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Analytical methods for determining major and trace elements in solid biofuels and ash

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Presentation content:

- Introduction to the topic
- Sample preparation
- Analytical techniques and methods

Introduction to the topic

- Wood pellets are made of compressed sawdust (wood industry waste).The pellets are held together by the natural lignin in the wood—typically no binder glue is needed. Lignin makes up approximately one quarter to a third of dry wood. It strengthens the wood as well as having water proofing properties.
- Wood pellets have a very low moisture content, typically 6%–10% which means that wood pellets are a very good source of energy since not too much energy from the burning of pellets is used to evaporate moisture. The general properties of wood pellets:

- Moisture: 3.5%–5.5%
- Ash: 0.2%–0.5%
- Calorific value: 8800 Btu/lb
- Bulk density: 600–750 kg/m

Introduction to the topic

- During the combustion of wood pellets i.e. biomass of various origins, most of the basic building elements including C, H, N, P, S and others are lost in the form of gaseous oxides and other gases.
- Consequently, the mineral composition of the biomass is concentrated in the ash in the form of oxides, oxo and other non-volatile salts

Introduction to the topic

- The mineral composition of the ash resulting from the combustion of pellets and other forms of wood biomass depends on the type and origin of the material, as well as the content and nature of the additives used during production.
- In general, the mineral composition can be divided into two categories in terms of the total content of elements:

- Major elements: Ca, K, Mg, P, S, Fe and Na
- Minor elements/trace elements: Mn, B, Cu, Zn and other heavy metlas including Pb, Cd, Ni, Cr, etc.

Introduction to the topic

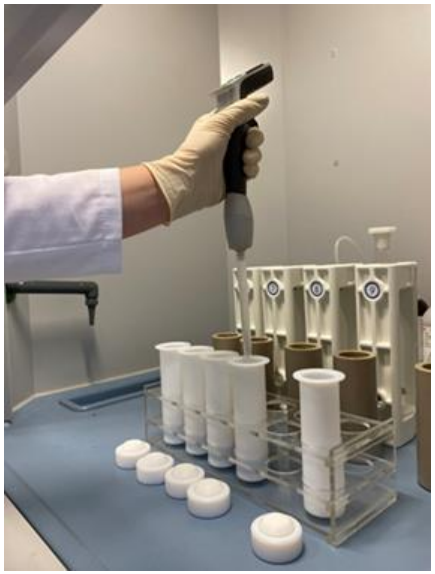
- The presence of major and minor elements in wood pellets and resulting ash is significant for assessing quality of biofuel of this kind.
- Apart from obvious impact on calorific value of pellets, the presence of certain elements may indicate soil pollution, and consequently biomass, and/or the addition of inadequate - harmful additives, and this data can help assess the impact on the environment, especially in terms of the presence of heavy metals.

Sample preparation

- Sampling techniques and preparation of wood pellet and ash samples can be significantly different in relation to the later applied analytical method.
- Sampling procedure must assume a representative laboratory or on-site sample that will minimally affect the measurement uncertainty, that is, the source of uncertainty is possible to control and quantify.

Sample preparation

Preparation of samples for optical methods of analysis such as atomic/ionic absorption or emission, and mass spectrometry includes the destruction of the sample with an appropriate mixture of mineral acids and oxidants, i.e. the derivatization of the sample by reducing the elements of interest to the ionic form in a homogeneous liquid (usually acidic) medium which is further subjected to concentration analysis.



Sample preparation

- Preparation of samples for non-destructive methods implies gravimetric processing of a representative sample, which is usually subjected to a spectrometric method by application of selected energy/wavelength X-rays.

- Pre-weighed samples are usually mixed with fixating agents such as wax to enable sample preservation and vacuum reading.

Analytical techniques and methods

- Analytical techniques include various classical and instrumental procedures for analysis based on certain scientific principles and are usually not completely selective, but can be applied to a larger number of analytes.
- Analytical methods more specifically describe procedures for the analysis of one or a group of related analytes using some of the analytical techniques.

Analytical techniques and methods

- Some written standards are commercially available that describe analytical procedures for the analysis of elements in wood materials and biomass that also include methods of sample preparation.
- The publishers of these standards are international, regional or national standardization institutions that develop standards based on the results of various researches – ISO, CEN/CENELEC, EPA, etc.

Analytical techniques and methods

- Some examples are:

- ***EPA 6020B Elemental analysis of wood or pulp***

  (Determining the content of S, Na, K, Ca, Fe, Cu, Mg, Mn, Si, and P in a wood or pulp powder sample)

- ***ISO 16967, Solid biofuels — Determination of major elements — Al, Ca, Fe, Mg, P, K, Si, Na and Ti***

- ***ISO 16968, Solid biofuels — Determination of minor elements***

However, existing standards are not validated for all types of sample matrices and composition, and a particular problem is the non-existence of reference materials of this type.

Analytical techniques and methods

- Techniques and methods used to determine the elemental composition of wood pellet and ash include various wet chemistry processes and non-destructive methods.
- Optics and gravimetric as primary methods ensure traceability of the measurement results, but for these and other methods, the application of appropriate certified reference materials is implied for the purpose of method validation.

Analytical techniques and methods

- The term elemental analysis is typically defined as the determination of the amount of an element in a given sample, usually a weight percent.
- As there are different elements in many different samples, there is a number of techniques more or less suitable for elemental analysis of a sample of interest.
- Some of the most common techniques used in the laboratories today are X-ray fluorescence (XRF), absorption atomic spectroscopy (AAS), and inductively coupled plasma (ICP) techniques: ICP-optical emission spectroscopy (ICP-OES) and ICP-mass spectrometry (ICP-MS).

Analytical techniques and methods

- Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is based upon the detection of wavelengths of light absorbed by an element (usually 190 nm to 900 nm).

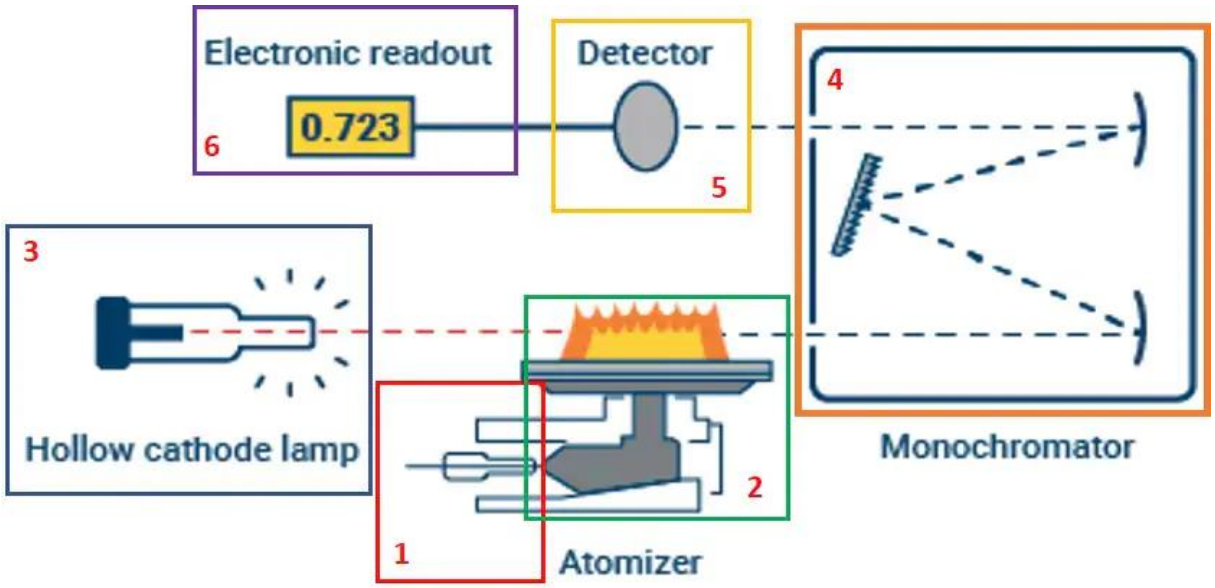
The AA spectrometer consists of a light source, a sample cell to atomize the sample and a detector. As a source of light, several lamps are typically used for different elements.

Analytical techniques and methods

- Atomic Absorption Spectroscopy (AAS)

There are two basic sample cells for atomization used in AAS: the flame burner and the electrothermal heating.

FAAS is used for elements present in higher concentrations, while ETAAS for trace analysis.



Analytical techniques and methods

- Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

Inductively coupled plasma spectrometry is a technique used for elemental analysis and trace analysis. The sample is injected into argon gas plasma in a liquid form. Solid samples require a preparation step prior to injection, such as extraction or acid digestion, but liquid and gas samples can be injected directly.

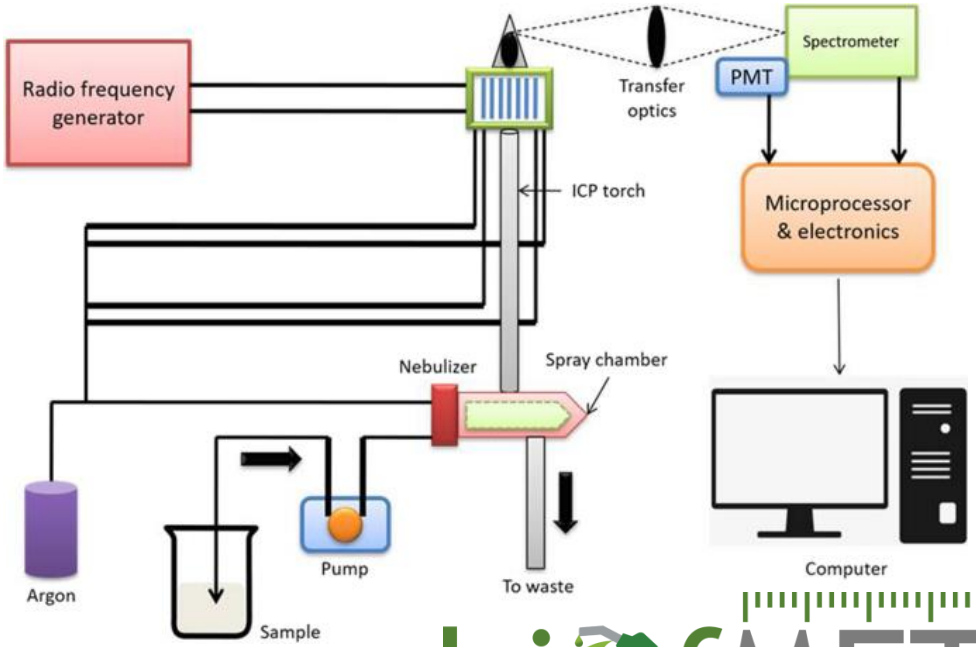
The sample solution gets converted to an aerosol which is quickly vaporized by ICP at a temperature of approximately 10 000 K. Elements are liberated as free atoms and possibly converted to ions. Both atoms and ions are promoted to the excited state. The photons emitted from these species are measured by optical spectrometry.

Analytical techniques and methods

- Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

Low detection limits ranging from parts per million (ppm) to parts per billion (ppb) are the main advantage of the ICP-OES technique.

The high temperature of the ICP allows excellent atomization and excitation of various species. This feature allows simultaneous analysis of more than 60 elements.

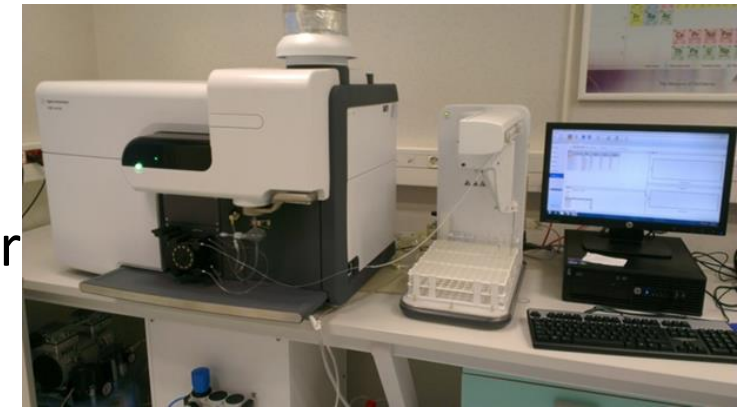


Analytical techniques and methods

- Microwave Plasma – Atomic Emission Spectroscopy (MWP-AES)

Very similar to ICP-OES. An optical instrument coupled with microwave nitrogen plasma ignited indirectly by means of temporary formed Argon plasma. The plasma temperature is around 6000°C and it emits high levels of microwave radiation.

Identification and quantification of the elements in plasma is done by optical detection of atomic and/or ionic emission spectral lines at selected wavelengths after atomization or ionization of sample. Detection covers near UV and visible part of the EM spectra enabling extensive elemental analysis.



Analytical techniques and methods

- Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

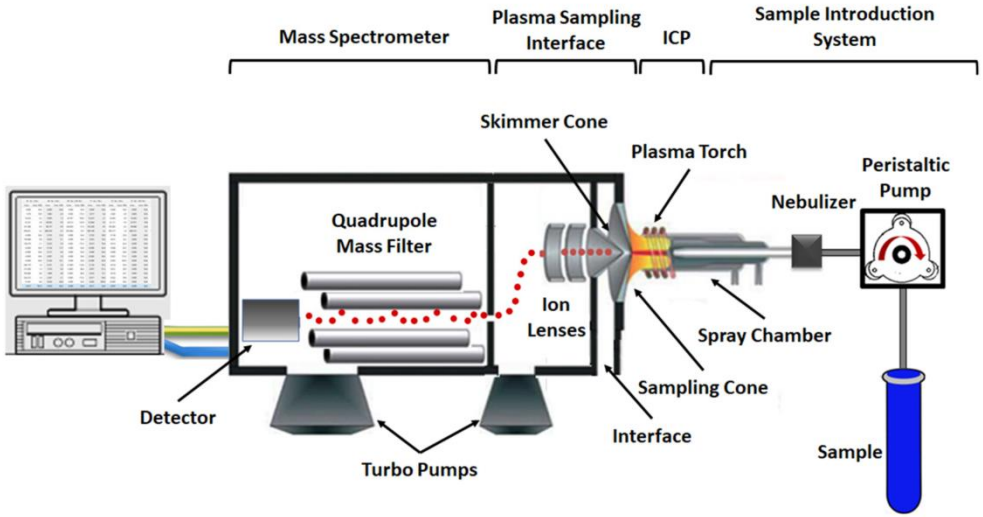
An ICP-MS combines a high-temperature inductively coupled plasma (ICP) source with a mass spectrometer (MS). Samples are introduced into an argon plasma in the form of aerosol drops. The aerosol is dried, the molecules dissociated and an electron removed from the components. The resulting singly-charged ions are filtered in the mass spectrometer. At a given time only one mass-to-charge ratio passes through the MS to the detector.

Analytical techniques and methods

- Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

The intensity of a resulting pulse in the detector is proportional to the concentration of the element.

One of the great advantages of the ICP-MS technique is the ability to measure the individual isotopes of each element. The other is extremely low detections limits of one part per trillion (ppt).



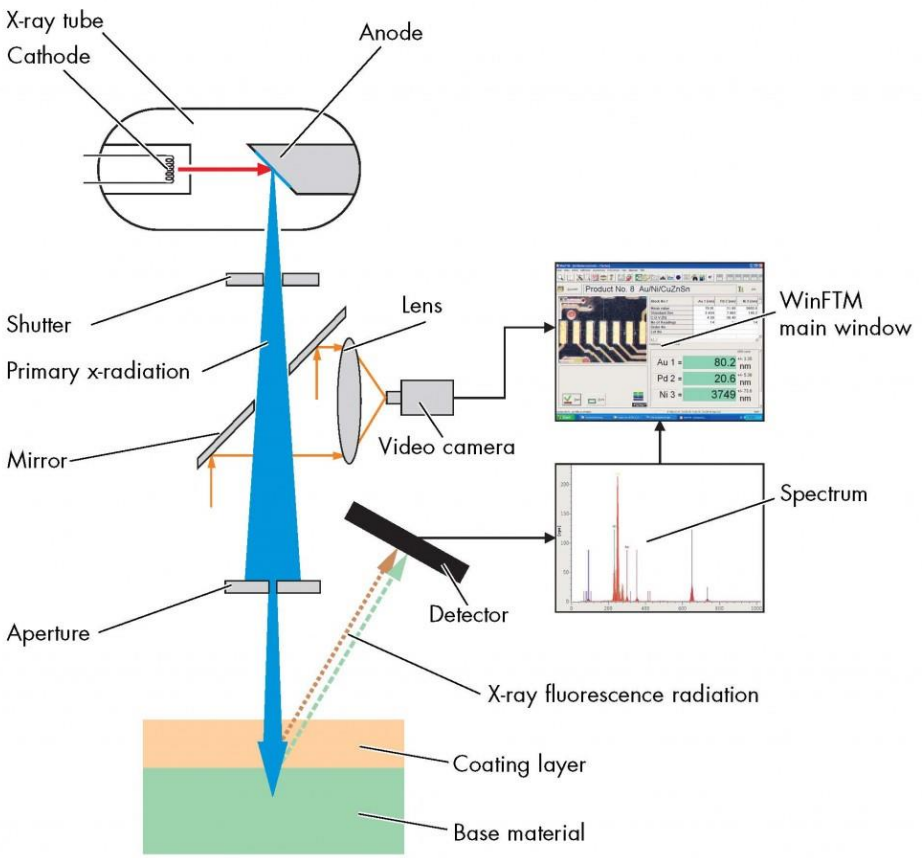
Analytical techniques applied

- X-ray fluorescence (XRF)

XRF is a non-destructive technique for the determination of elemental composition.

A primary X-ray source radiates the sample causing excitation. The sample consequentially emits fluorescent (or secondary) X-ray which is measured by the instrument.

Each element produces a specific set of fluorescent X-rays. This set is unique for a given element and is thus called “a fingerprint”.



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Analytical techniques applied

- Wavelength-dispersive X-ray fluorescence

WDXRF uses crystals to disperse the fluorescence spectrum into individual wavelengths of each element, providing high resolution and low background spectra for accurate determination of elemental concentrations.

The types of crystals used in WDXRF include minerals, metallic, organic and synthetic multi-layers.

Synthetic thin film multilayer crystals are increasing in popularity because they offer higher sensitivity and resolution for enhanced light element analysis.

Analytical techniques applied

- Wavelength-dispersive X-ray fluorescence

WDXRF systems are based on Bragg's law, which states that crystals will reflect x-rays of specific wavelengths and incident angles when the wavelengths of the scattered x-rays interfere constructively. While the sample position is fixed, the angles of the crystal and detector can be changed in compliance with Bragg's law so that a particular wavelength can be measured. Only x-rays that satisfy Bragg's law are reflected.

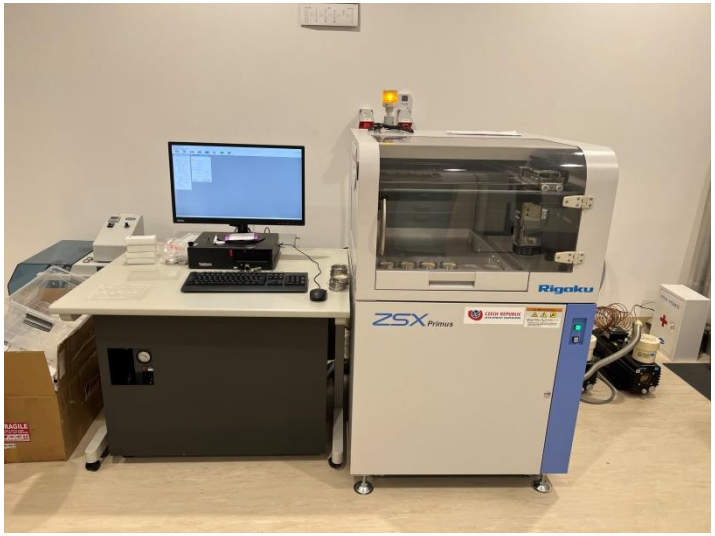
Collimators further improve resolution by providing different angular divergences to restrict unwanted secondary x-rays from reaching the detector. Larger collimators can be used when high intensity is favored over resolution.

Analytical techniques applied

- WD-XRF

Enables rapid quantitative determination of major and minor atomic elements, from beryllium (Be) through uranium (U), in a wide variety of sample types.

Enables non-destructive analysis of various samples.



Questions?

Thank you for your attention