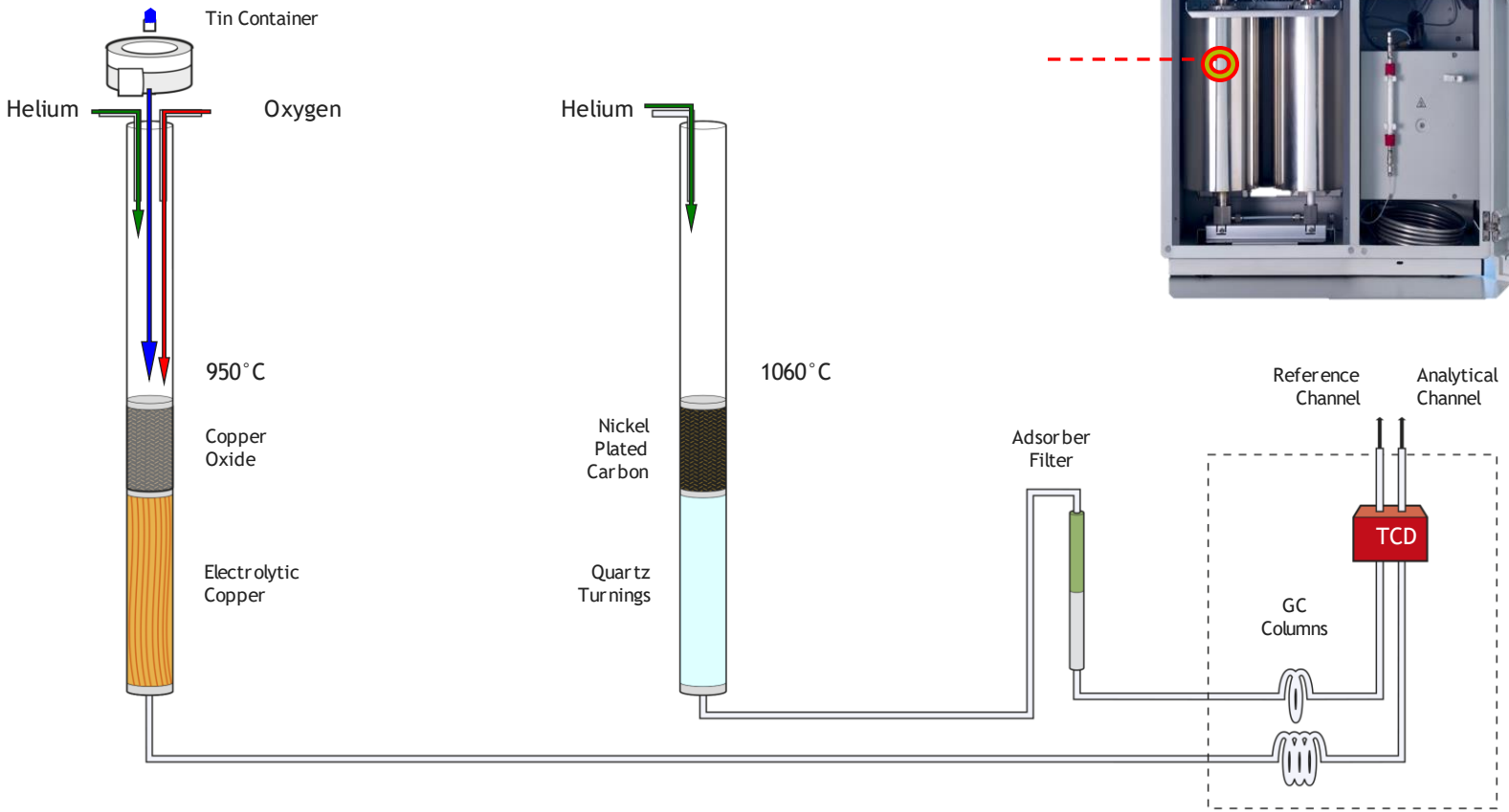


High purity



- Introduced into the combustion reactor by and auto sampler

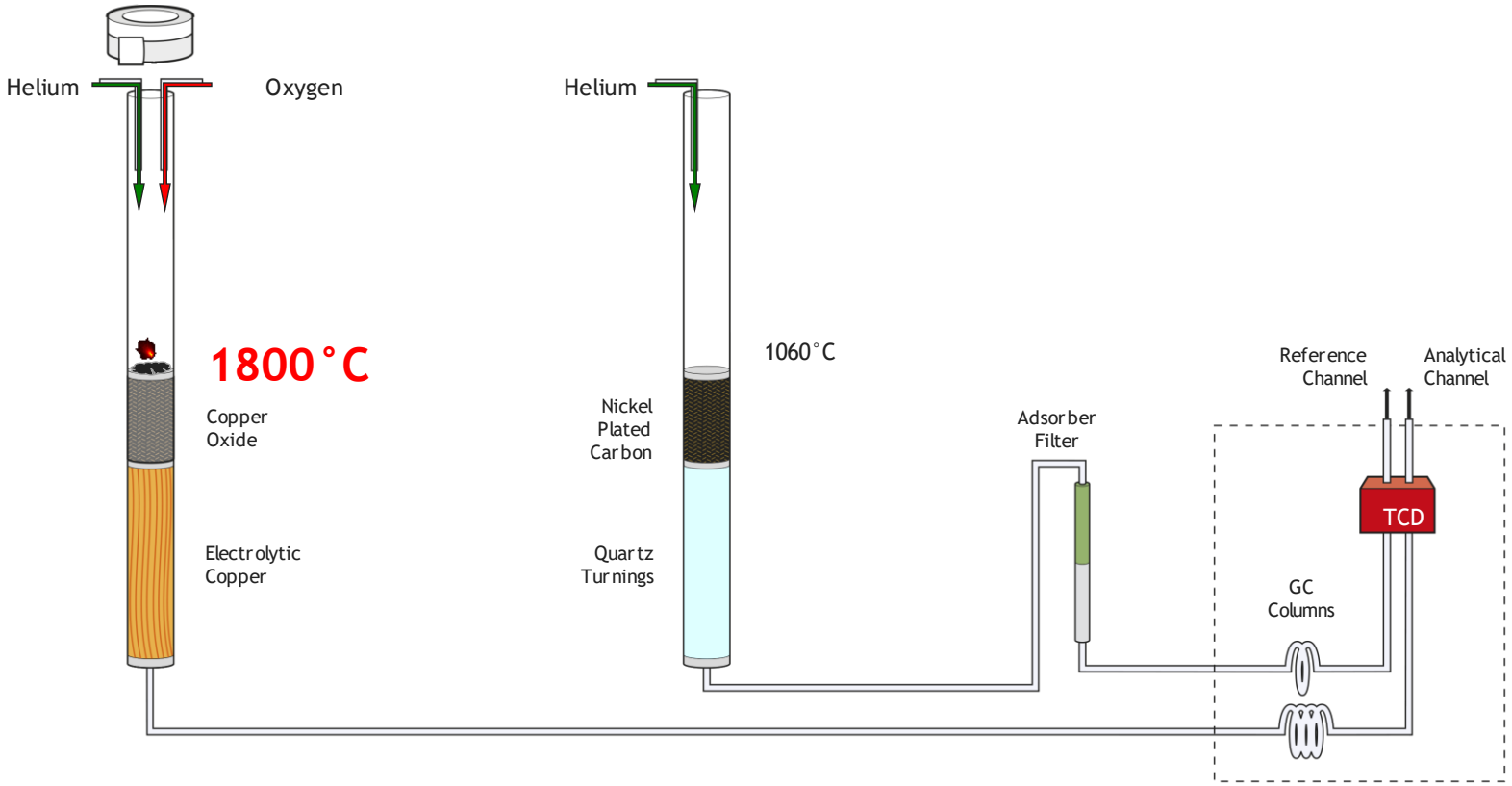
CHNS Analytical configuration



- Inserted in the special furnace heated at 950 °C
- A small volume of pure oxygen is added to the system and helps to burn the sample

CHNS Analytical configuration

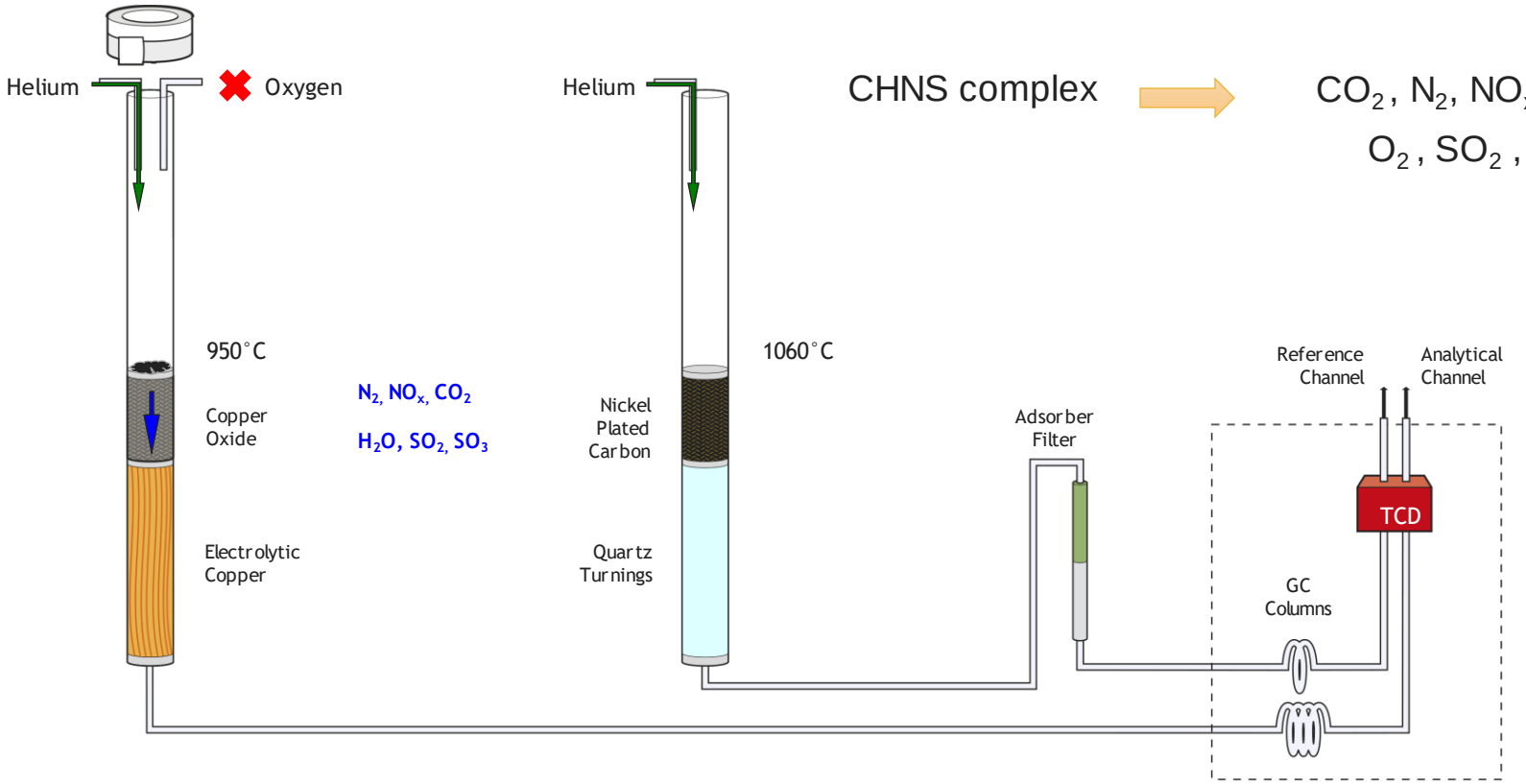
$O_2 + Sn \rightarrow SnO_2 + 1800\,^oC$



CHNS Analytical configuration

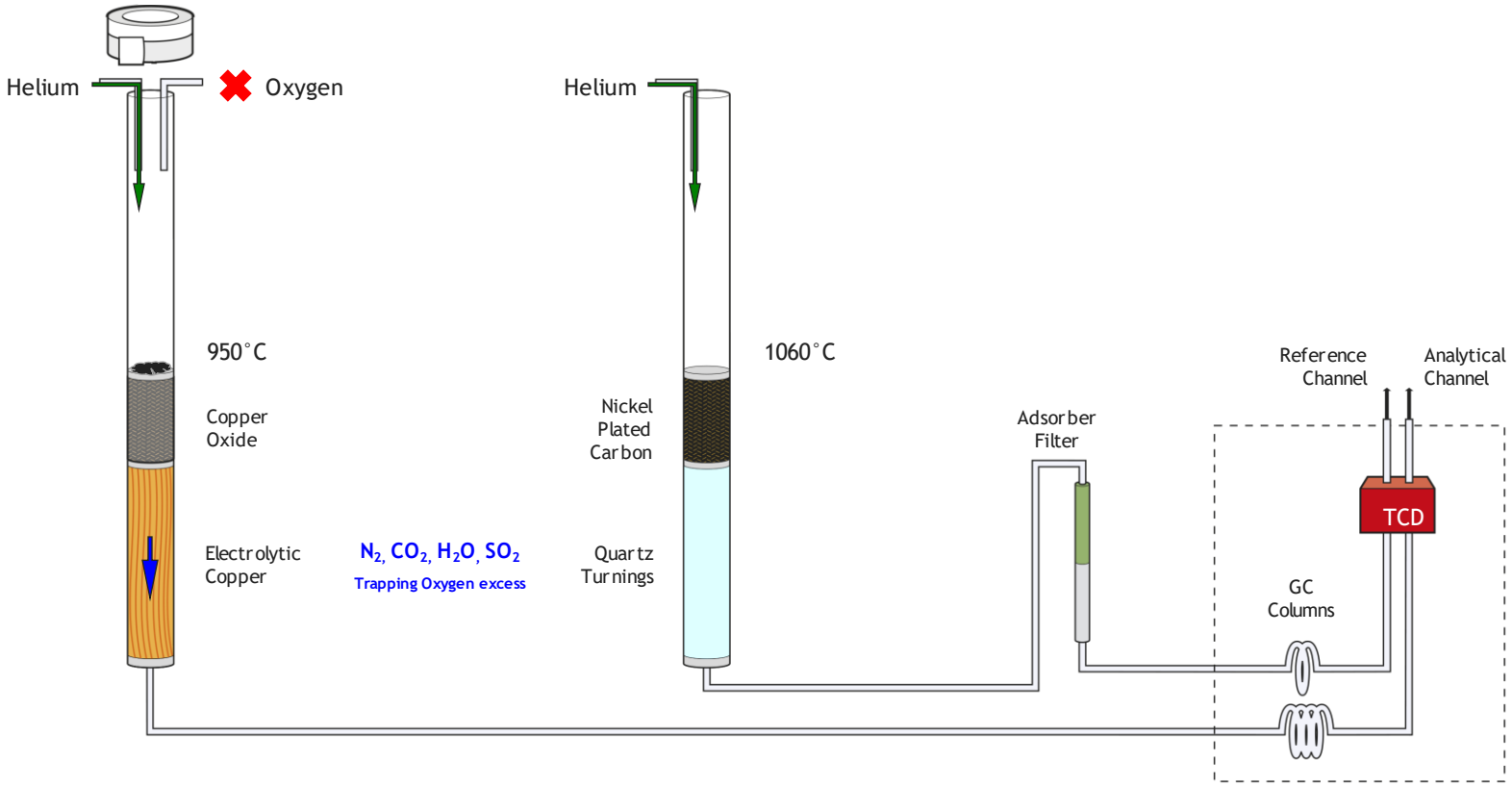
$O_2 + Sn \rightarrow SnO_2 + 1800\,^oC$

CHNS complex $\rightarrow$ CO_2, N_2, NO_x, H_2O, O_2, SO_2, SO_3



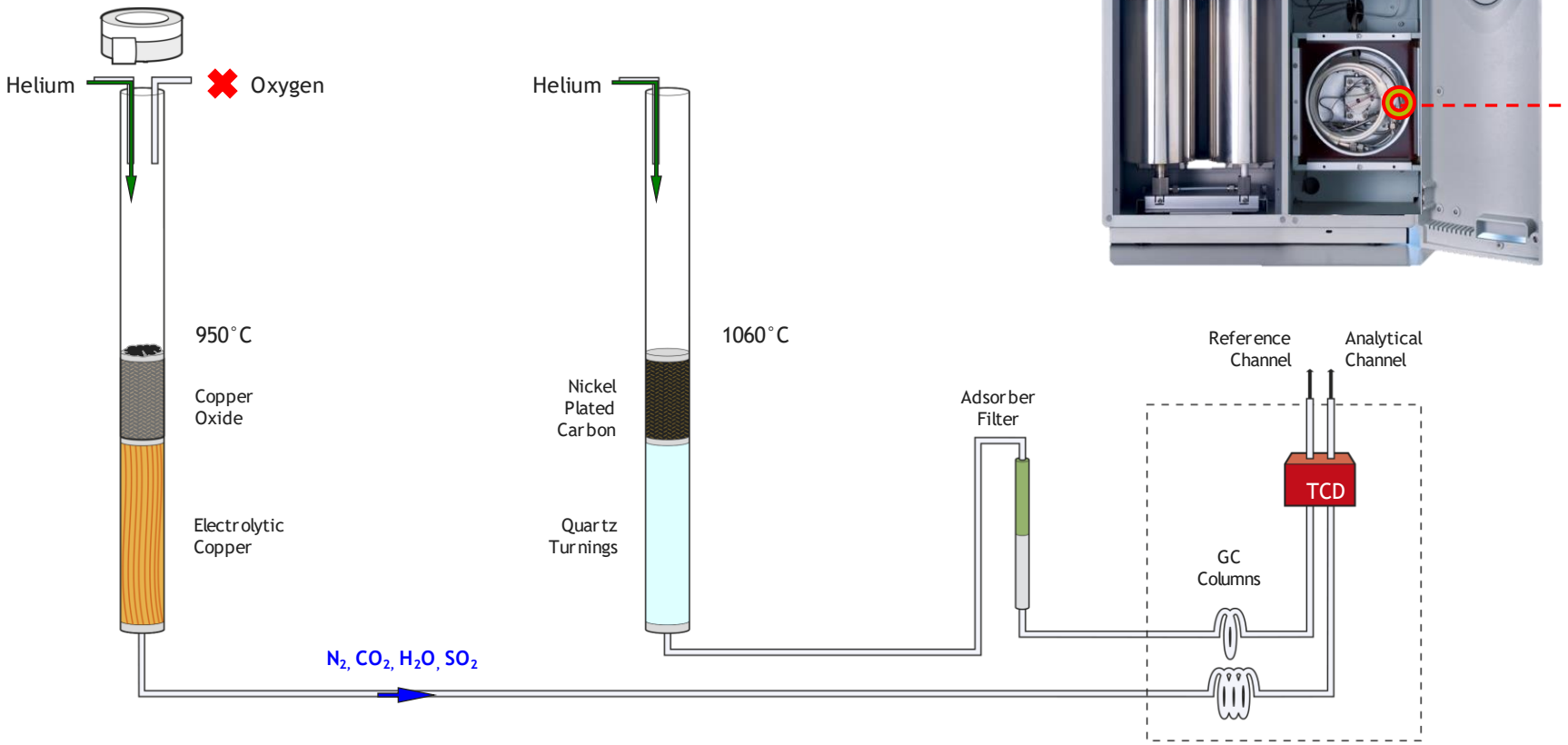
CuO Convert any CO to CO_2, N to, NOx, S to SOx, and H_2 to H_2O

CHNS Analytical configuration



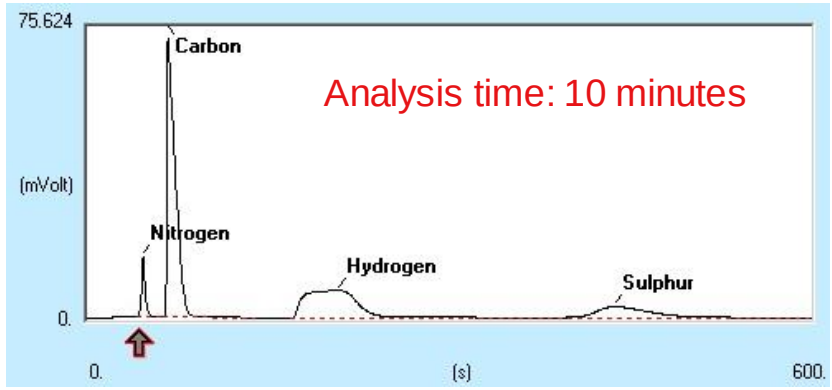
- Reduction "using Copper" converting the sample into element gases
- Reduces NOx to N_2 and SOx to SO_2 and removes the excess O_2

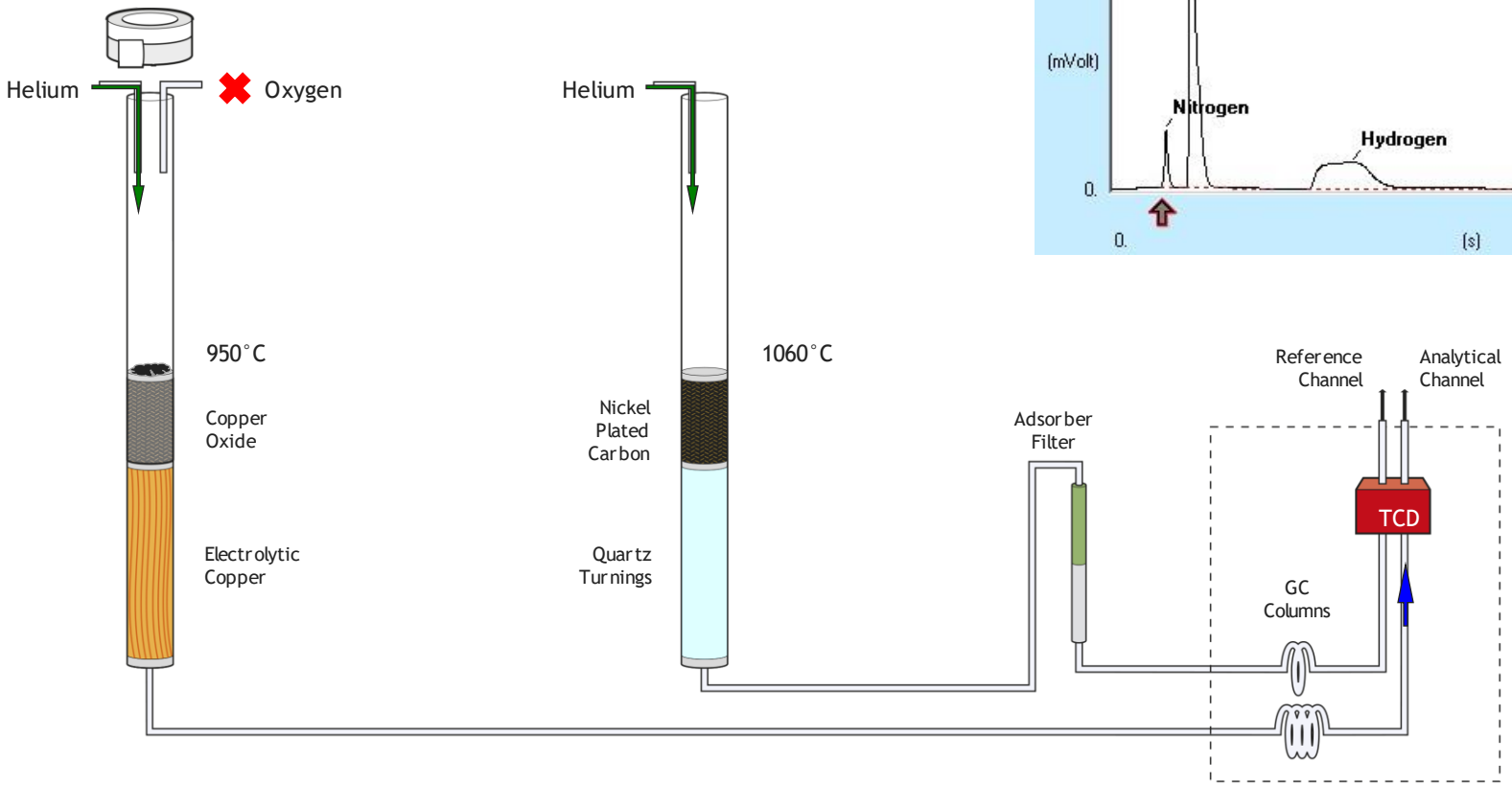
CHNS Analytical configuration



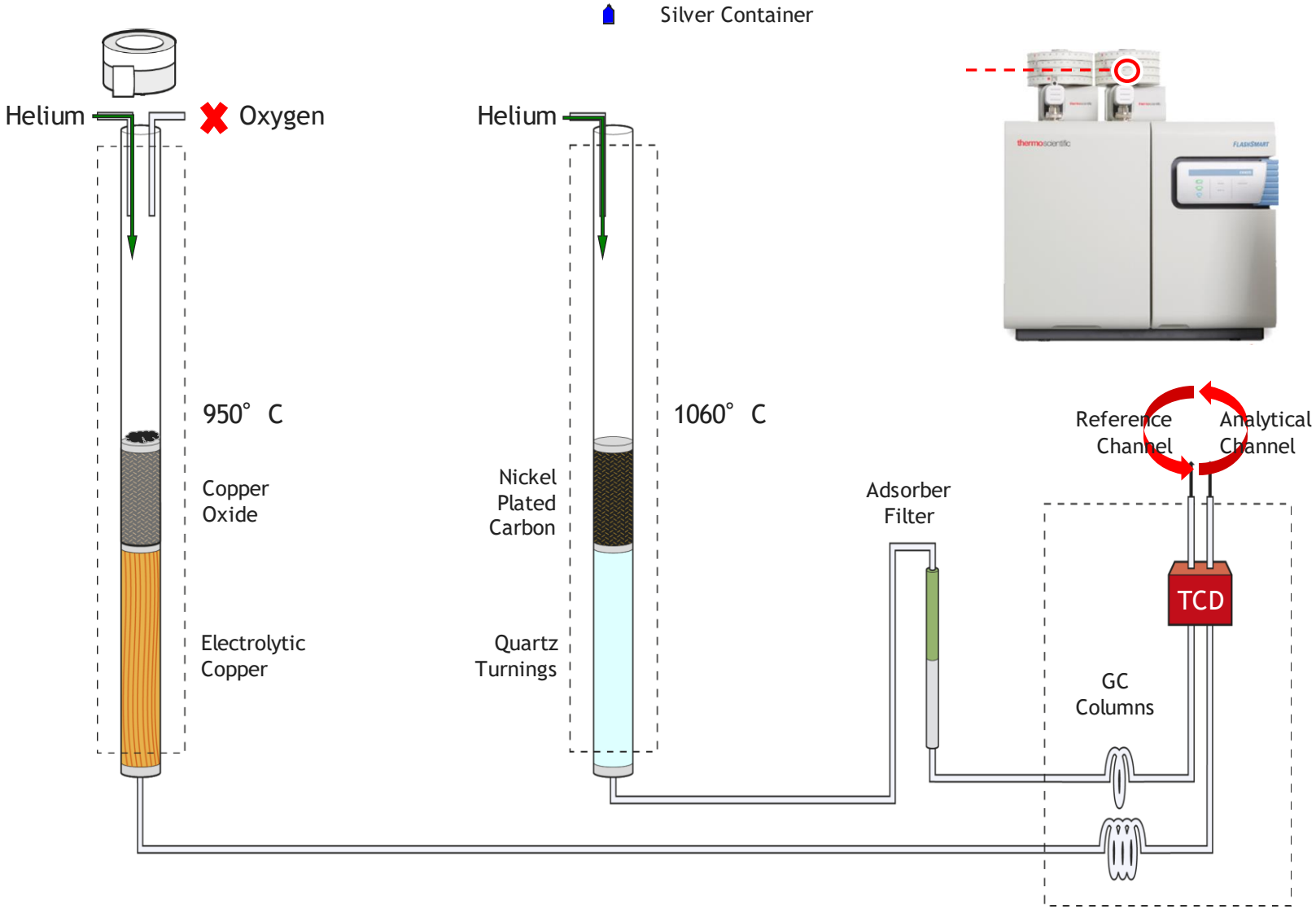
- A separation column and TCD detector allows the user to determine elements

CHNS Analytical configuration

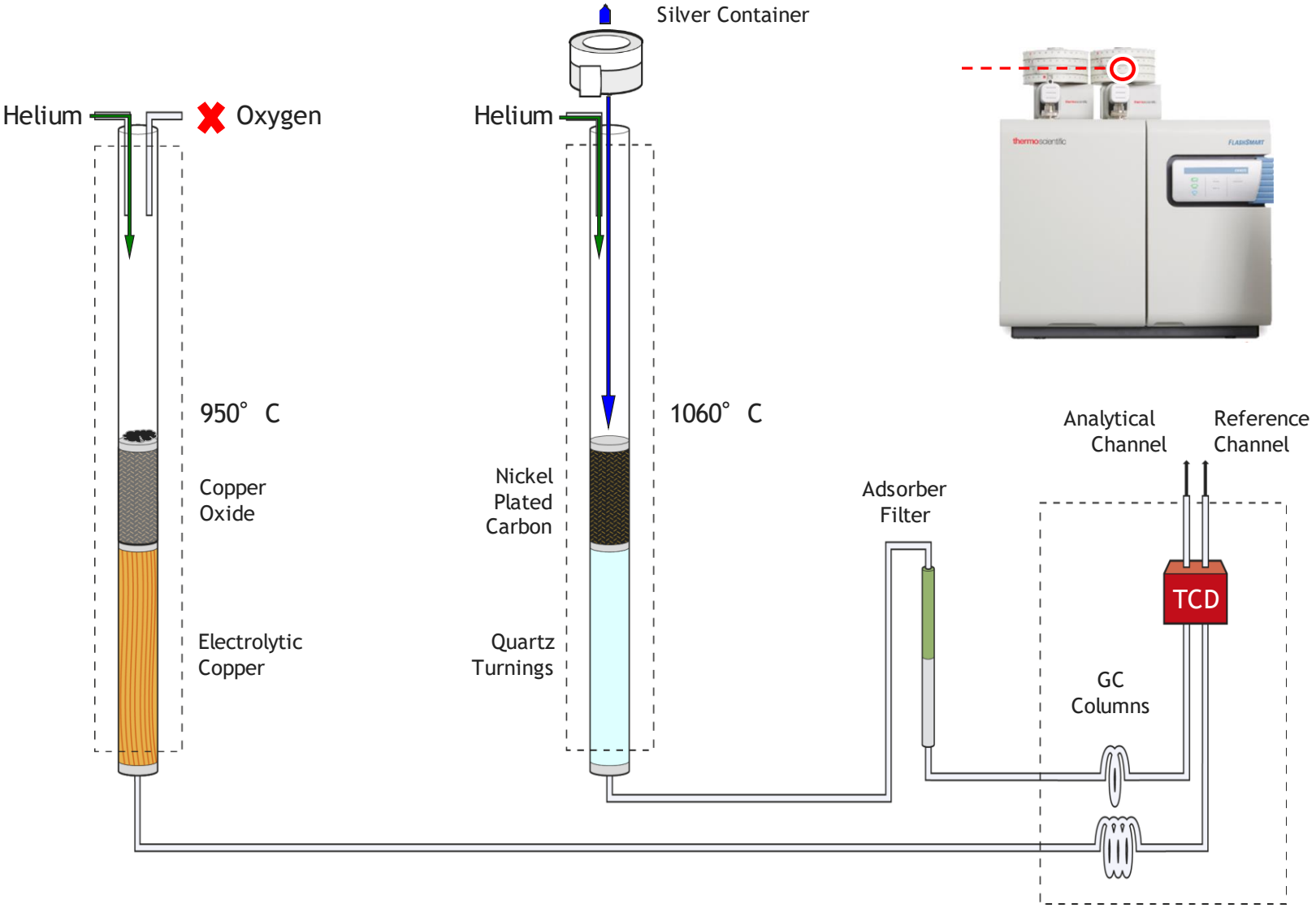




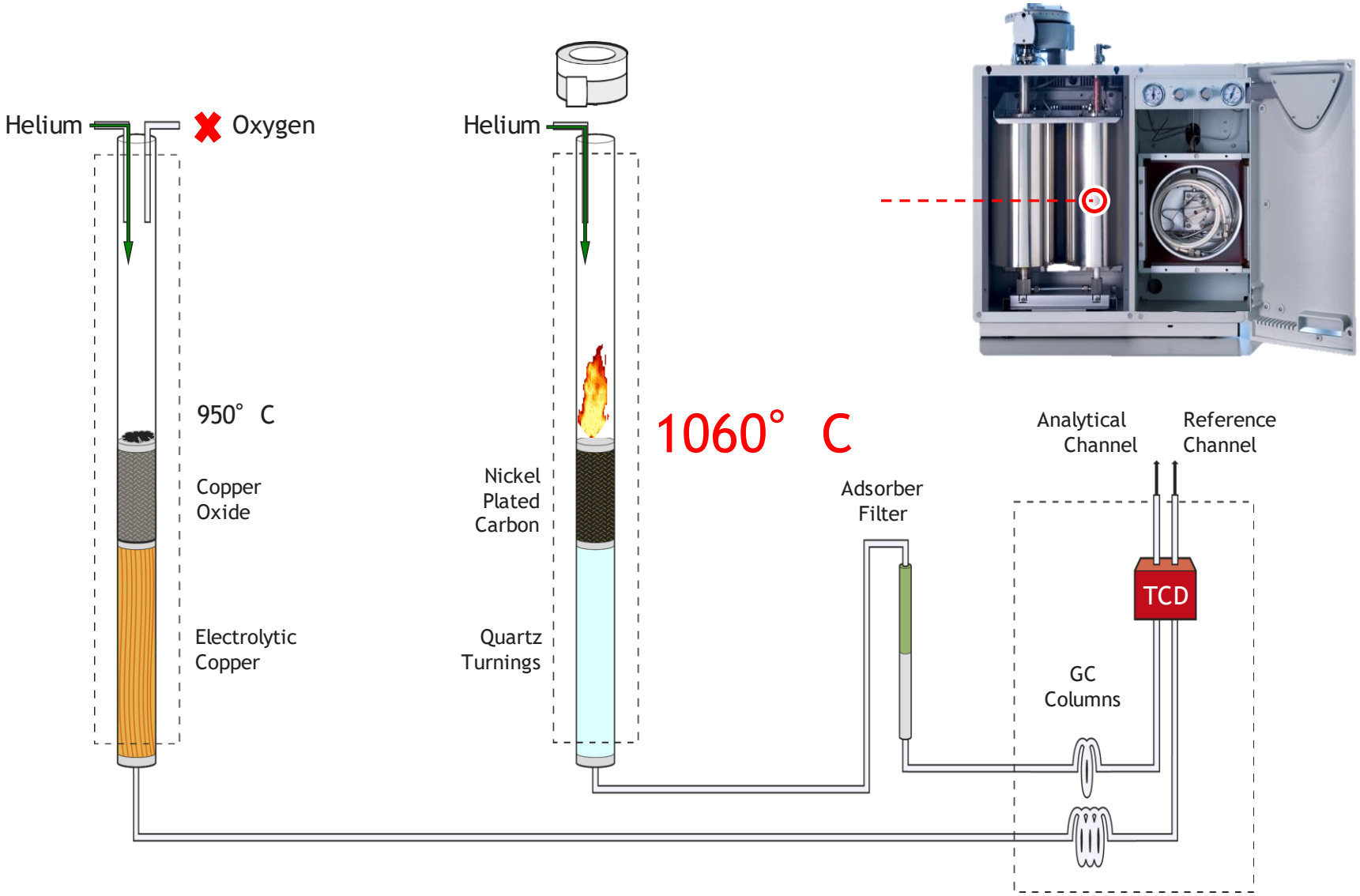
Oxygen Analytical configuration



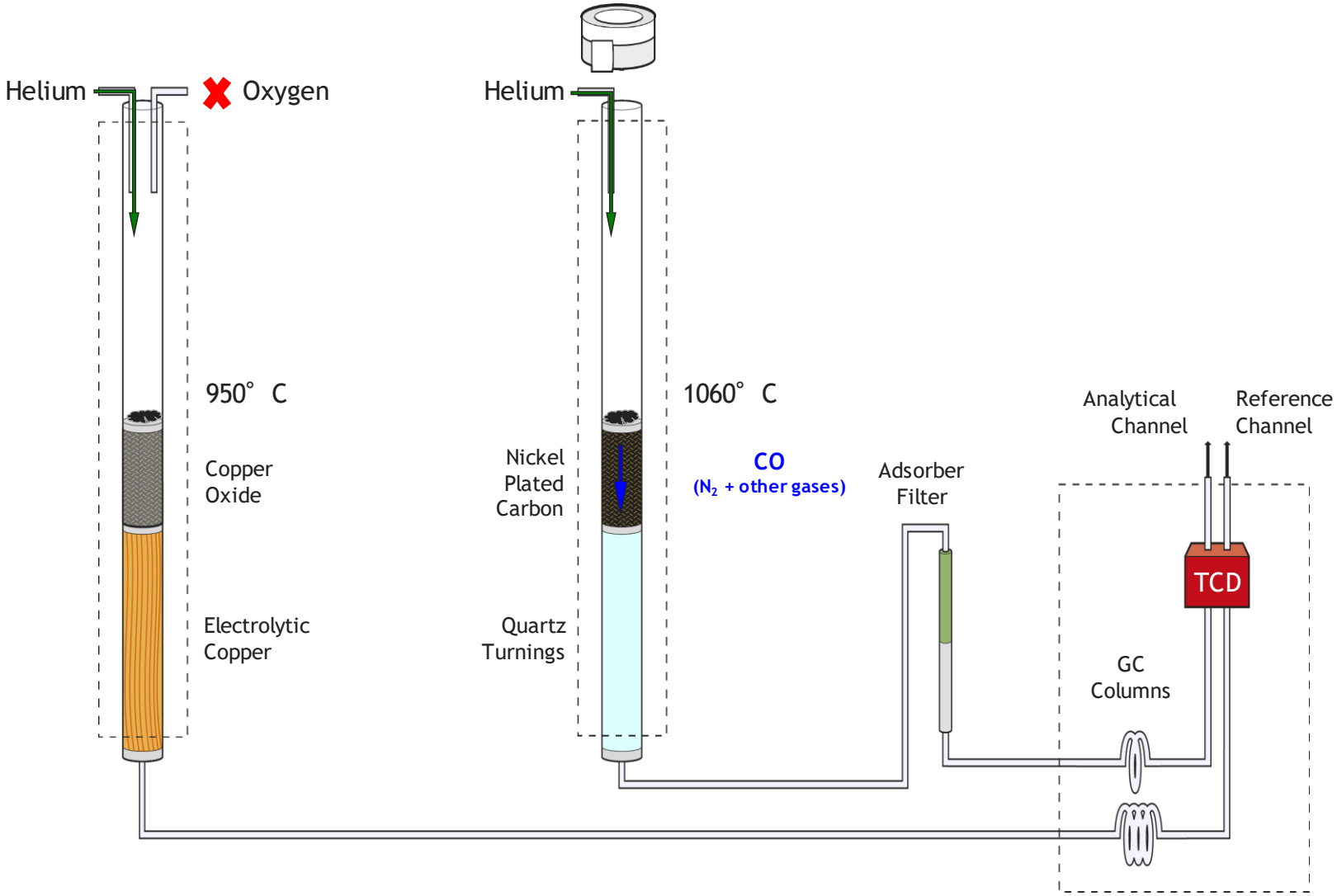
Oxygen Analytical configuration



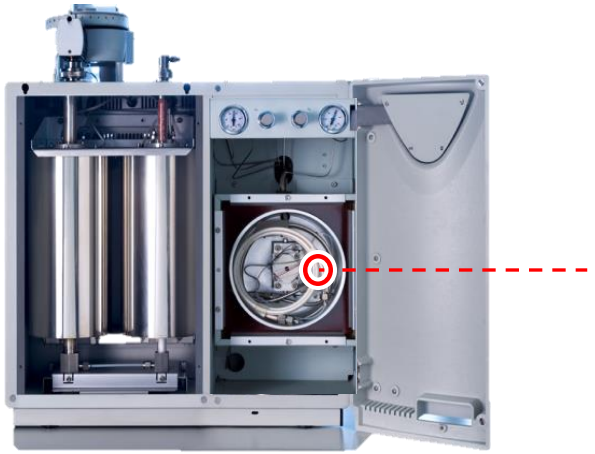
Oxygen Analytical configuration



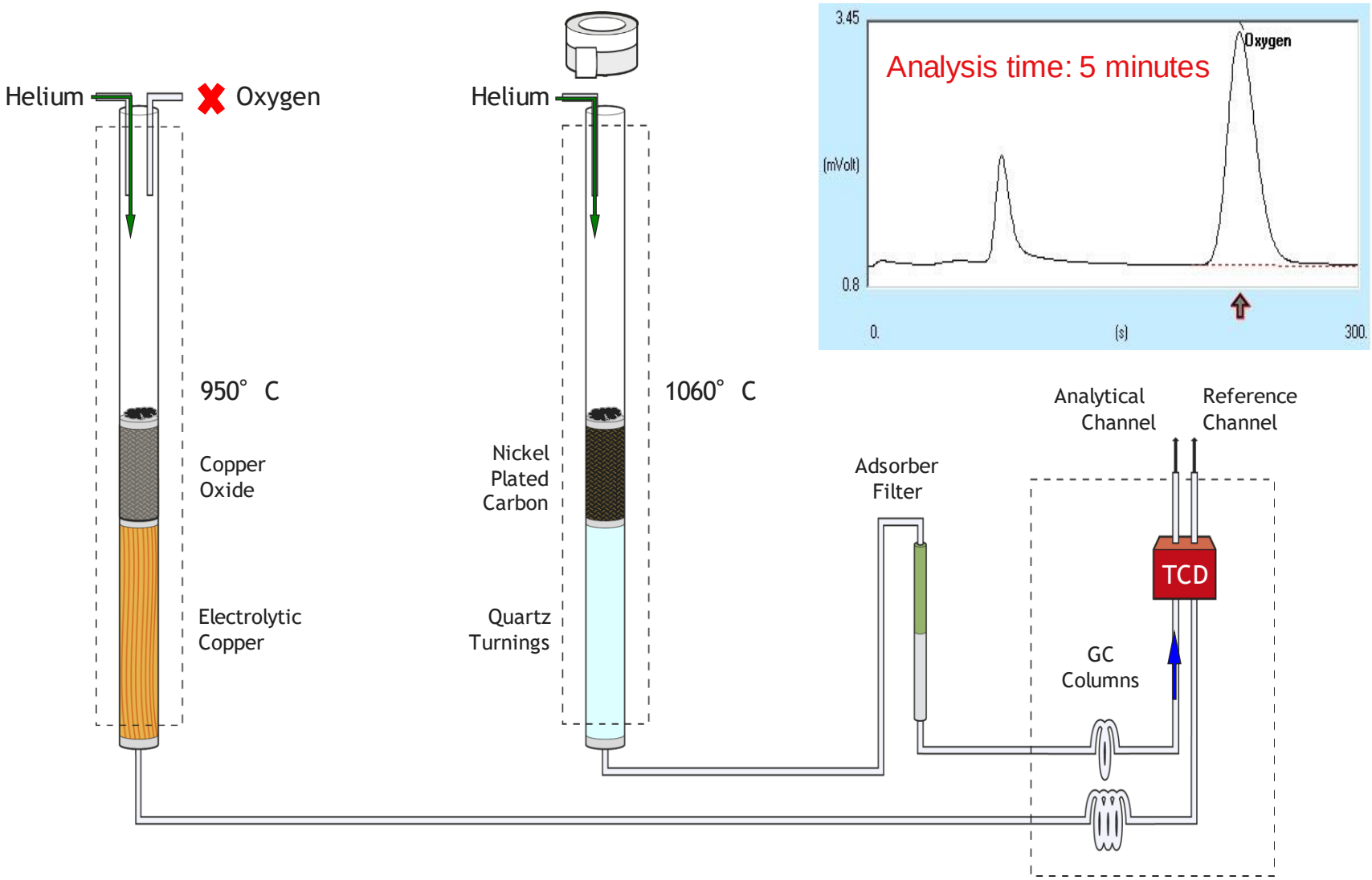
Oxygen Analytical configuration



Oxygen Analytical configuration

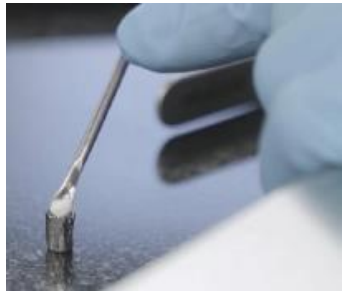


Oxygen Analytical configuration

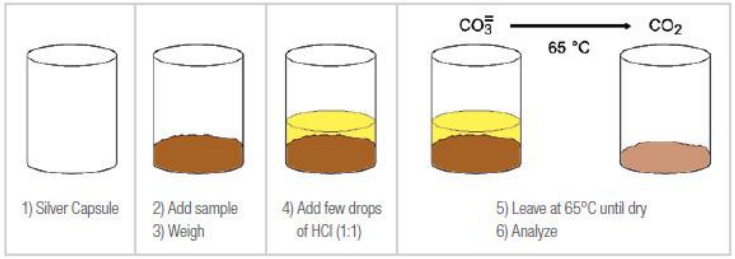


Sample Preparation

Most materials are often non-homogeneous, and an appropriate homogenization procedure is required to obtain high-quality data. The reproducibility of results is independent of the sample size but strongly dependent on the sample homogeneity.



Tin Capsule



TOC was determined after removing carbonate minerals by acidification of the sample with HCl

Agronomy: Soil NCS and TOC

Drill in several points

Representative sample

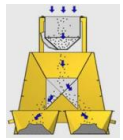
Sieve 1.5 cm

Take 1 kg

Dry at room temperature or at 35-40 °C in a oven up to constant weight

Crush with wooden rolling pin on brown paper.

Sieve to 2 mm



Take 250 grams by a sample splitter

Take 20 grams

Homogenization by a mortar or ball mill

Analysis

Sieve to 500 um

Dry at 105°C up to constant weight. Determine the humidity.

Tin caps.

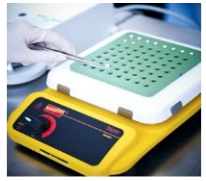
For NC, S an.

Weight the sample

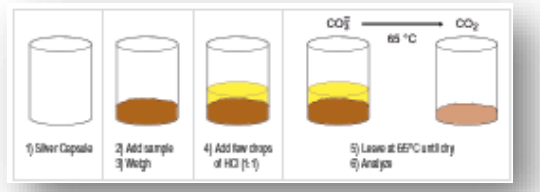
Introduce the sample into the MAS Plus Autosampler

Analysis of NC, S and TOC det.

Silver caps. for TOC an.



Acidification with HCl 1:1 for TOC



Agronomy & Animal Feed: NCS

Leaves

Representative sample

Take 25 grams of the fresh mixture

Dry at room temperature or at 70 °C in a oven up to constant weight

Determine the humidity

Homogenization at 1mm by a mill

Analysis

Take 30 gr of sample

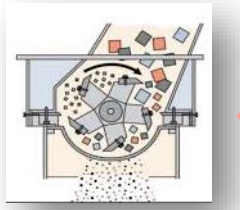
Smaller Sieve

Representative sample

Homogenization at 2 cm by a crusher

Take 3 kg of the fresh mixture

Dry first at 65° C and then at 105 oC in an oven up to constant weight. Determine the humidity.



Homogenization at 3 mm by a knives mill

Sieve 500 mg of dry sample

Take 100 mg of dry sample

Ultra Centrifugal Mill at 1 mm and then at 200 um

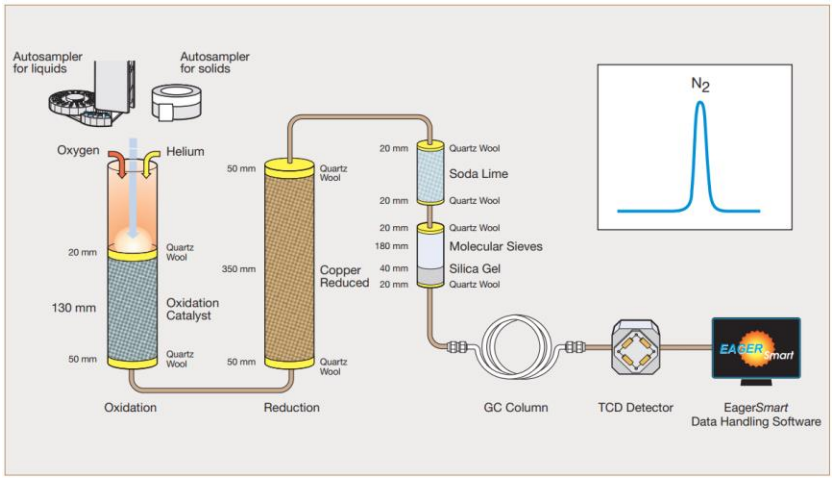
Fertilizer

Nitrogen determination of fertilizers according to AOAC 993.13 Official Method : applicable to the determination of 1 – 67 % total nitrogen content in liquid and solid fertilizer materials

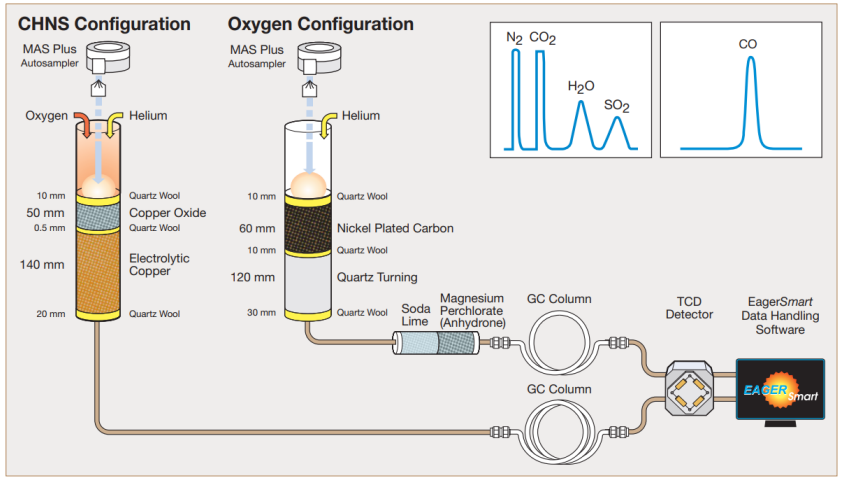
Homogenization
By Mortar or mill

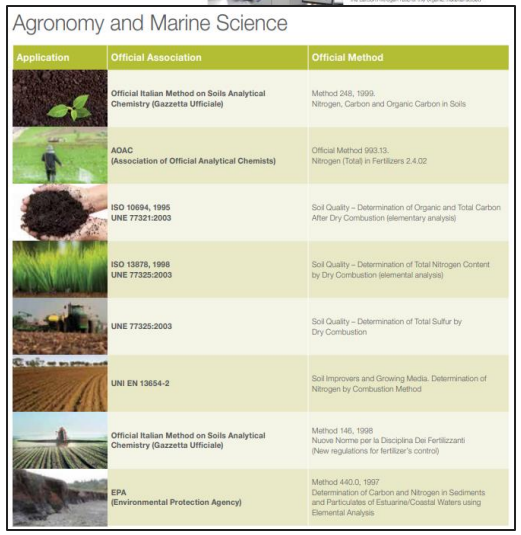
Sieve No.20

0.85 mm



*ประกาศกระทรวงเกษตรและสหกรณ์ เรื่อง กำหนดกรรมวิธีการตรวจวิเคราะห์ปุ๋ยเคมี

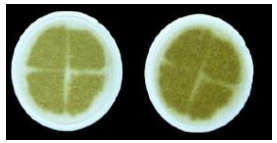


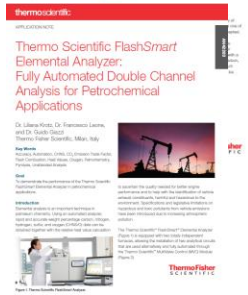


Applications: Access more applications: become the reference laboratory in your field

Petrochemistry: gasoline, diesel, lubricants, oils


Environmental and Marine Science: Wastewater, Particulate matter, Biomass, Plankton



Food: cheese, chocolate, cocoa, flours, pasta, starch, juice, wine, milk, yoghurt



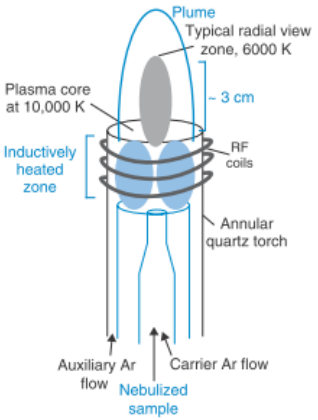



Materials: paper, cotton, textile fibers, polyethylene film


Organic Chemistry & Pharm

Techniques routinely used for soil analysis

	Organic element analyzer	Discrete analyzer	IC	Accelerated Solvent Extraction	GC & GC-MS	X-ray Fluorescence	ICP-OES & ICP-MS
Nutrient Analysis	●	●	—	—	—	●	●
Metal Contaminants	—	—	—	—	—	●	●
Inorganic Anions	—	—	●	—	—	—	—
Organic Contaminants	—	—	—	●	●	—	—



ppb to %

- The ICP-OES and ICP-MS are used to provide information of major plant nutrients (P, K), secondary plant nutrients (Ca, S, Mg), micronutrients such as B, Mn, Fe, Cu, Zn, Mo and Se, also the toxic elements (As, Cd, Pb and Hg)

What is ICP-OES?

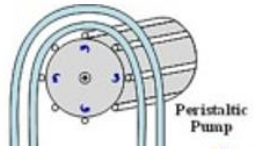
thermo scientific
by Thermo Fisher Scientific

Spectrometer

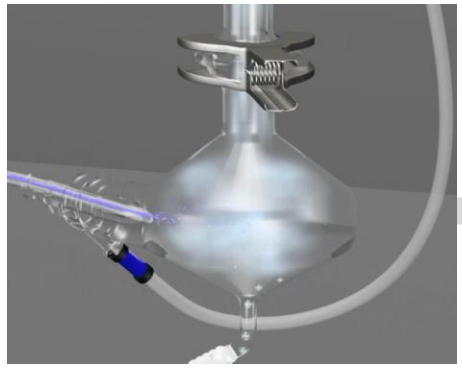
Sample introduction → Inductively Coupled Plasma → Wavelength Separator → Detector → Readout

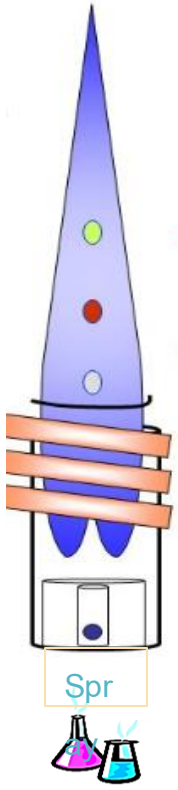
Delivers all the sample to the plasma which provide a *non-effect to plasma stability*

Convert all forms of sample into *free Atom/Ions* and Excite free Atom/Ions turn to *Excited state*



3% TDS

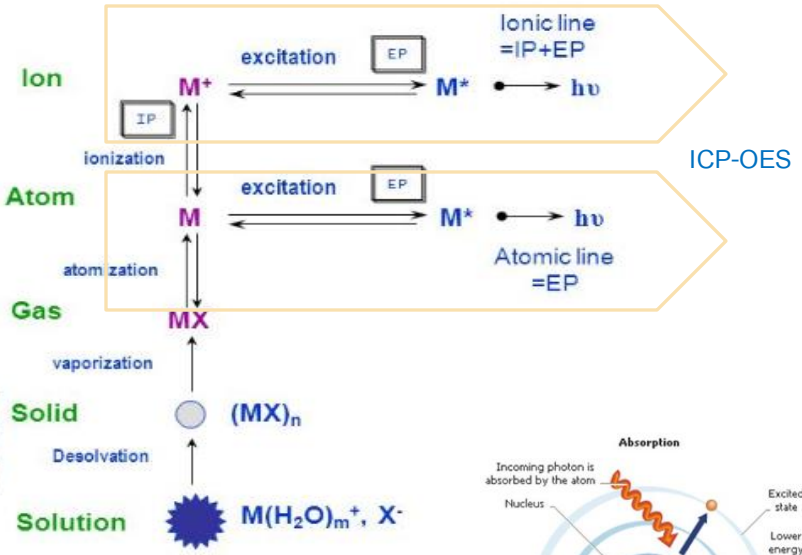




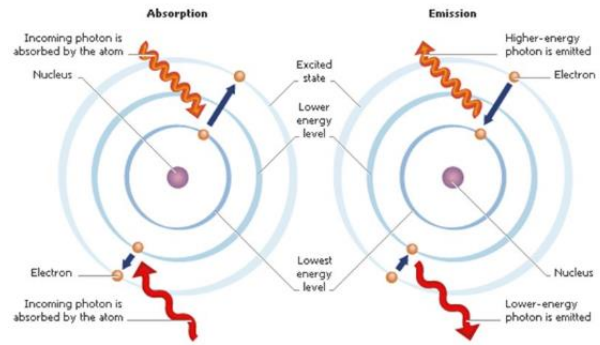
Spr

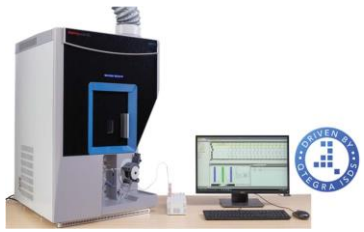
Nebulization

SOULTION SAMPLE



ICP-OES





What is ICP-OES?

Spectrometer

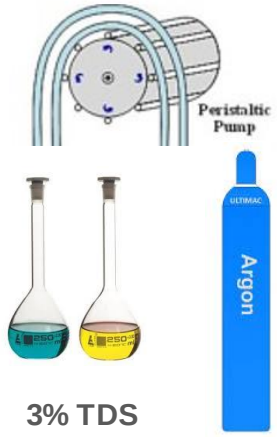
Sample introduction → Inductively Coupled Plasma → Wavelength Separator → Detector → Readout

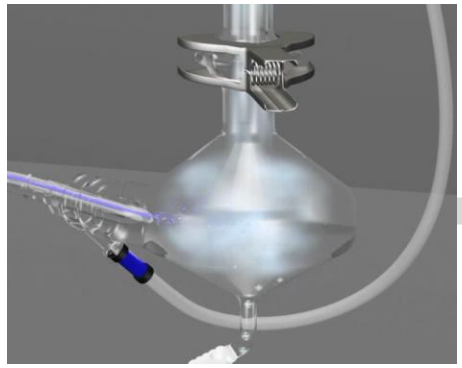
Delivers all the sample to the plasma which provide a *non-effect to plasma stability*

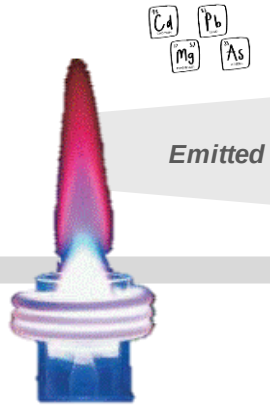
Convert all forms of sample into *free Atom/Ions* and Excite free Atom/Ions turn to *Excited state*

Distinguish emission light from each elemental Atom/Ions and Detect the intensity of each wavelength

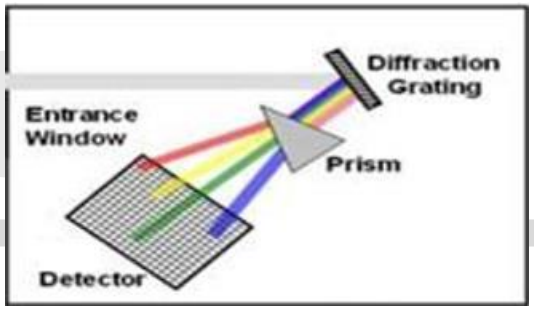
Provide all important information when required but in a simple way.

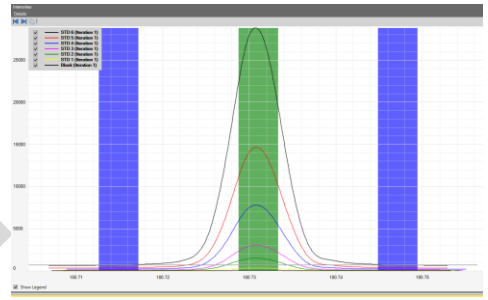


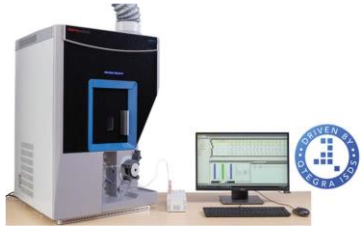




Emitted Light

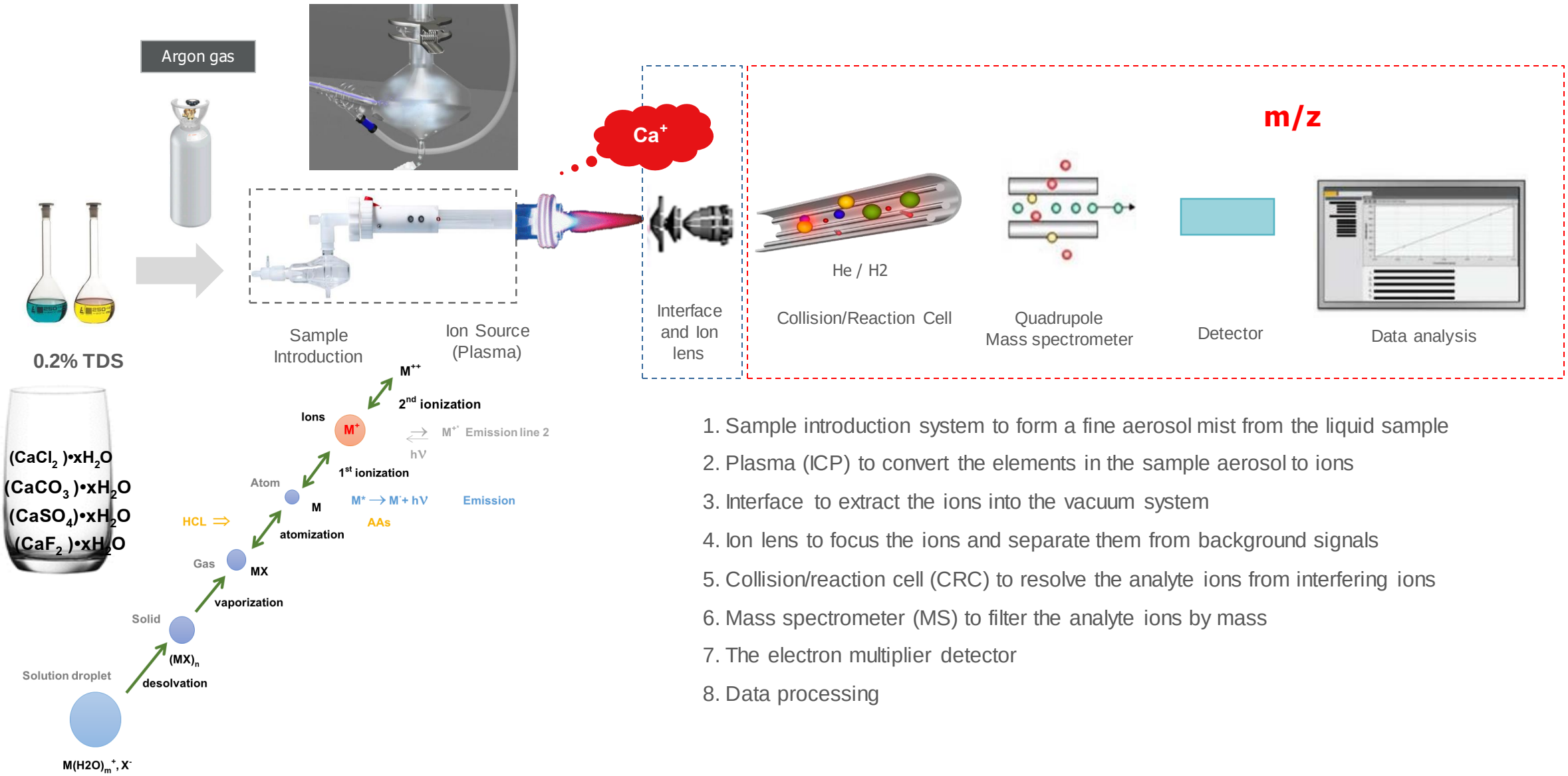






What is ICP-MS?

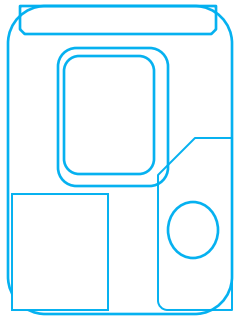
ICP-MS is an elemental analysis technique and uses an argon (Ar) plasma – the ICP – to convert the sample into ions that are then measured using a mass spectrometer



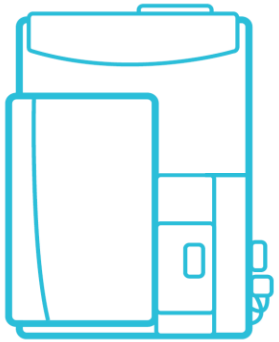
1. Sample introduction system to form a fine aerosol mist from the liquid sample
2. Plasma (ICP) to convert the elements in the sample aerosol to ions
3. Interface to extract the ions into the vacuum system
4. Ion lens to focus the ions and separate them from background signals
5. Collision/reaction cell (CRC) to resolve the analyte ions from interfering ions
6. Mass spectrometer (MS) to filter the analyte ions by mass
7. The electron multiplier detector
8. Data processing

Select the right techniques for metal analysis in your lab

Field	Typical Applications	Commonly used Techniques		
		AA	ICP-OES	ICP-MS
Environmental	Water			
	Soil			
	Air			
Food	Food safety			
	Nutritional labeling			
Pharmaceutical	Drug / Clinical			
Petrochemical	Petroleum refining			
	Lubricants and oil			
Chemical / Industrial	QC/Product testing			
Agriculture	Soil / Fertilizer / Plant			
Geochemical/Mining	Exploration			
	Research			
Bio-monitoring	Biological Fluids			
Semiconductor	Wafers			
	High-Purity Chemicals			
Nuclear Energy	Low-level waste			
	Process water			
Renewable Energy	Biofuels			
	Solar panels			
Nano materials	Research			



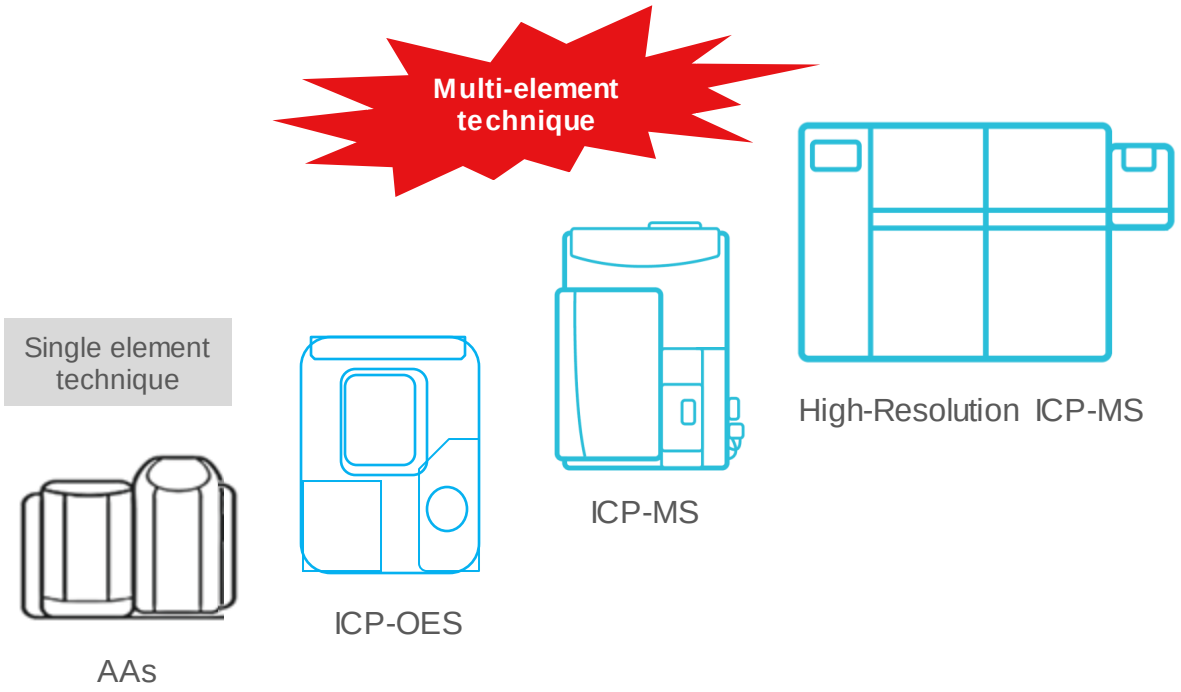
ICP-OES



ICP-MS

Frequency of Technique Used

Select the right techniques for metal analysis in your lab



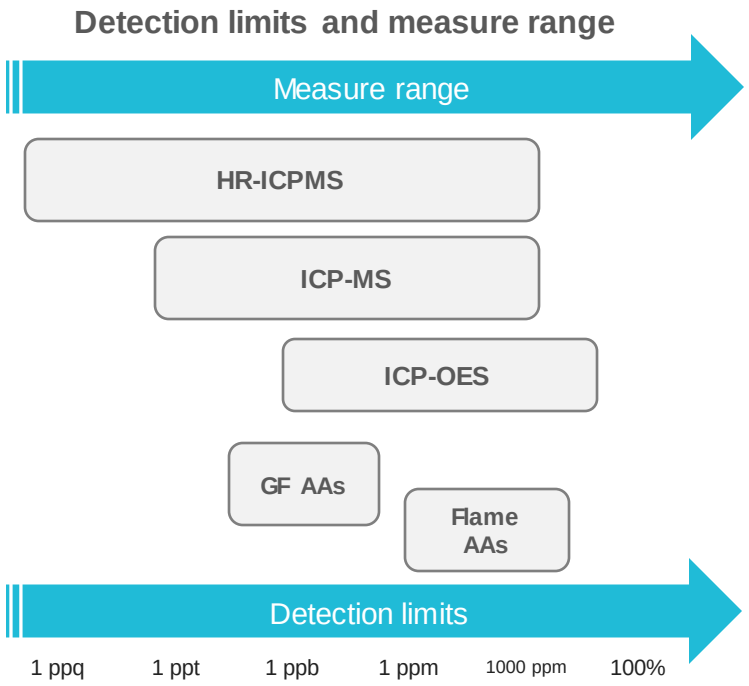
ICP-OES

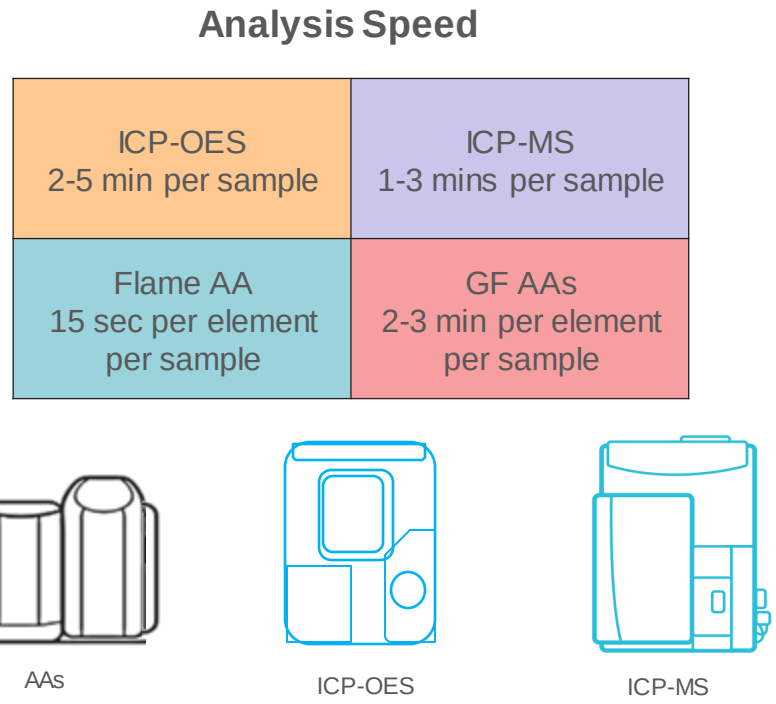
- Simultaneous
- Multi-elements
- ppb to %
- Highest matrix tolerance
- High sample throughput
- Ease to use

ICP-MS

- Multi-elements
- High dynamic range and lowest limits of detection
- Detection limits in ppt range
- High sensitivity
- High sample throughput
- Ease to use

Considers for instrument selection



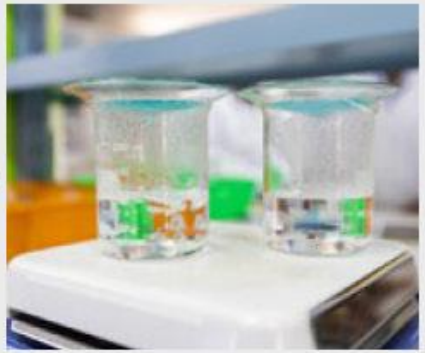


- ✓ ICP-MS offers high dynamic range and lowest limits of detection
- ✓ ICP-OES has highest matrix tolerance
- ✓ GFAAs offers sensitivity, best for few elements
- ✓ Flame AA offers fast analysis, and economical sol.

Low (<5)	Number of Elements	High (>15)
One matrix	Sample Matrix	Difference matrix
ppm	Detection limits	ppb or lower
Low (<20)	Sample throughput	High (>100)

Elemental analysis workflow

Standard preparation



Sample preparation

Sample dilution

Sample introduction

Sample analysis

Data

Be aware of contamination sources.

Minimize handling and transfer steps.

Use high-purity reagents.

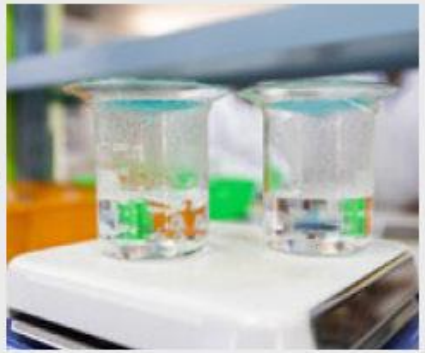
Use ultrapure water.

Measure weights and volumes with accuracy.

Apply proper skill, technique, and attention to detail.

Elemental analysis workflow

Standard preparation



Sample preparation

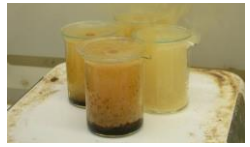
Sample dilution

Sample introduction

Sample analysis

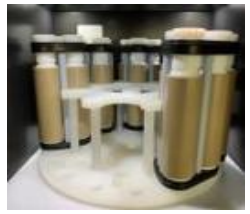
Data

Acid Leaching



Wet digestion : Hot plate

Block Acid digestion



Microwave digestion

Dry ashing

EPA United States Environmental Protection Agency

Standard Methods

Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry

EPA Method 6010D (SW-846) Inductively Coupled Plasma - Atomic Emission Spectrometry

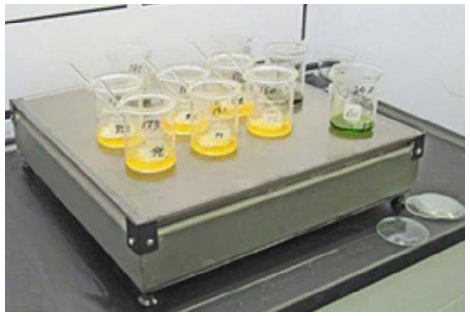
Hazardous Waste Test Methods / SW-846

EPA Method 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry

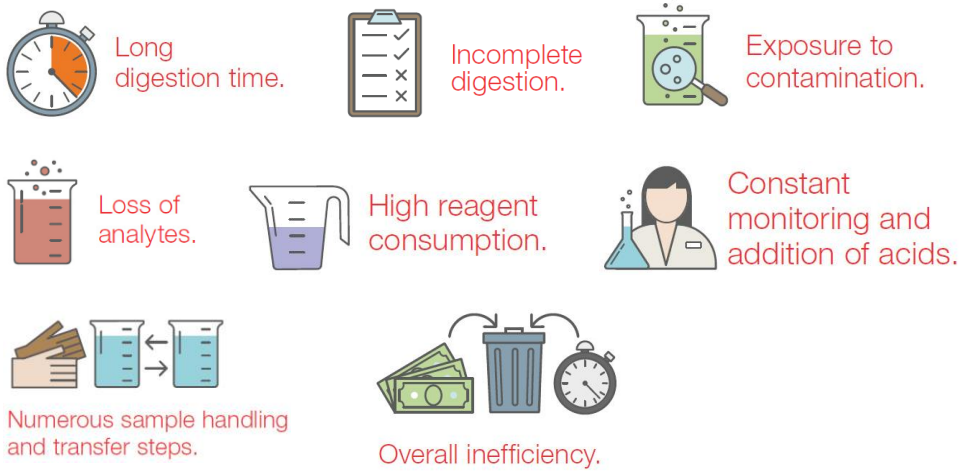
EPA Method 6020B (SW-846) Inductively Coupled Plasma - Mass Spectrometry, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

Sample preparation techniques

Hot plate acid digestion



- ✓ Simple and inexpensive set-up involving the use of commonplace laboratory apparatus and a hot plate
- ✓ Procedures are standardized and uncomplicated
- ✓ Higher sample sizes (e.g., > 1 gram) are possible, which may be required for multiphasic, heterogeneous samples



Hot block acid digestion

- ✓ Reduced sample handling and transfers
- ✓ Exposure to contamination is reduced.
- ✓ Elimination of issues associated with glassware.

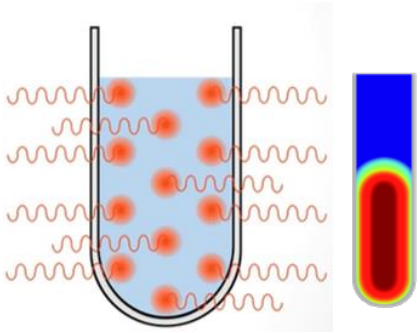
(adsorption of analytes to container walls or leaching of elemental impurities to the sample solution, are eliminated)

X However, the duration of the digestion process is still extensive, reagent consumption is high, and exposure to contamination from the atmosphere may be possible since it is an open system.

Sample preparation techniques - Microwave digestion

- Microwaves are a form of electromagnetic radiation with relatively low energy. It promotes the rotation of specific molecules in a reaction mixture, this rotation results in increased molecular collision and the generation of heat
- Combining the sample matrix and acids (HCl, HNO_3, H_2SO_4, and H_2O_2) in a pressurized close container and elevating the solution past the boiling point of the acid
- Temperatures in the range of 200-260 °C
- Typical microwave digestion takes just 20-40 minutes

Microwave heating



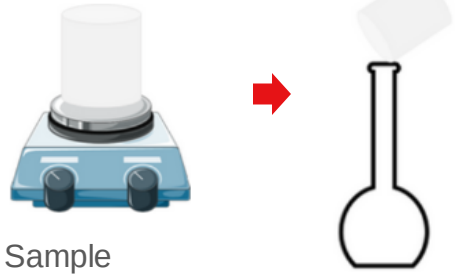
- ✓ Speed of digestion
- ✓ Quality digestion
- ✓ Reduced exposure to contamination
- ✓ Reduced reagent consumption
- ✓ Retention of analyte

Key considerations	Open vessel acid digestion		Closed vessel acid digestion
	Hot plate	Hot block	Microwave
Initial investment	$	$$	$$$
Ease of set-up	Easiest	Easier	Easy
Consumables	N/A	Required	Optional
Maintenance and cleaning	High	Low	Medium
Sample handling	Highest handling	Lowest handling	Medium handling
Contamination exposure	Highest risk	Medium risk	Lowest risk
Reagent consumption	High	High	Low
Retention of analyte	Lowest	Medium	Highest
Digestion quality	Low	Medium	High
Batch size	Lowest	Highest	Medium
Digestion time	Hours	Hours	Minutes
Sample throughput	Lowest	Medium	High
Recommended for ultra-trace elemental analysis	Not recommended	Recommended	Highly recommended
Overall efficiency	Low	Medium	High

Soil, Sediment and Solid waste

- Nutritional elements: Al, Ba, Ca, Fe, K, Mg, Mn, P and Zn
- Trace elements: Cd, Co, Cr, Pb, Mo, Ni, V, etc.
- EPA Method 6010D (SW-846) – ICP-OES

Wet digestion



Sample
+ HNO_3
+ H_2O_2
+ HCl

EPA 3010A

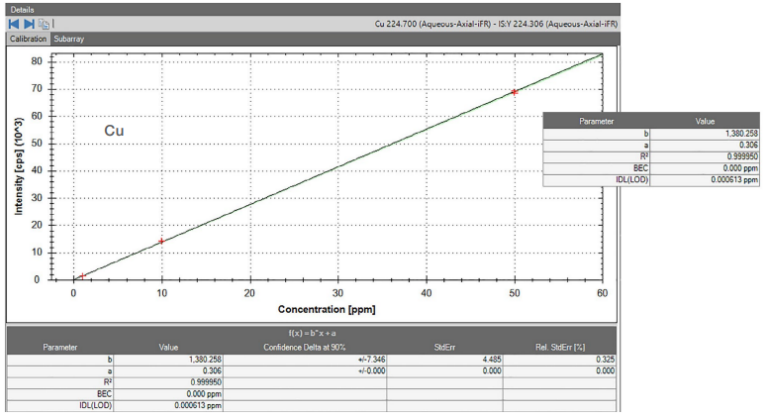
Microwave digestion

Sample
+ HNO_3
+ HCl

EPA 3051A

Analysis by ICP-OES

All elements in single run



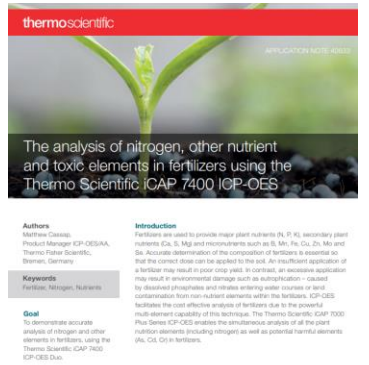
Fertilizer (AOAC 2017.02)

Elemental Categories in Fertilizer

Class	Elements
Primary Nutrients	N, P, K
Secondary Nutrients	Ca, Mg, Fe, Mn, Na, Cu, Zn, Mo, B, S,
Micronutrients	Al, Co, V, Se, Ni
Harmful trace elements	As, Cd, Cr, Pb

Regulatory Limits of Elements in Fertilizers in Thailand

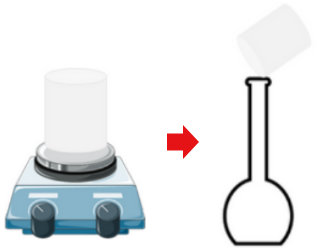
Element	Regulatory Concentration (mg/kg)
As	50
Cd	5
Cr	300
Pb	500



1 g sample

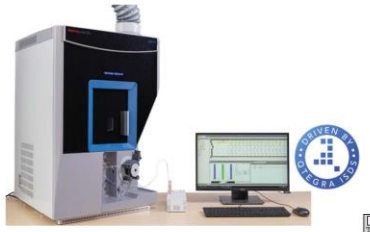
+ HNO3

+ HCl



100 mL with DI water

All elements in single run



Analysis by ICP-OES

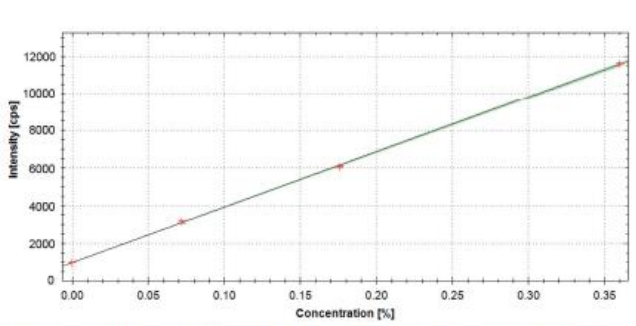


Figure 2. Calibration curve for N 174.272 nm with an R^2 of 0.9998.

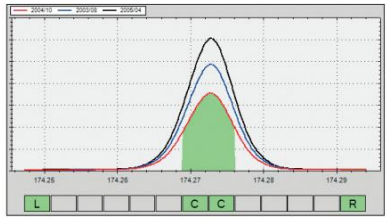


Figure 1. Subarray plot of N 174.272 nm.

0.1-0.5 sample

+ HNO3

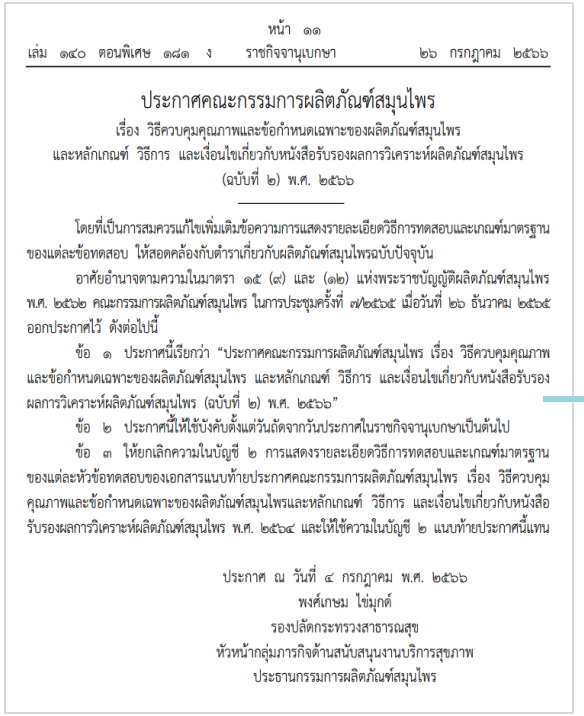
+ HCl

100 mL with DI water

Cannabis / Kratom / Herbal

Raw Materials and Products

- Liquid soap
- Soap bar
- Cannabidiol oil
- Caring oil
- Face cream
- Skin cream organic
- Gel cream organic



หน้า ๑๑
เล่ม ๑๔๐ ตอนพิเศษ ๑๘๑ ง ราชกิจจานุเบกษา ๒๖ กรกฎาคม ๒๕๖๖

ประกาศคณะกรรมการผลิตภัณฑ์สมุนไพร
เรื่อง วิธีควบคุมคุณภาพและข้อกำหนดเฉพาะของผลิตภัณฑ์สมุนไพร
และหลักเกณฑ์ วิธีการ และเงื่อนไขเกี่ยวกับหนังสือรับรองผลการวิเคราะห์ผลิตภัณฑ์สมุนไพร
(ฉบับที่ ๒) พ.ศ. ๒๕๖๖

โดยที่เป็นการสมควรแก้ไขเพิ่มเติมข้อความการแสดงรายละเอียดวิธีการทดสอบและเกณฑ์มาตรฐานของแต่ละข้อทดสอบ ให้สอดคล้องกับตำราเกี่ยวกับผลิตภัณฑ์สมุนไพรฉบับปัจจุบัน

อาศัยอำนาจตามความในมาตรา ๑๕ (๙) และ (๑๒) แห่งพระราชบัญญัติผลิตภัณฑ์สมุนไพร พ.ศ. ๒๕๖๒ คณะกรรมการผลิตภัณฑ์สมุนไพร ในการประชุมครั้งที่ ๗/๒๕๖๕ เมื่อวันที่ ๒๖ ธันวาคม ๒๕๖๕ ออกประกาศไว้ ดังต่อไปนี้

ข้อ ๑ ประกาศนี้เรียกว่า "ประกาศคณะกรรมการผลิตภัณฑ์สมุนไพร เรื่อง วิธีควบคุมคุณภาพและข้อกำหนดเฉพาะของผลิตภัณฑ์สมุนไพร และหลักเกณฑ์ วิธีการ และเงื่อนไขเกี่ยวกับหนังสือรับรองผลการวิเคราะห์ผลิตภัณฑ์สมุนไพร (ฉบับที่ ๒) พ.ศ. ๒๕๖๖"

ข้อ ๒ ประกาศนี้ให้ใช้บังคับตั้งแต่วันถัดจากวันประกาศในราชกิจจานุเบกษาเป็นต้นไป

ข้อ ๓ ให้ยกเลิกความในบัญชี ๒ การแสดงรายละเอียดวิธีการทดสอบและเกณฑ์มาตรฐานของแต่ละหัวข้อทดสอบของเอกสารแนบท้ายประกาศคณะกรรมการผลิตภัณฑ์สมุนไพร เรื่อง วิธีควบคุมคุณภาพและข้อกำหนดเฉพาะของผลิตภัณฑ์สมุนไพรและหลักเกณฑ์ วิธีการ และเงื่อนไขเกี่ยวกับหนังสือรับรองผลการวิเคราะห์ผลิตภัณฑ์สมุนไพร พ.ศ. ๒๕๖๔ และให้ใช้ความในบัญชี ๒ แนบท้ายประกาศนี้แทน

ประกาศ ณ วันที่ ๔ กรกฎาคม พ.ศ. ๒๕๖๖
พงศ์เกษม ไข่มุกด์
รองปลัดกระทรวงสาธารณสุข
หัวหน้ากลุ่มภารกิจด้านสนับสนุนงานบริการสุขภาพ
ประธานกรรมการผลิตภัณฑ์สมุนไพร

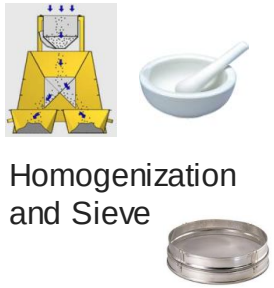
*	Type	Pb	As	Cd	Hg
World Health Organization	Herbal medicines	10 mg/kg	-	0.3 mg/kg	-
Canada	Raw herbal materials	10 mg/kg	5 mg/kg	0.3 mg/kg	0.2 mg/kg
China	Raw herbal materials	10 mg/kg	5 mg/kg	1.0 mg/kg	0.5 mg/kg
Malaysia	Finished herbal materials	10 mg/kg	5 mg/kg	-	0.5 mg/kg
Singapore	Finished herbal materials	20 mg/kg	5 mg/kg	-	0.5 mg/kg
Thailand*	Raw herbal materials	10 mg/kg	5 mg/kg	0.3 mg/kg	0.5 mg/kg

Cannabis / Kratom / Herbal

Sample

Rinse with Trap water and DI water

Dry at Room temp. until constant weight

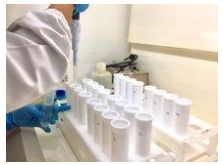


Homogenization and Sieve

Acid digestion & Analysis by ICP-MS

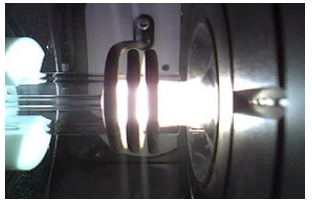
Weight 0.25 - 0.5 g

Add conc. HNO_3, HCl, H_2O_2



Microwave digestor

Adjust the final volume to 25 ml with ultrapure water



Qtegra Intelligent Scientific Data Solution (ISDS) Software

Technical Note: 43106 — Thermo Scientific Qtegra ICP-MS software for 21 CFR Part 11 compliant labs

Raw mat.	HNO3	HCl	H2O2
Flower	✓	✓	✓
Leave	✓	✓	
Seed	✓		✓
Root	✓		✓
Products	✓	✓	✓

Step	Temperature (°C)	Heat time (min)	Hold time (min)
1	160	5	5
2	200	5	25

Applications: Access more applications: become the reference laboratory in your field

thermo scientific
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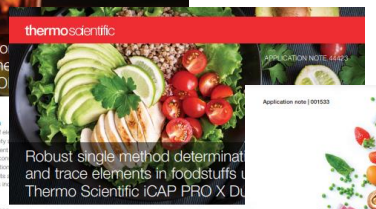

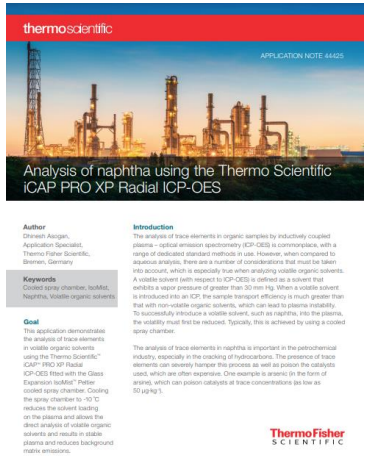

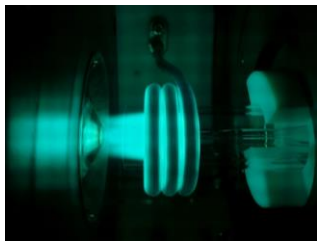

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Thank You

Q & A

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