Elemental Analysis in Soil and Fertilizer

PRESENTED BY

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What to analyze in Soil and Fertilizer?

O_2, CO_2  H_2O

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

Major nutrients

Nitrogen (N)
Phosphorus (P)
Potassium (K)

Micronutrients

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

Secondary nutrients

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

Toxic

Arsenic (As)
Cadmium (Cd)
Chromium (Cr)
Mercury (Hg)
Lead (Pb)
Copper (Cu)
Manganese (Mn)
Nickel (Ni)
Selenium (Se)

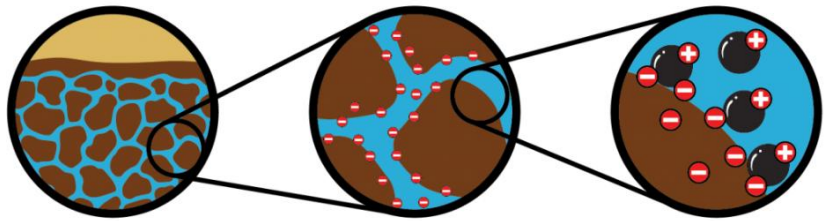
Fertilizer

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

- Raw materials
- Finish products
- N, P, K, C/N ratio

โลหะหนักที่อยู่ในรูปประจุบวกPb As Cd Hg

ธาตุที่ตรึงบนผิวเม็ดดินที่ในรูปประจุลบ เช่น P N O C



Soil and Fertilizer Regulation

Soil: Regulation in Thailand

ประกาศคณะกรรมการสิ่งแวดล้อมแห่งชาติ เรื่องกำหนดมาตรฐานคุณภาพดิน 2564

Element	mg/kg	
	ดินประเภทที่ 1 อยู่อาศัย	ดินประเภทที่ 2 เพื่อการเพาะปลูก
As	6	25
Cd	67	762
Cr	17.5	212
Cu	2920	35040
Pb	400	800
Hg	22	263
Ni	436.5	5205
Mn	1710	19640
Se	365	4380

Animal feed

Human food

Fertilizers: Regulation in Thailand

ประกาศกรมวิชาการเกษตร เรื่อง กำหนดเกณฑ์ปุ๋ยอินทรีย์ / ปุ๋ยหมัก 2557

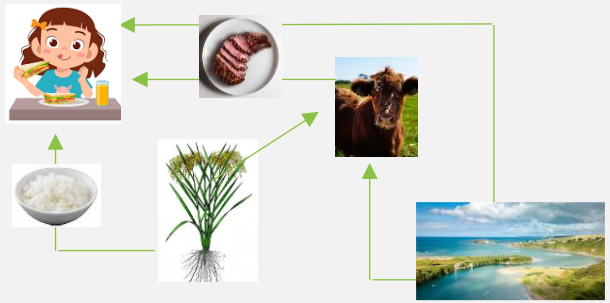
Element	mg/kg
As	50
Cd	5
Cr	300
Cu	500
Pb	500
Hg	2

Element	% โดยน้ำหนัก
N	>1
P	>0.5
K	>0.5
C/N ratio	20:1
Na	<1

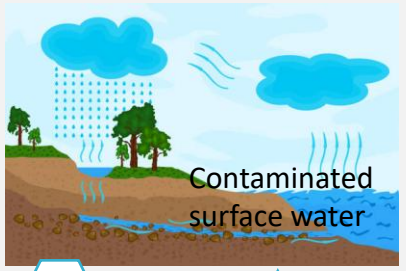
Heavy metal

Anthropogenic

Geogenic

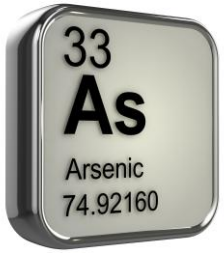


Biogenic

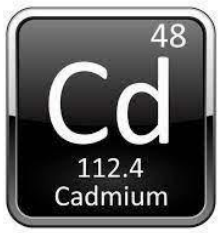


As Minerals

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



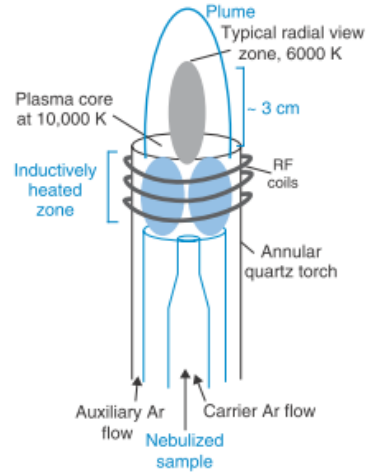
- พิษต่อตับและไต
- ตับอับกเสบ
- ทำลายสมอง



- โรคไต
- กระดูกผุ ปวดบริเวณเอวและหลัง
- เป็นสารก่อมะเร็ง โดยเฉพาะมะเร็งปอด มะเร็งต่อมลูกหมากและไต
- โรคอิไต อิไต

Techniques routinely used for soil / Fertilizer 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	—	—	—	●	●	—	—



trace (ppm to ppb)
ultra-trace (ppb to ppt)

100 ppm to 100 %

CHNS

Oxygen

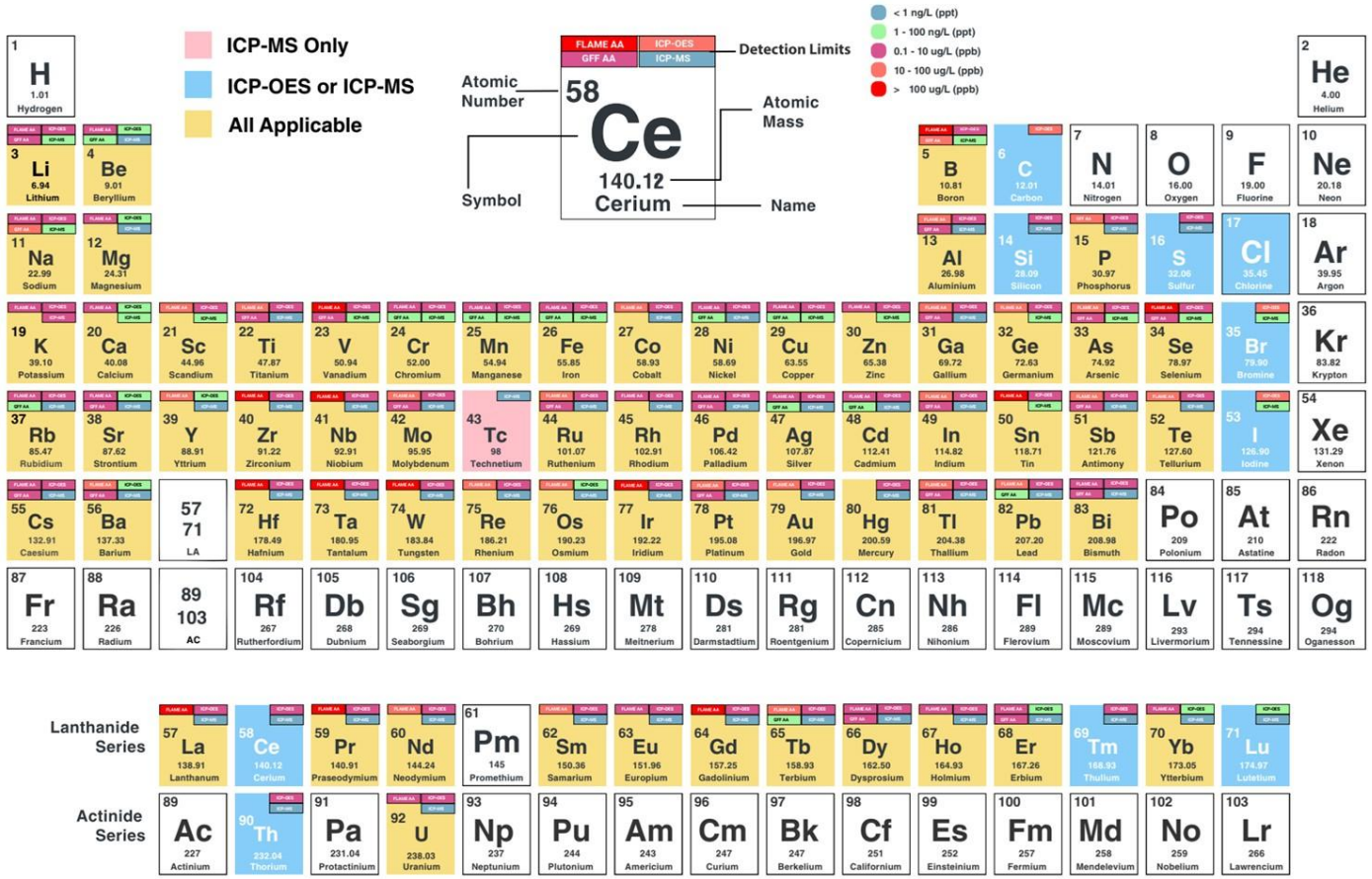
1800°C
Flash Combustion

Organic Elemental Analysis (Combustion)

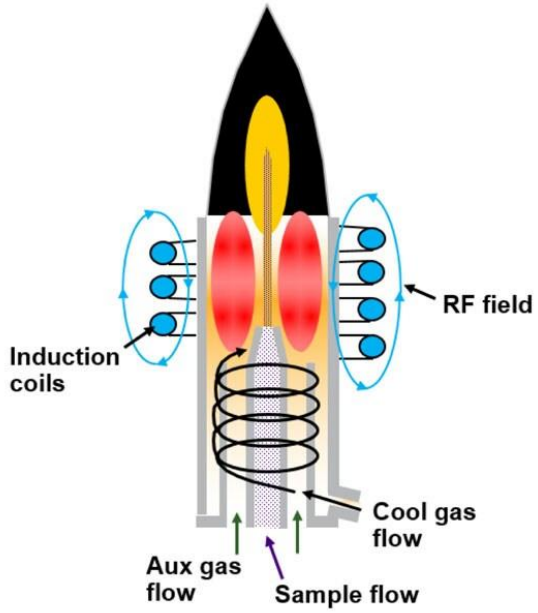
- The Organic Elemental Analyzer is used for Carbon, Hydrogen, Nitrogen, Sulphur, and Oxygen analysis
- The ICP-OES and ICP-MS are used to provide information of major plant nutrients (N, P, K), secondary plant nutrients (Ca, S, Mg), micronutrients such as B, Mn, Fe, Cu, Zn, Mo and Se, also the toxic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

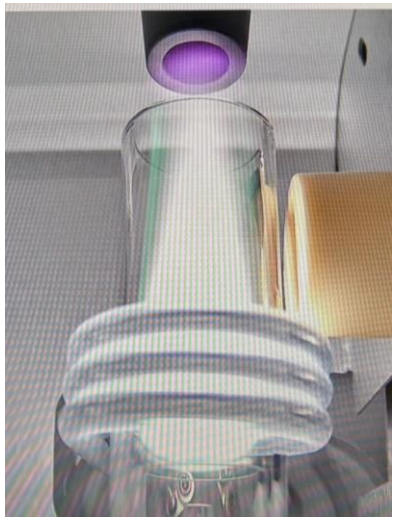
What is Inductively Coupled Plasma (ICP)?

PERIODIC TABLE CHART



- The Inductively Coupled Plasma (ICP) is an ionization source that fully decomposes a sample into its constituent elements and transforms those elements into ions.
- It is typically composed of argon gas, and energy is "coupled" to it using an induction coil to form the plasma.

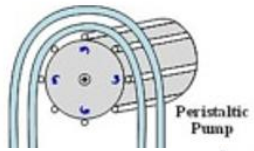




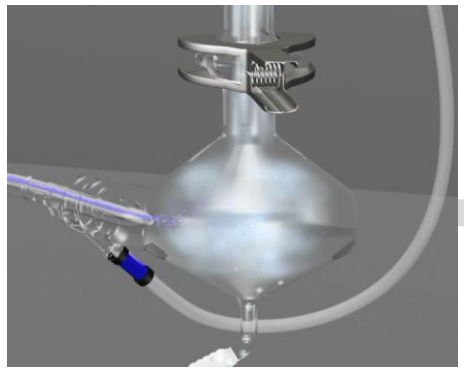
What is ICP-OES?

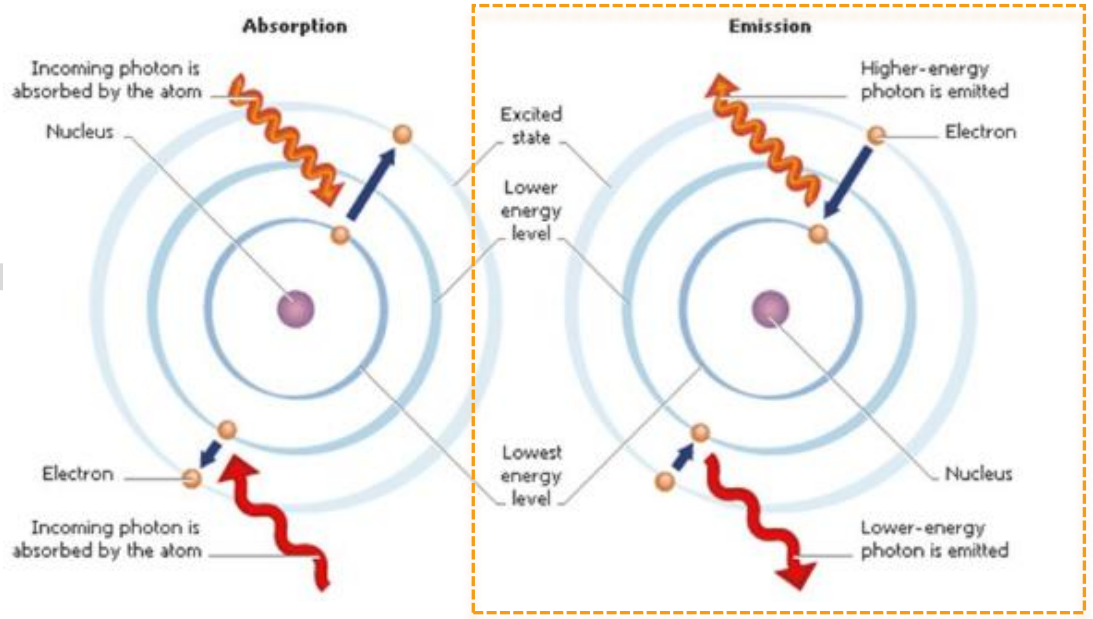
Spectrometer

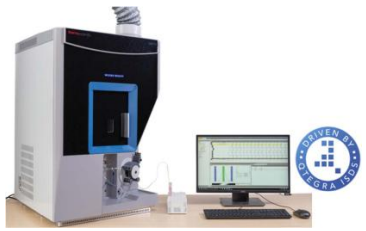
Sample introduction	Inductively Coupled Plasma	Wavelength Separator	Detector	Readout
Delivers all the sample to the plasma which provide a *non-effect to plasma stability*	Convert all forms of sample into *free Atom/Ions* and Excite free Atom/Ions turn to *Excited state*	Distinguish emission light from each elemental Atom/Ions and Detect the intensity of each wavelength		Provide all important information when required but in a simple way.



3% TDS



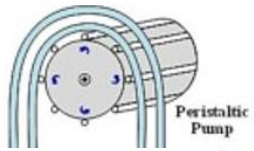




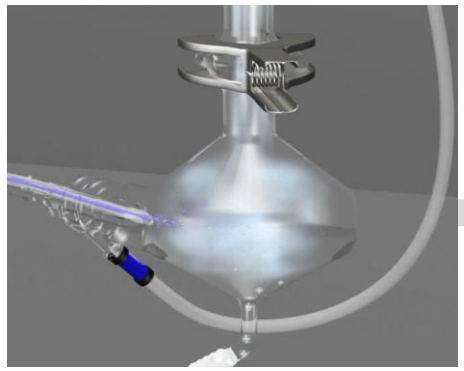
What is ICP-OES?

Spectrometer

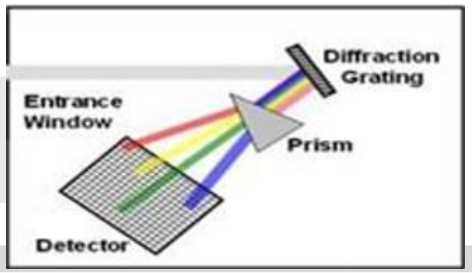
Sample introduction	Inductively Coupled Plasma	Wavelength Separator	Detector	Readout
Delivers all the sample to the plasma which provide a *non-effect to plasma stability*	Convert all forms of sample into *free Atom/Ions* and Excite free Atom/Ions turn to *Excited state*	Distinguish emission light from each elemental Atom/Ions and Detect the intensity of each wavelength		Provide all important information when required but in a simple way.

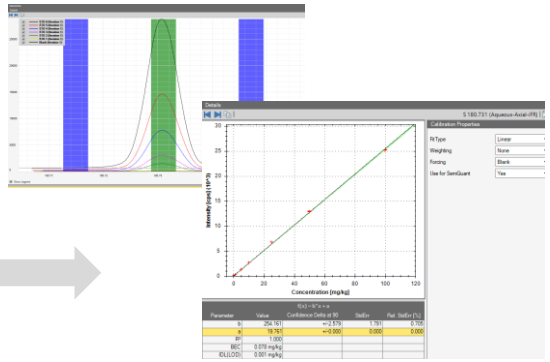


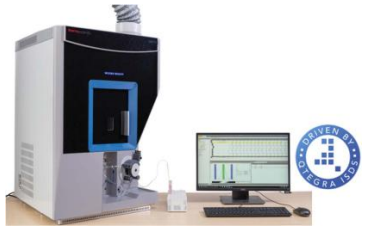
3% TDS



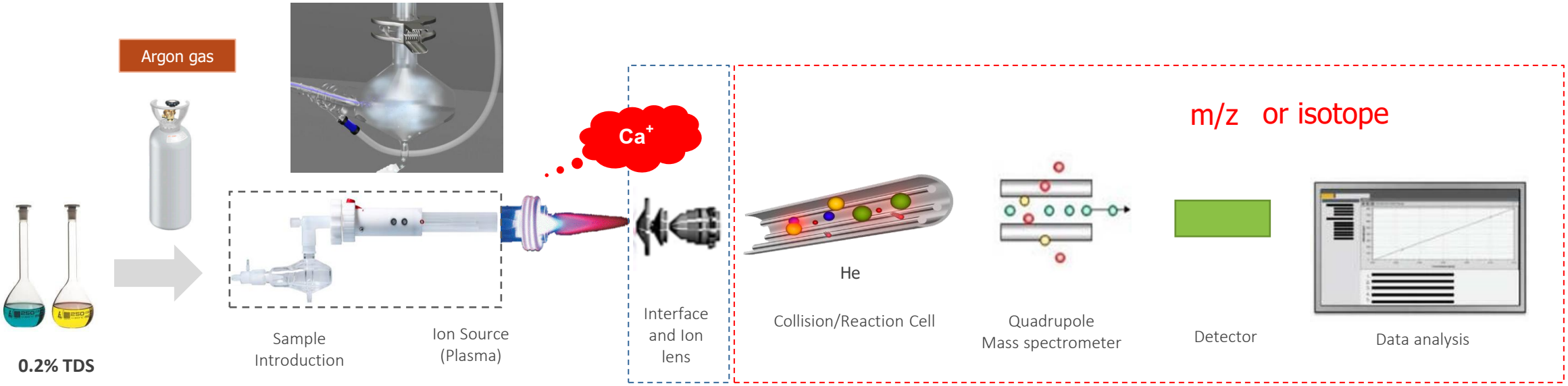
Emitted Light







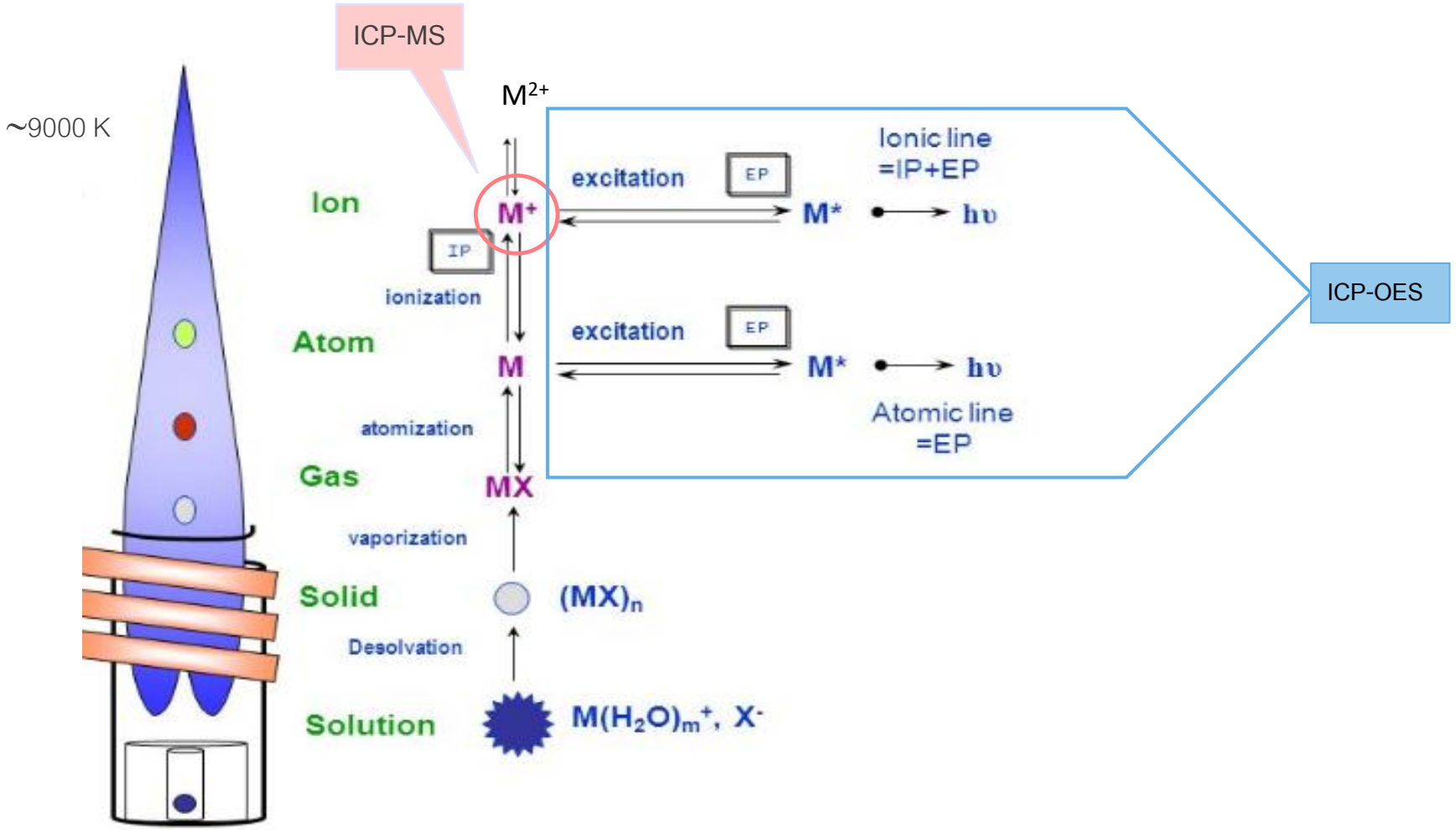
What is ICP-MS?

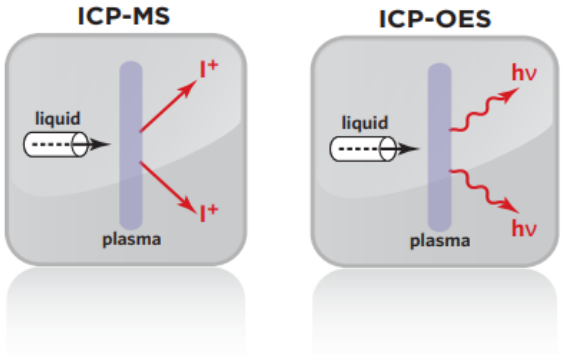


Sample preparation

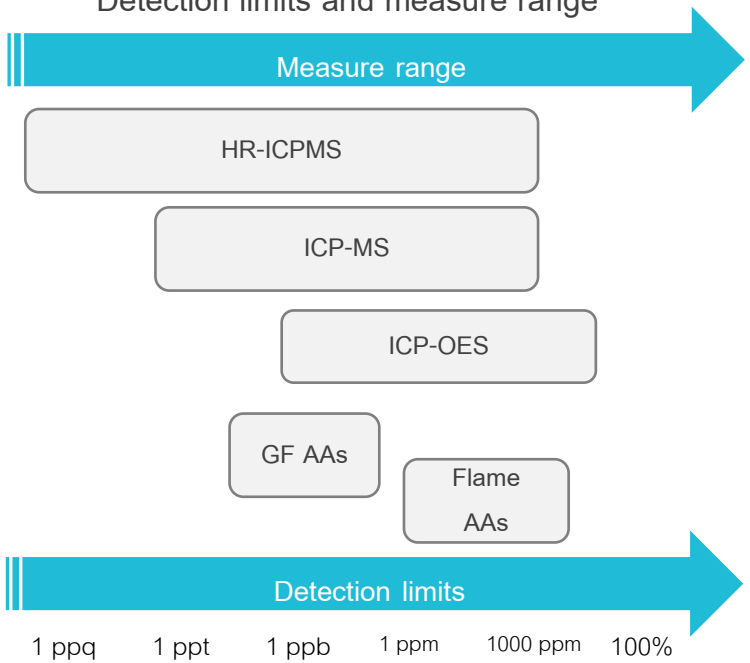
1. Sample introduction system to form a fine aerosol mist from the liquid sample
2. Plasma (ICP) to convert the elements in the sample aerosol to ions
3. Interface to extract the ions into the vacuum system
4. Ion lens to focus the ions and separate them from background signals
5. Collision/reaction 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 & Data processing

Plasma





How to choose Techniques?



Analysis Speed

ICP-OES 2-3 min per sample	ICP-MS 2-3 mins per sample
Flame AA 15 sec per element per sample	GF AAs 2-3 min per element per sample

- ✓ 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.

PERFORMANCE | SENSITIVITY AND DETECTION LIMIT | ANALYSIS SPEED | EASE OF USE AND MAINTENANCE | COST PER SAMPLE

ICP-OES

- ➢ Simultaneous
- ➢ Multi-elements
- ➢ Sub ppb to %
- ➢ Highest matrix tolerance
- ➢ High sample throughput

ICP-MS / ICP-MSMS

- ➢ Multi-elements
- ➢ High dynamic range and lowest limits of detection
- ➢ ppb to ppt range
- ➢ High sensitivity
- ➢ High sample throughput

How to choose Techniques?

AAs

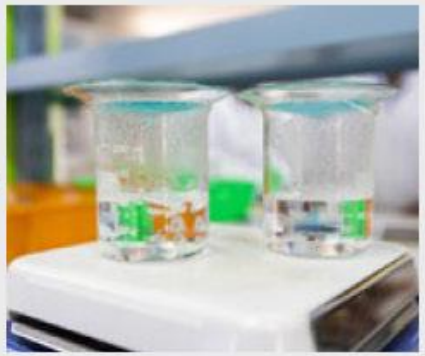
ICP-OES

ICP-MS

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.

Sample Preparation for Soil and Fertilizers

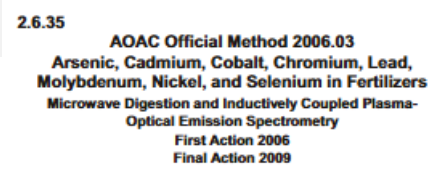
United States Environmental Protection Agency

Test Method 3010A, 3051A

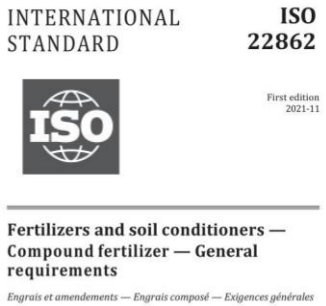
Hazardous Waste Test Methods / SW-846

- EPA Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry
- EPA Method 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry
- EPA Method 6010D (SW-846) Inductively Coupled Plasma - Atomic Emission Spectrometry
- EPA 6020B ((SW-846)) Inductively Coupled Plasma Mass Spectrometry

- **Fertilizer** : Sampling of the fertilizer material should follow accepted guidelines e.g. the International Organization for Standardization (ISO), the Association of Official Agricultural Chemists (AOAC 2017.02), EN method or other applicable protocols


2.6.35

AOAC Official Method 2006.03
Arsenic, Cadmium, Cobalt, Chromium, Lead, Molybdenum, Nickel, and Selenium in Fertilizers
Microwave Digestion and Inductively Coupled Plasma-Optical Emission Spectrometry
First Action 2006
Final Action 2009


INTERNATIONAL STANDARD

ISO 22862

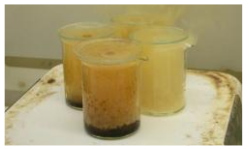
First edition 2021-11

ISO

Fertilizers and soil conditioners — Compound fertilizer — General requirements

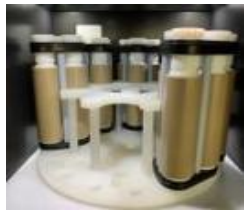
Engrais et amendements — Engrais composé — Exigences générales

Method 200.8, Revision 5.4	Method 6020B (SW-846)
• Used for drinking water and wastewater compliance monitoring programs under the SDWA and CWA. • Applies to the analysis of dissolved elements in groundwaters, surface waters, and drinking water. • Applies to the analysis of total recoverable elements in groundwaters, surface waters, wastewaters, sludges, and soils.	• In support of RCRA, SW-846 Method 6020B was developed for the ICP-MS analysis of various environmental samples: soils, sediments, sludges, groundwater, surface water, aqueous samples with suspended solids, and industrial wastes requiring a measure of the total leachable elements. • This is a performance-based method, used for guidance, not for compliance testing.



Wet digestion
Hot plate

Block Acid digestion



Microwave digestion

Sample preparation methods are given in the SW-846 Compendium, Chapter Three, "Inorganic Analytes." The following methods are specified for the digestion of samples prior to ICP-MS analysis: Methods 3005A, 3010A, 3015A, 3020A, 3050B, 3051A, and 3052.

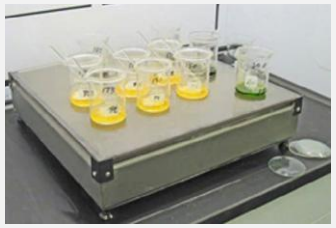
Method 3050B – Acid Digestion of Sediments, Sludges and Soils

Method 3051A – Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils

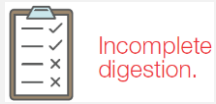
Sample preparation techniques

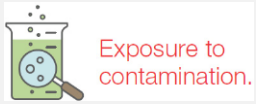
Open vessel acid digestion

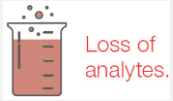
Hot plate

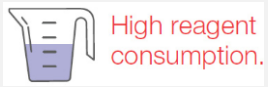


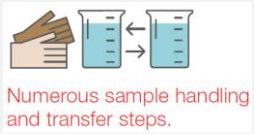
- ✓ Simple and inexpensive set-up involving the use of commonplace laboratory apparatus and a hot plate
- ✓ Procedures are standardized and uncomplicated
- ✓ Higher sample sizes (e.g., > 1 gram)











Hot block

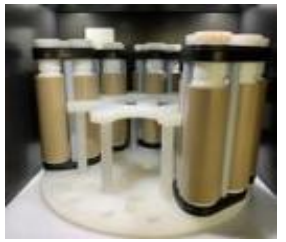
- ✓ Reduced sample handling and transfers
- ✓ Exposure to contamination is reduced
- ✓ Elimination of issues associated with glassware

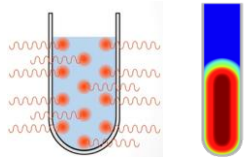
(adsorption of analytes to container walls or leaching of elemental impurities to the sample solution, are eliminated)

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

Closed vessel acid digestion

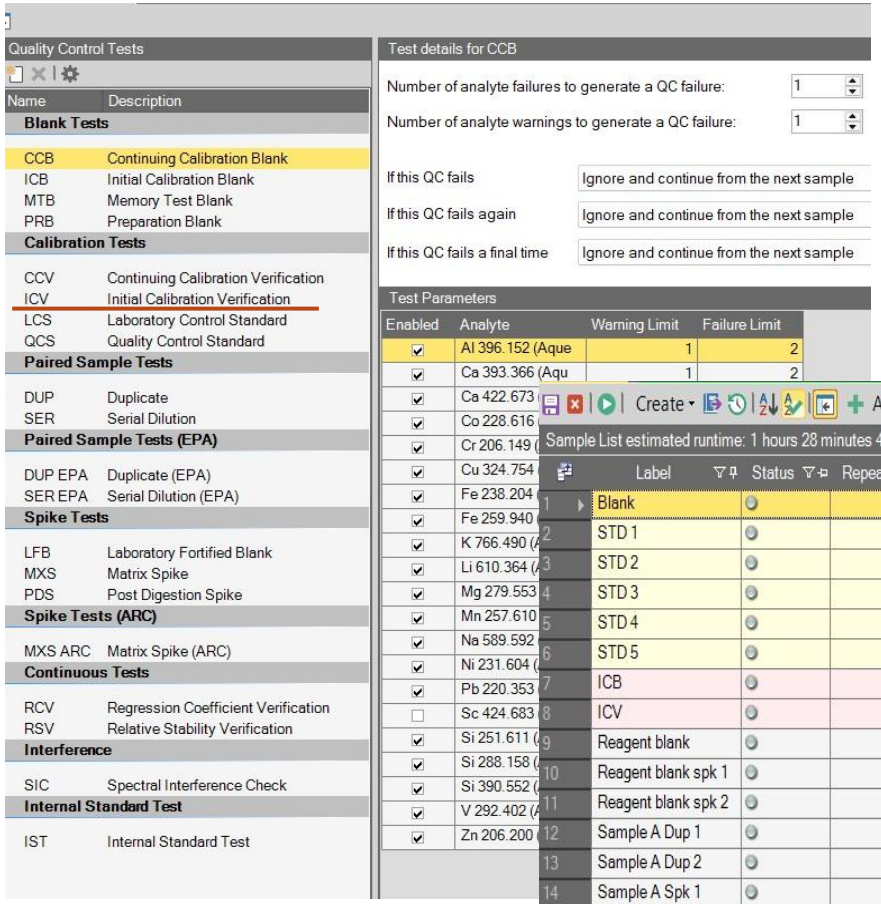
Microwave

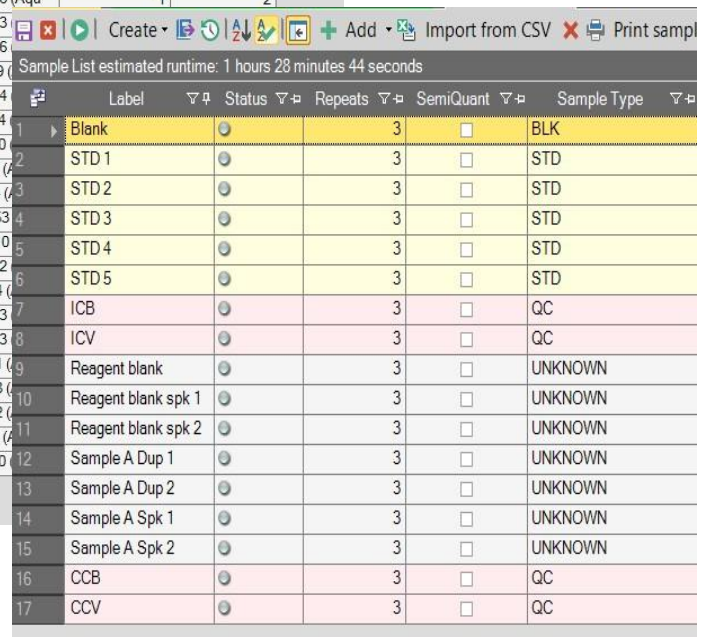




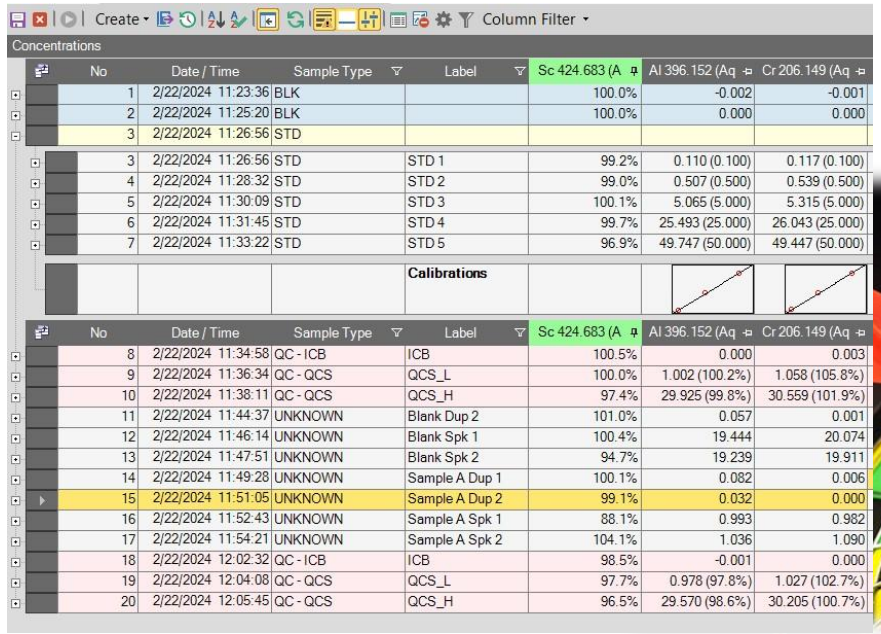
- ✓ Speed of digestion
- ✓ Quality digestion
  - ✓ Complete decomposition of the matrix
  - ✓ Cleaner digestate
  - ✓ Better analyte recoveries
- ✓ Reduced exposure to contamination
- ✓ Reduced reagent consumption
- ✓ Retention of analyte

Quality Control





- Calibration
- Requirements for initial and continuing calibration verification are given in Sections 7.24 and 7.25 of Method 6020B Quality control
  - ICB, ICV, CCB, CCV
- Spiked method blank
- Spiked sample (Matrix spiked)
- Spiked Internal standard



Soil, Sediment and Solid Waste

EPA Method 6010D (SW-846)

Dry at RT or at 35-40 °C in an oven at constant weight

3010A

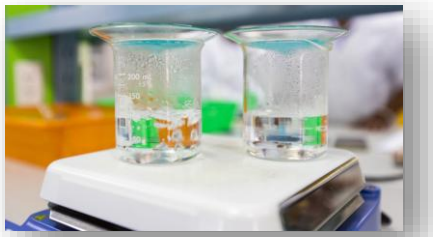
3050B

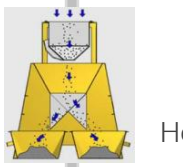
HNO_3

HCl, H_2O_2....

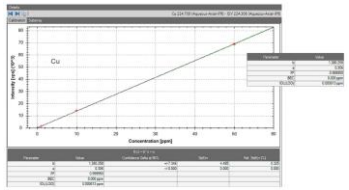
3015A

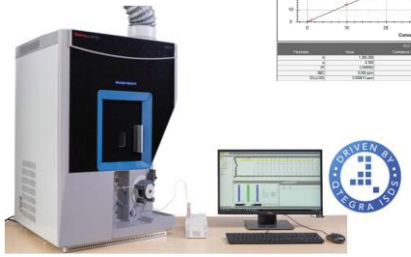
3051A





Homogenization





Sampling

Fertilizer

AOAC 2017.02: Arsenic, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Selenium, and Zinc in Fertilizers: Microwave Acid Digestion and ICP-OES Detection

Elemental Categories in Fertilizer

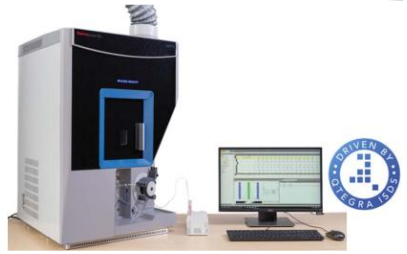
Class	Elements
Primary Nutrients	N, P, K
Secondary Nutrients	Ca, Mg, Fe, Mn, Na, Cu, Zn, Mo, B, S
Micronutrients	Al, Co, V, Se, Ni
Harmful trace elements	As, Cd, Cr, Pb

0.5-1 g

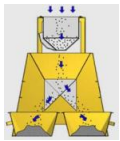
+ HNO_3

+ HCl,

Homogenization and sieve



Herbal
Big four: As Cd Pb Hg





0.25 - 0.5 g

Homogenization
and Sieve

Dry at Room temp.
until constant weight

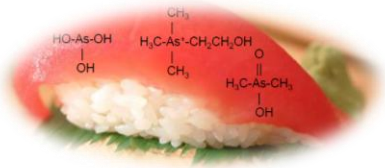
Rinse with Trap water
and DI water

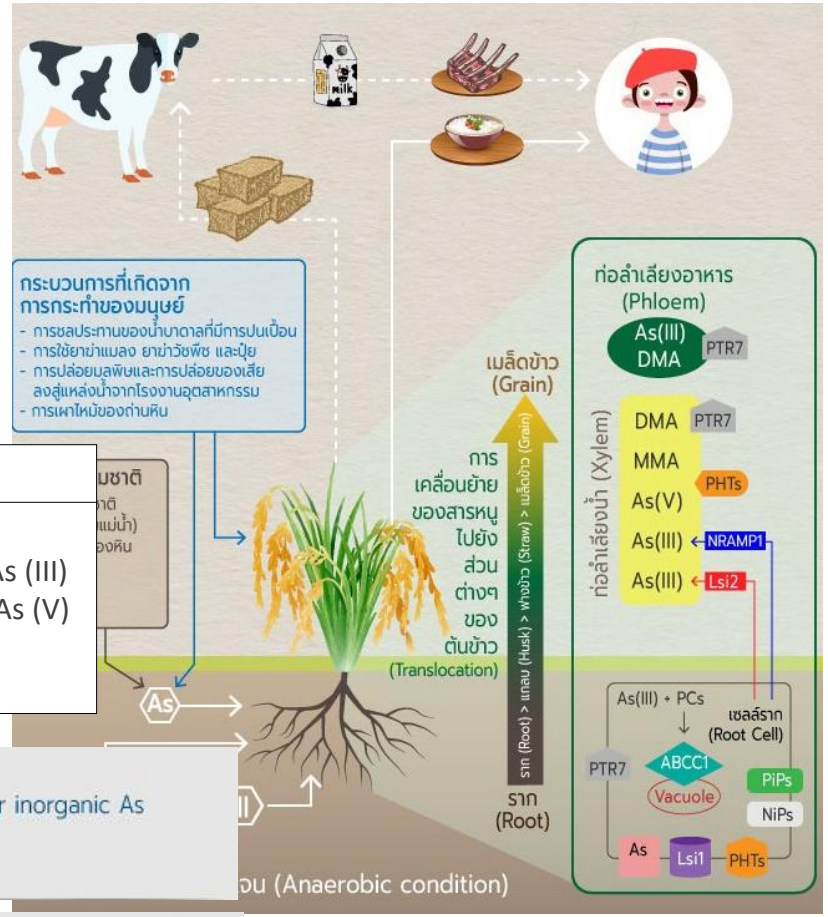



+. HNO_3, HCl, H_2O_2

	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

Speciation analysis of As in Rice



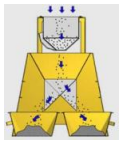
Mildly Toxic	Toxic
Organic: AsB AsC DMA MMA	Inorganic: Arsenite, As (III) Arsenate, As (V)

หน่วยงาน:	FAO/WHO
Guideline:	Maximum levels for inorganic As in rice
ความเข้มข้น:	0.2 mg kg^{-1}

หน่วยงาน:	EU
Guideline:	Maximum levels of inorganic As in food for infants and young children
ความเข้มข้น:	0.1 mg kg^{-1}

Biswas *et al.* (2020)
https://mx.nimt.or.th/?p=13683

Herbal
Big four: As Cd Pb Hg





0.25 - 0.5 g


Homogenization
and Sieve

Dry at Room temp.
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Rinse with Trap water
and DI water




+. HNO_3, HCl, H_2O_2

	Type	Pb	As	Cd	Hg
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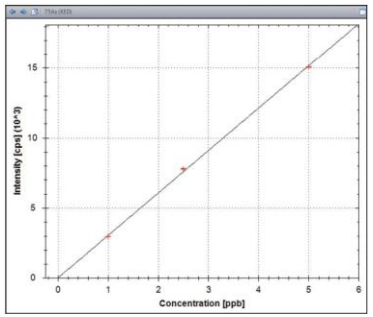
China	Raw herbal materials	10 mg/kg	5 mg/kg	1.0 mg/kg	0.5 mg/kg
Malaysia	Finished herbal materials	10 mg/kg	5 mg/kg	-	0.5 mg/kg
Singapore	Finished herbal materials	20 mg/kg	5 mg/kg	-	0.5 mg/kg
Thailand*	Raw herbal materials	10 mg/kg	5 mg/kg	0.3 mg/kg	0.5 mg/kg

speciation analysis of As in Rice

Sample preparation → **Chromatography IC, HPLC** + **ICP-MS**



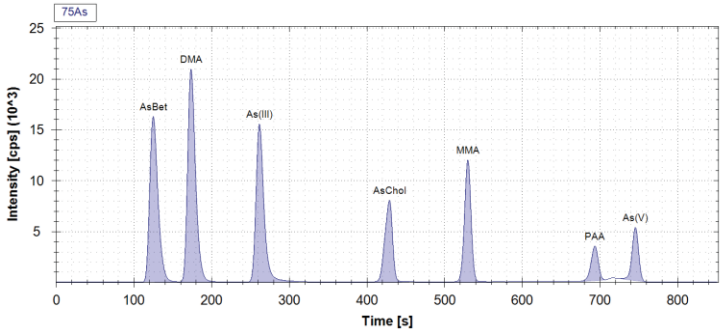
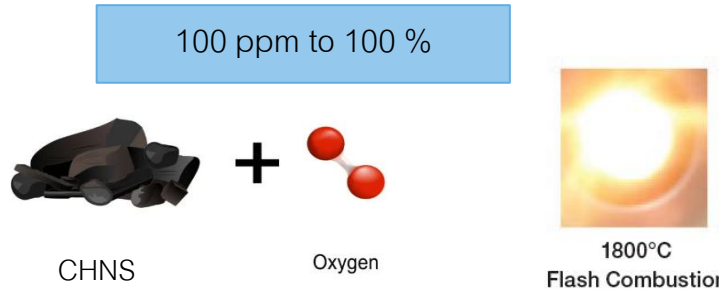


Table 1. Ion Chromatography operating conditions.

Parameter	Value			
Columns	Dionex IonPac AG7 (4x50 mm) and AS7 (4x250 mm)			
Injection Volume	100 µL			
Eluents	A: Ultrapure water B: 100 mM $(NH4)_2CO_3$ + 3% MeOH, pH 10.3			
Gradient	Time min	Flow mL·min^{-1}	% A	% B
	0-5	0.7	95	5
	5.1-10	1.5	70	30
	10.1-13	1.5	40	60
	13.1-14	0.7	95	5

Techniques routinely used for soil / Fertilizer 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	—	—	—	●	●	—	—

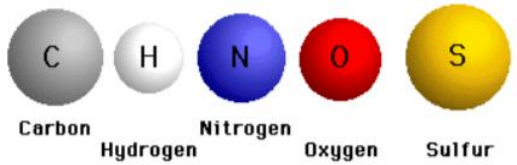


- The Organic Elemental Analyzer is used for Carbon, Hydrogen, Nitrogen, Sulphur

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 the characterization of

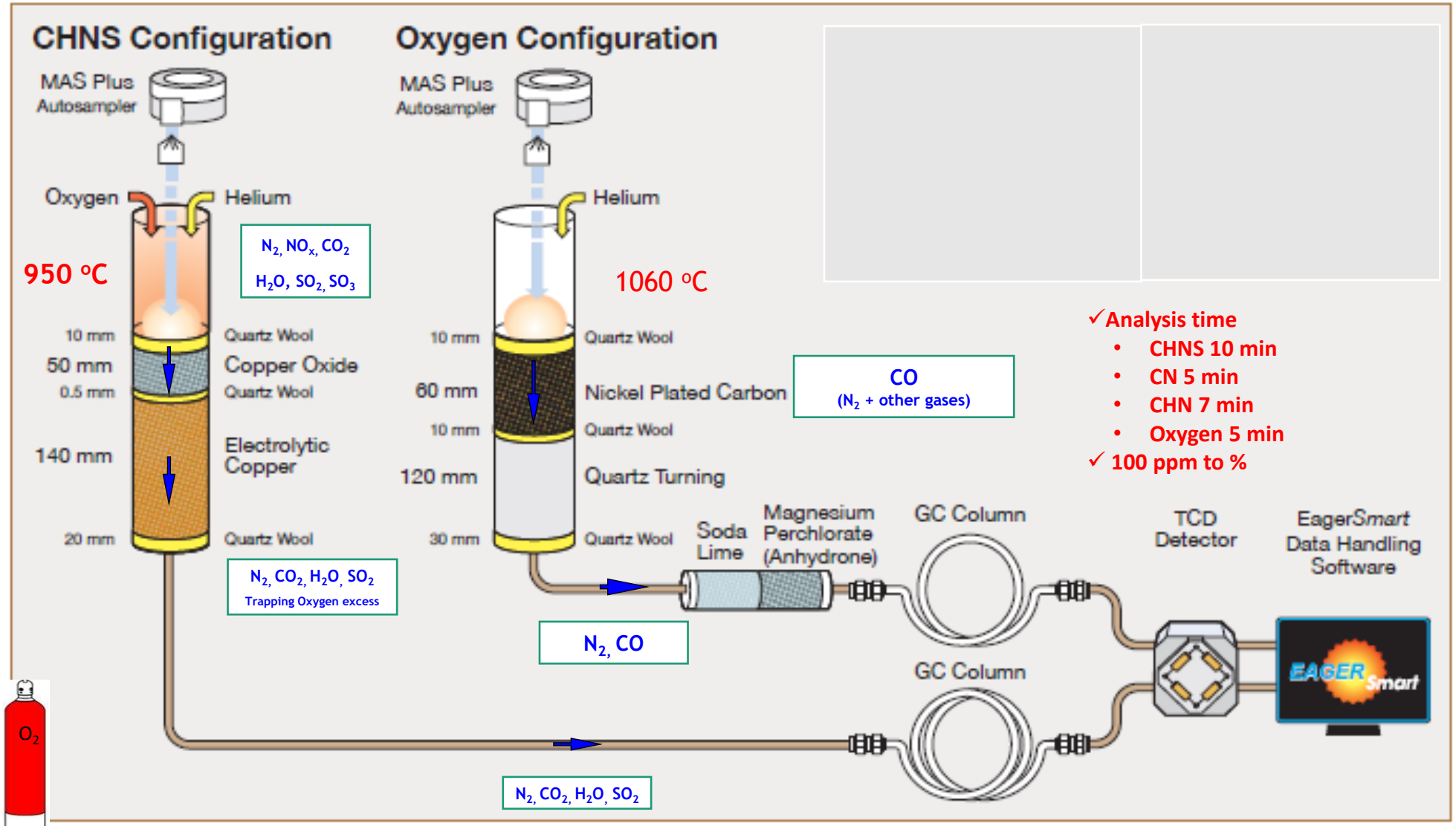
- Soils
- Leaves, Plants, Crops, and other materials
- Fertilizer



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. Thus, the ratio of the elements in the original sample is determined. C, H, N, and S can all be determined simultaneously, whereas Oxygen by pyrolysis.

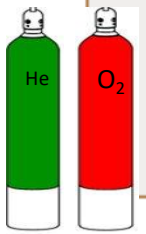
Quantification of the sample	Weighting
Quantitative oxidation of the sample	Combustion
Reduction of combustion gases	Reduction
Separation of the oxidation gases	Chromatography
Generation of signal	Detection

CHNS/O Analyzer principle



✓Analysis time
- CHNS 10 min
- CN 5 min
- CHN 7 min
- Oxygen 5 min

✓ 100 ppm to %



99.995% purity

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

%C, %H, %N, %S

Agronomy: Soil / Fertilizer

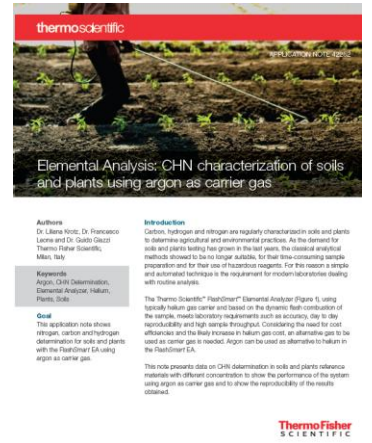
Drill in several points

Representative sample

Sieve 1.5 cm

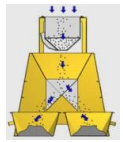
Take 1 kg

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

Sieve to 500 um

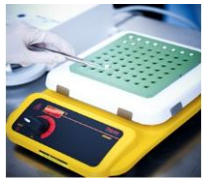
Dry at 105°C up to constant weight. Determine the humidity.

Analysis

Tin caps.

For NC, S an.

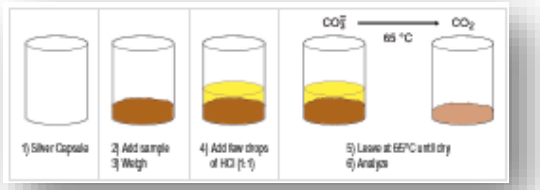
Silver caps. for TOC an.



Acidification with HCl 1:1 for TOC

Weight the sample

Introduce the sample into the MAS Plus Autosampler



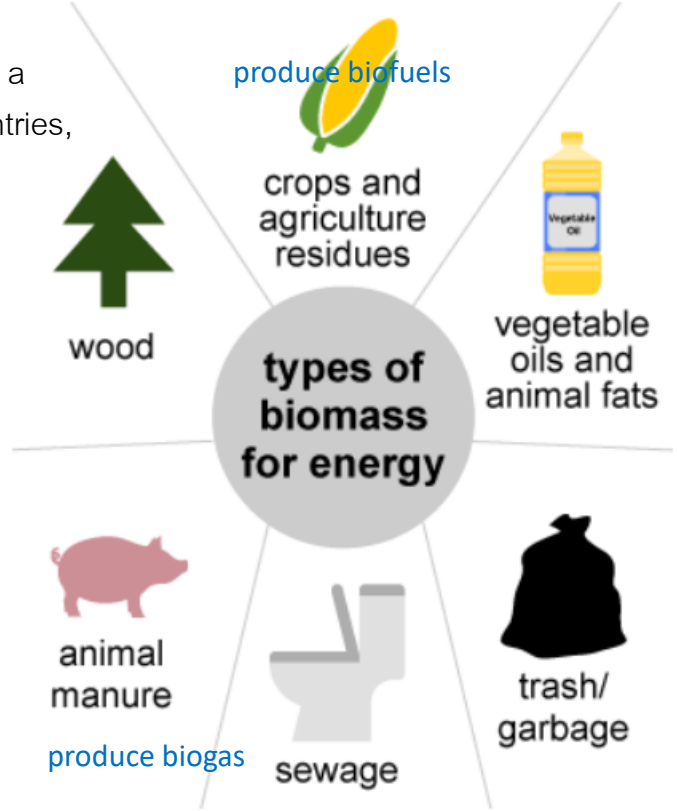
Analysis of NC, S and TOC det.

Biomass, Biochar and Carbon credits

- Biomass is renewable organic material that comes from plants and animals.
- Biomass is used for heating and electricity generation and as a transportation fuel. Biomass is an important fuel in many countries, especially in developing countries for cooking and heating.
  - Combustion
  - Gasification
  - Fermentation
  - Hydrothermal liquefaction

Properties of Biomass Sources

- Moisture Content <50%
- Calorific value
- Proportion of Fixed Carbon and Volatile
- Ash/ Residue Content
- Alkali metal: Na K Mg Ca P
- Cellulose/ Lignin Ratio
- Size and Bulk density



Source: U.S. Energy Information Administration (public domain)

- ✓ ทรัพยากรหมุนเวียน : เป็นแหล่งชีวมวลที่ยั่งยืน
- ✓ เป็นกลางทางคาร์บอน : ลดการเพิ่มของก๊าซเรือนกระจกสุทธิสู่ชั้นบรรยากาศ
- ✓ การลดของเสีย
- ✓ ความมั่นคงด้านพลังงาน
- ✓ ประโยชน์ทางเศรษฐกิจ
- ✓ ความคล่องตัว ชีวมวลสามารถแปลงเป็นพลังงานรูปแบบต่างๆ ได้ เช่น ความร้อน ไฟฟ้า และเชื้อเพลิงชีวภาพ (เช่น เอธานอลและไบโอดีเซล)
- ✓ การปล่อยมลพิษต่ำ : มี S น้อยไม่สร้างปัญหาฝนกรด
- ✓ การปรับปรุงดิน เช่นขี้เถ้า
- ✓ การผลิตพลังงานจากพื้นที่ที่เพาะปลูกยาก

Biochar and Carbon credits

- Thermal conversion of Biomass
- Biochar is produced during pyrolysis or gasification (350-700 ^{o}C)

Porosity

- Water Holding Capacity
- Nutrient Retention
- Microbial Habitat
- Low Bulk Density
- Heavy Metal Adsorption
- Cation Exchange Capacity (CEC)
- High Carbon Content >50%

Cycle of biochar production, modification and applications in the

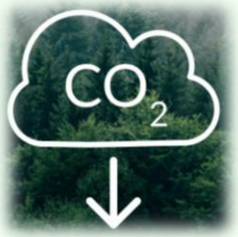
Agro-residue

Thermal decompositi
(350-650 °C)

Pyrolysis

Biochar

- ✓ Carbon sequestration
- ✓ Soil structure improvement
- ✓ Pollution control
- ✓ Waste management



nical activation

Biochar functionalized

Source: Patel and Panwar (2023), Castillo *et al*. (2022)

Agricultural residue and Biochar analysis

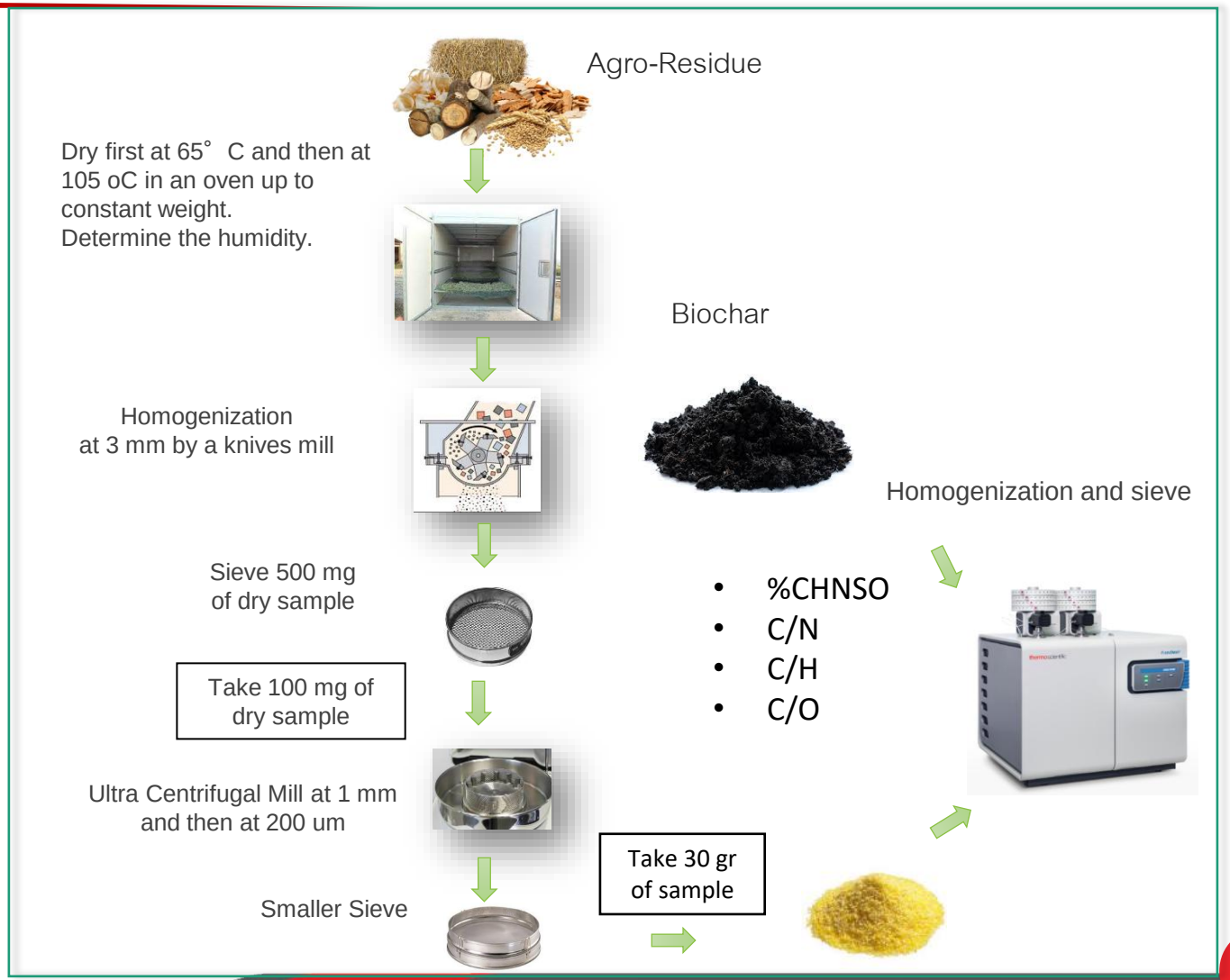
Agro-Residue

- Organic carbon (%)
- C/N ratio
- Total P, K, N

Biochar

- Organic carbon (35-95%)
- C/H < 0.7 (0.4 for Premium)
- C/O < 0.4
- C/N
- Total P, K, Mg, Ca, Fe, S
- Heavy metal

รายการ	โลหะปนเปื้อน	เกณฑ์การปนเปื้อนโลหะสูงสุด (mg/kg น้ำหนักแห้ง)		
		เกษตรกรรม	อุตสาหกรรม	
			ชั้นคุณภาพที่ 1	ชั้นคุณภาพพิเศษ
1	สารหนู (As)	20	ไม่กำหนด	13
2	แคดเมียม (Cd)	5	ไม่กำหนด	1.5
3	โครเมียม (Cr)	200	ไม่กำหนด	100
4	ปรอท (Hg)	2	ไม่กำหนด	1
5	นิกเกิล (Ni)	100	ไม่กำหนด	50
6	ตะกั่ว (Pb)	300	ไม่กำหนด	120
7	ทองแดง (Cu)	200	ไม่กำหนด	140
8	สังกะสี (Zn)	1 000	ไม่กำหนด	420



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