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Techniques for analysis of major elements in solid biofuels ash and establishment of results' traceability

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Presentation content:

- Introduction to the topic
- Sample preparation
- Analytical techniques applied
- MWP-AES method
- WD-XRF method
- Preliminary results

Introduction to the topic

- During the combustion of 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 the ash is significant both from a quantitative and qualitative aspect.
- Qualitatively, 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.

Introduction to the topic

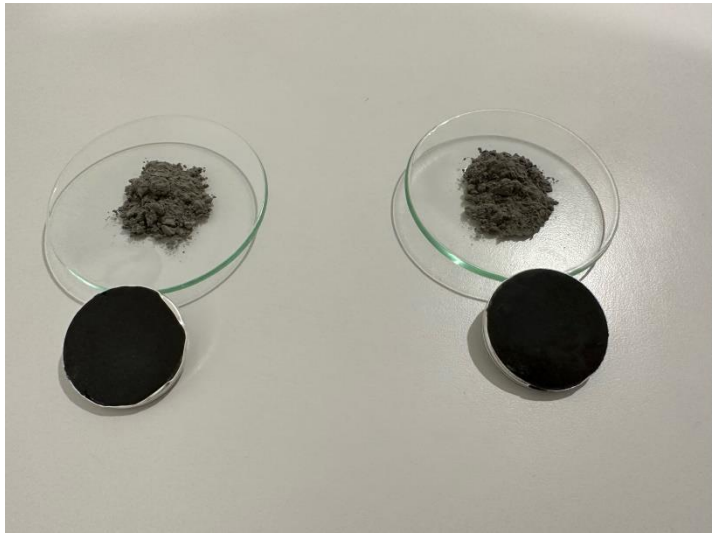
- Quantitatively, the presence of major elements indicates the efficiency of the combustion process, the origin and nature of the biomass, and refers to the pH potential of the waste/ash and serves as a basis for planning further remediation of the impact on the environment

Introduction to the topic

- Techniques and methods used to determine the composition of 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.

Introduction to the topic

- There are currently no reference materials for biomass ash on the market that can be used for the traceability of quantitative non-destructive methods of testing the composition of ash.
- This study aims to the development of calibrators for in-situ and lab X-ray composition analysis techniques of ash samples.



Sample preparation

- Sampling techniques and preparation of 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.
- Preweighed samples are usually mixed with fixating agens such as wax to enable sample preservation and vakuum reading.

Analytical techniques applied

- In this study, two analytical techniques were used:
- atomic emission spectrometry and
- wavelength-dispersive x-ray fluorescence

Analytical techniques applied

- Atomic emission spectrometry

MWP-AES (Microwave plasma – atomic emission spectrometer) – 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.

Analytical techniques applied

- Atomic emission spectrometry

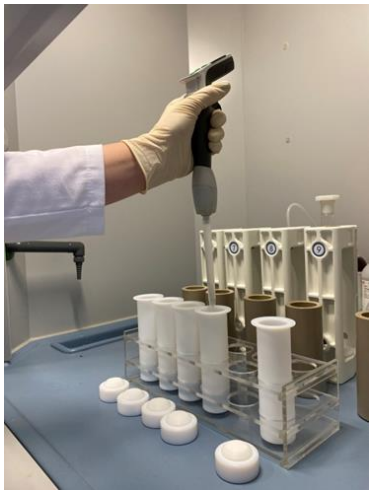
Identification and quantification of the elements in plasma is done by optical detection of atomic and/or ionic emission spectral lines at selected wavelengths after atomization or ionization of sample. Detection covers near UV and visible part of the EM spectra enabling extensive elemental analysis.

Analytical techniques applied

- Sample preparation

- Ash samples were prepared by controlled burning of a part of raw wood material in clean oven in order to obtain more concentrated samples composed of metallic oxides.
- Obtained ash samples were further processed by mechanical homogenization and subjected to digestion by means of microwave digestion technique using a mixture of acids.

Digestion procedure
0.25 g of sample + 8 mL HNO_3 + 1 mL $HClO_4$ + 1 mL HF Temperature/power: 1. 25 min: 1800 W and 230° 2. 15 min: 1800 W and 230°



Analytical techniques applied

- Sample preparation

Analytical techniques applied

- Instrumental parameters were optimized using standard solutions of known concentrations prepared by dilution of traceable standards.
- Instrumental parameters include the selection of appropriate analytical wave lines. Viewing position in plasma for each line and nebulizer pressure was optimized prior to the analysis using sample solutions (matrix effect included). Calibration fit selected was a weighted straight line with a squared correlation coefficient r^2 > 0,995, concentration intervals cover were optimizied to match concentration of elements in sample.

- For the purpose of quality control four types of checks were routinely used:
- calibration blank – nitric acid 2% in demineralized water to check for the presence of interferences (silicon) in media used for the preparation of standard solutions
- calibration control standard – standard solution prepared independently from the calibration standards read after the calibration curve has been formed (several times if needed) in order to check for the consistency and validity of readings
- sample blank – sample containing all chemicals used when conducting sample digestion in the absence of the sample to check for the presence of interferences (purity of chemicals, cleanliness of digestion vessels, etc.)
- spike QC sample and CRM – sample containing known amount of each element of interest digested in the same manner as samples used for recovery.

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.

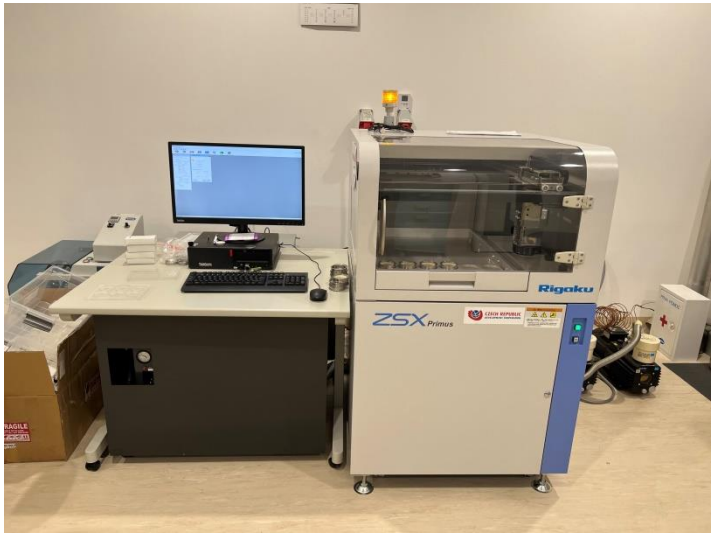
Collimators further improve resolution by providing different angular divergences to restrict unwanted secondary x-rays from reaching the detector. Larger collimators can be used when high intensity is favored over resolution.

Analytical techniques applied

- WD-XRF

Rigaku ZSX Primus delivers 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.



Preliminary results

TUBITAK-UME has prepared ash samples from two types of biomass - straw ash and wood chips ash. Each sample was submitted as 4 subsamples.

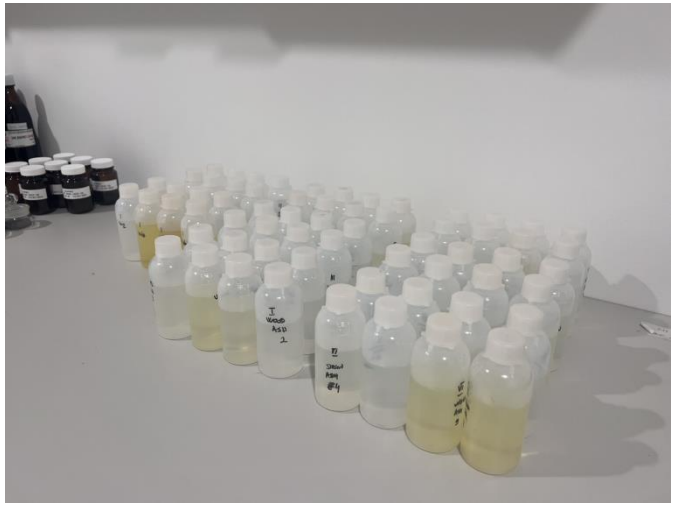
In cycles of controlled drying at 105˚C, the moisture content was determined for the purposes of concentration calculation to dry mass.

Preliminary results

Each sub-sample was analyzed in 8 replicates for 5 major elements: K, Mg, Ca, Na and Fe by means of previously presented MPAES method.

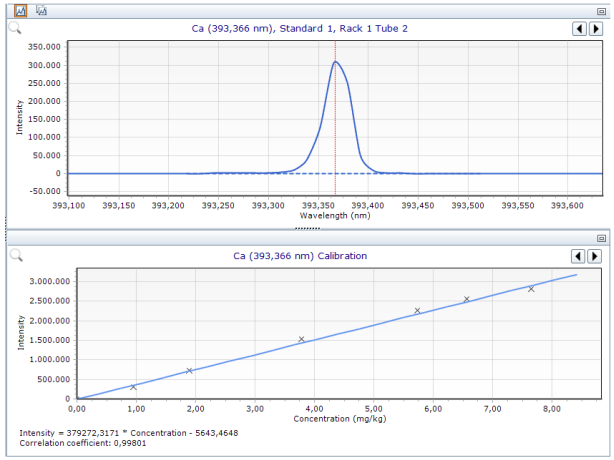
About 0.25 g of each replicate was accurately weighed and subjected to microwave digestion with a mixture of nitric and hydrocloric acids and hydrogen peroxide.

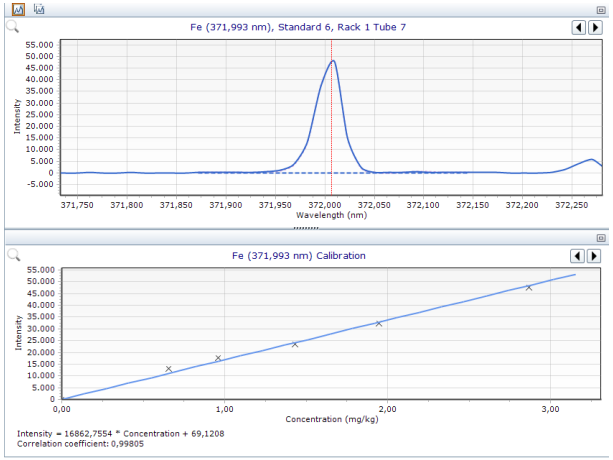
After digestion the liquid samples were quantitatively transferred in plastic vessels and prepared gravimetrically.

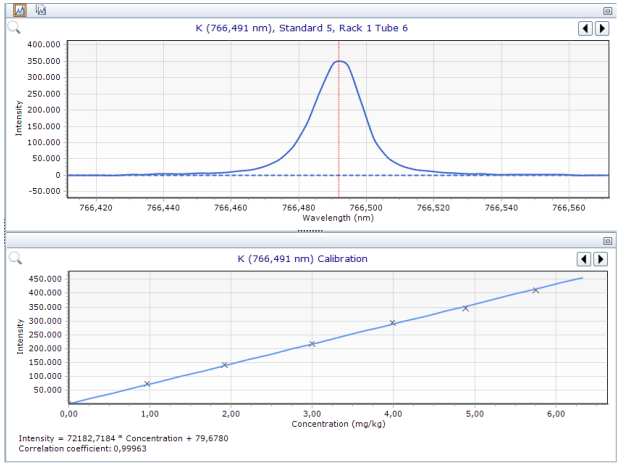


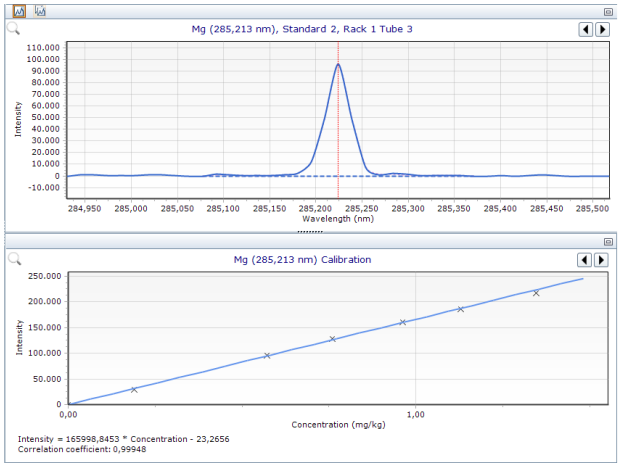
Preliminary results

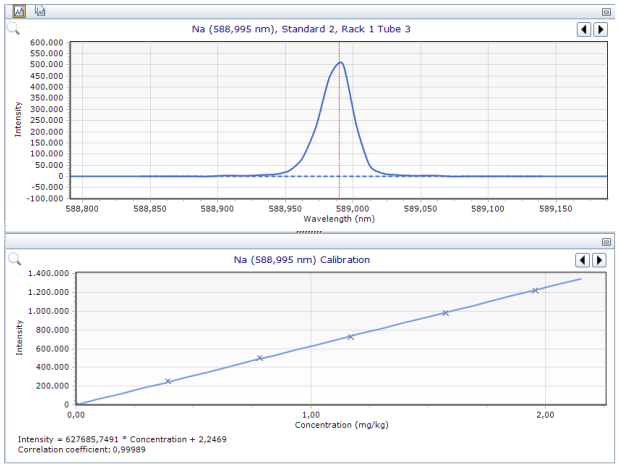
Sample calibration curves for selected elements:











Preliminary results

F and T test were conducted on replicates for each subsample for two types of ash – straw and wood chips:

Sample/ compound	Fe		Ca		K		Mg		Na	
	*Fexp**	*Texp***	*Fexp**	*Texp***	*Fexp**	*Texp***	*Fexp**	*Texp***	*Fexp**	*Texp***
straw	2.3517	1.7610	2.8701	2.0529	3.6707	1.0941	3.3705	1.5487	2.8393	0.5882
wood	2.5761	1.4462			1.7520	2.1284	2.6663	1.4460	1.9897	1.0655

Fe_straw	* Two tailed, α=0.05, 95% confidence df1=7 df2=7 (n-1), Ftab = **3.787** **Two tailed, α=0.05, 95% confidence df =14 (n1+n2-2), Ttab = **2.145**
Fe_wood	* Two tailed, α=0.05, 95% confidence df1=6 df2=6 (n-1), Ftab = **4.284** **Two tailed, α=0.05, 95% confidence df =12 (n1+n2-2), Ttab = **2.179**
Na_straw & wood	* Two tailed, α=0.05, 95% confidence df1=7 df2=7 (n-1), Ftab = **3.787** **Two tailed, α=0.05, 95% confidence df =14 (n1+n2-2), Ttab = **2.145**
Mg_straw	* Two tailed, α=0.05, 95% confidence df1=7 df2=7 (n-1), Ftab = **3.787** **Two tailed, α=0.05, 95% confidence df =14 (n1+n2-2), Ttab = **2.145**
Mg_wood	* Two tailed, α=0.05, 95% confidence df1=6 df2=7 (n-1), Ftab = **3.833** **Two tailed, α=0.05, 95% confidence df =13 (n1+n2-2), Ttab = **2.160**
K_straw	* Two tailed, α=0.05, 95% confidence df1=7 df2=7 (n-1), Ftab = **3.787** **Two tailed, α=0.05, 95% confidence df =14 (n1+n2-2), Ttab = **2.145**
K_wood	* Two tailed, α=0.05, 95% confidence df1=6 df2=7 (n-1), Ftab = **3.833** **Two tailed, α=0.05, 95% confidence df =12 (n1+n2-2), Ttab = **2.179**
Ca_straw	* Two tailed, α=0.05, 95% confidence df1=6 df2=7 (n-1), Ftab = **3.833** **Two tailed, α=0.05, 95% confidence df =11 (n1+n2-2), Ttab = **2.201**

Preliminary results

For the purpose of testing the X-ray method the following values were assigned as % concentrations of each element of interest:

Assigned values	% on dry basis
Fe_straw	0.36
Fe_wood	0.91
Na_straw	0.17
Na_wood	0.32
Mg_straw	2.49
Mg_wood	2.64
K_straw	17.01
K_wood	8.20
Ca_straw	4.62

Preliminary results

- The assigned values for each element were used to calibrate the WDXRF method.
- Several differenet method settings were used in the process of optimisation:

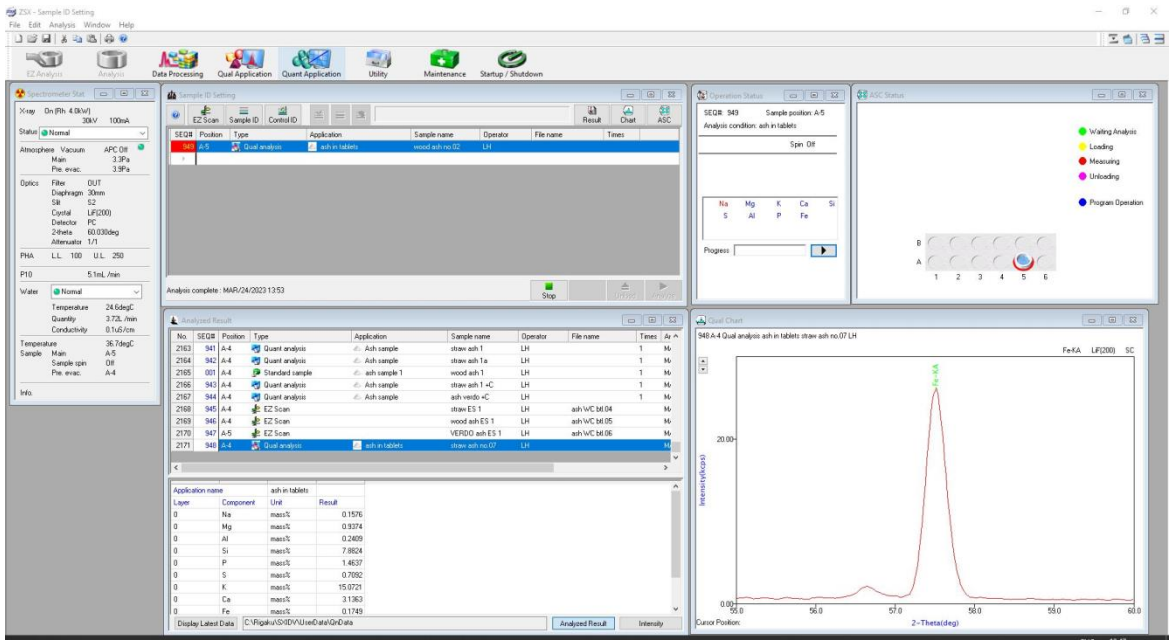
- EASY SCAN that gives opportunity to scan the sample for total composition
- EASY SCAN qualitative – enables scaning the selected elements
- Quantitative method

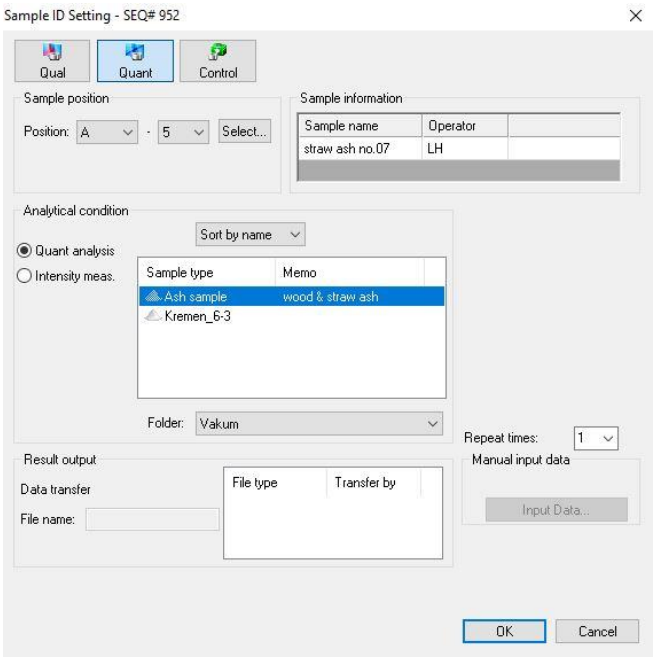
Preliminary results

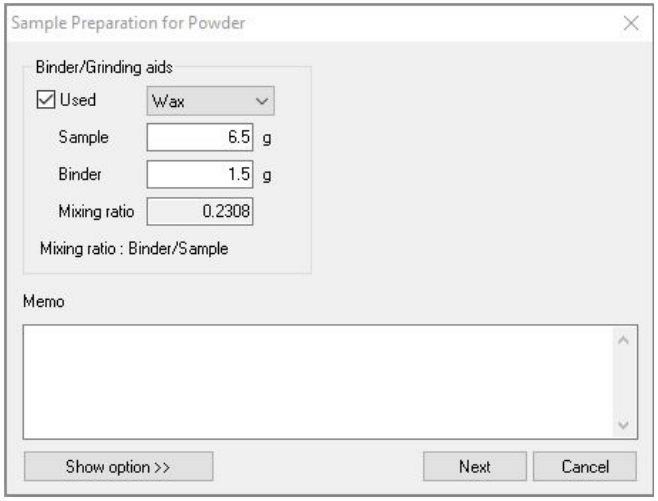
- The samples for WDXRF analysis were prepared as tablets in Al holders using wax as binding material for ash samples.
- These types of samples can be used multiple times.

Preliminary results

Instrumental setup:

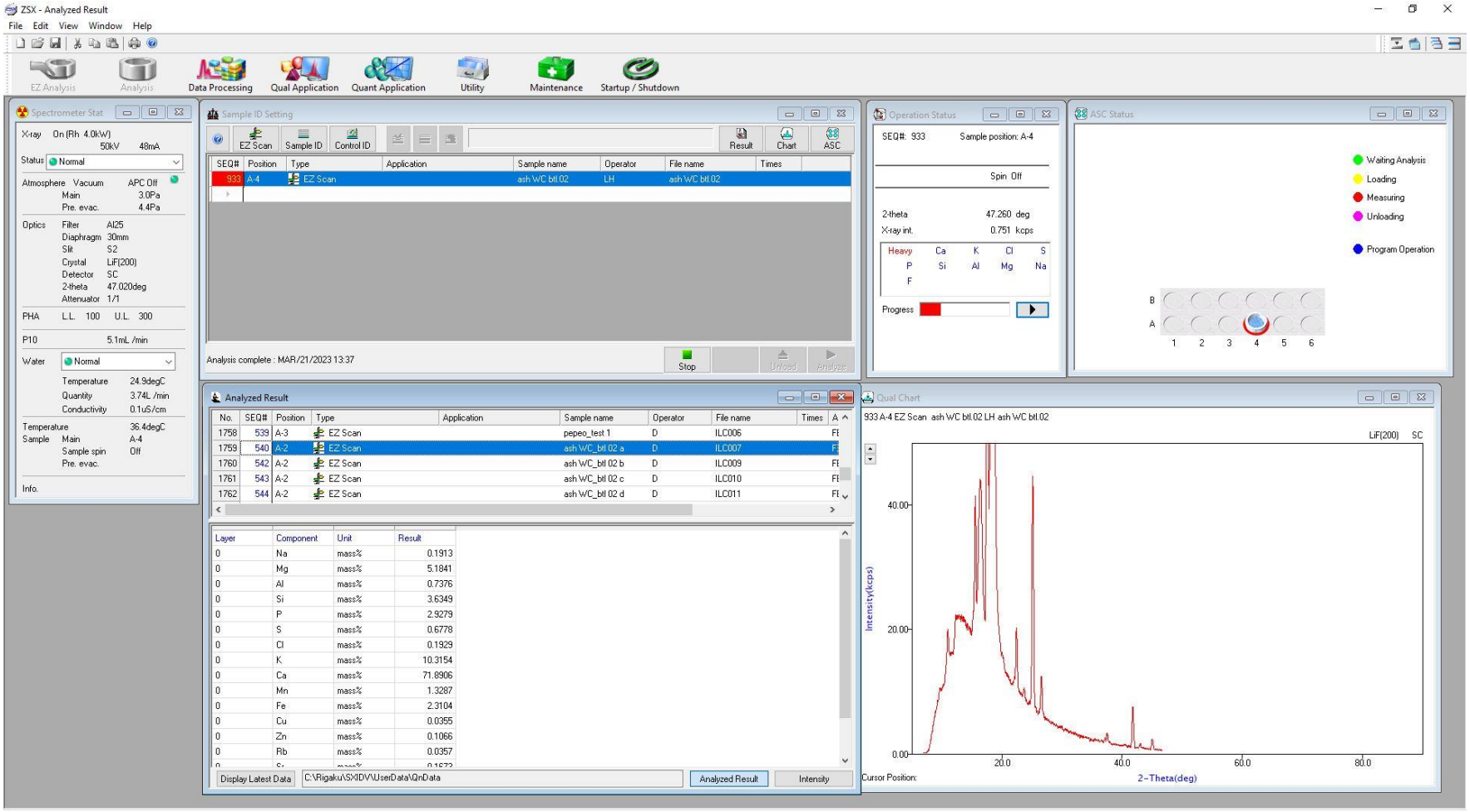






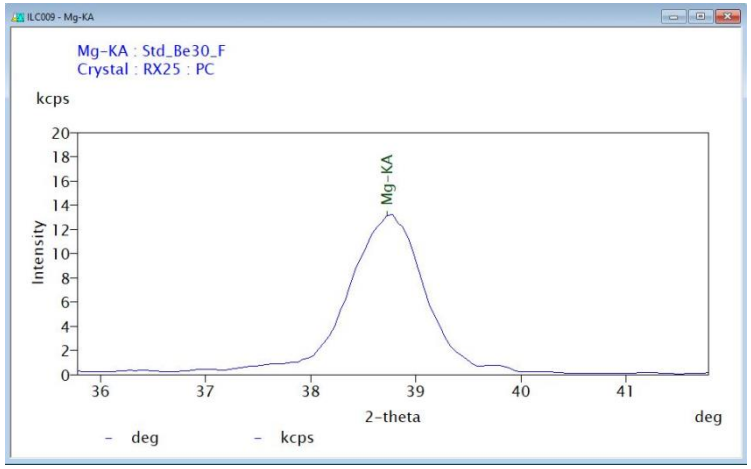
Preliminary results

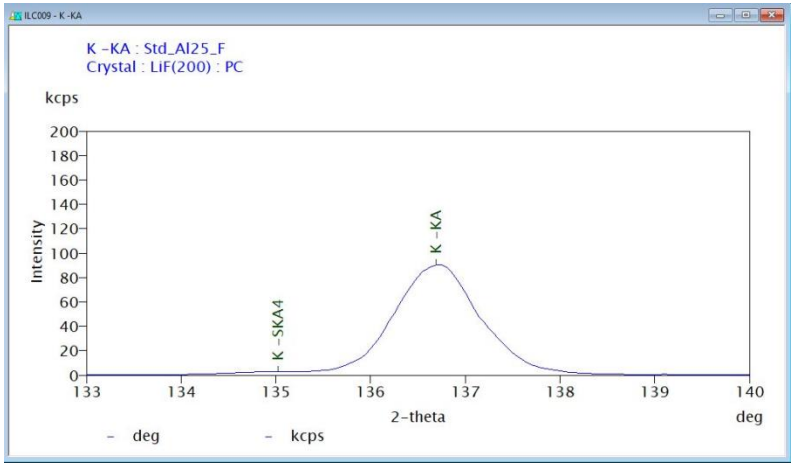
Instrumental setup:

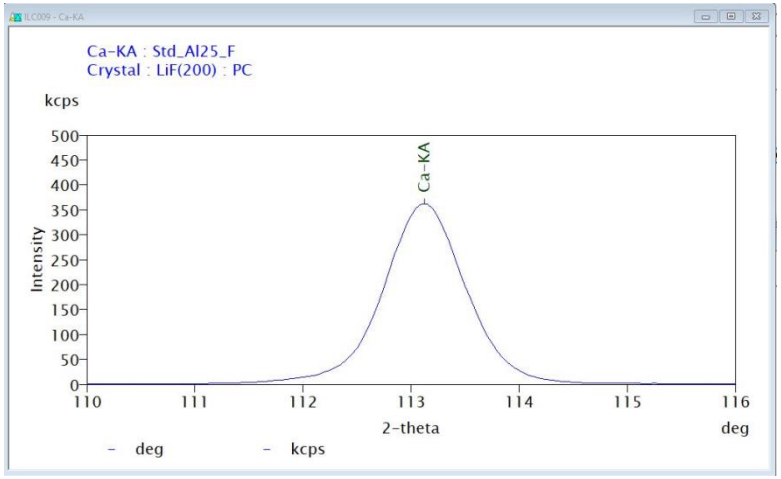


Preliminary results

Example :







Preliminary results

Easy scan method example results

SQX Calculation Result

Sample : straw ES 1
Application : F-U_Solid_N_000
Binder : S-BLEND

Sample type : Oxide Powder
Ratio : 0.2602
Sample film corr. :
File : ash WC btl.04

Date analyzed : MAR/24/2023 11:57
Balance : C
Matching library :
Impurity corr. :

No.	Component	Result	Unit	El. line	Intensity	Analyzing depth
1	Na	0.148	mass%	Na-KA	0.6586	0.0079
2	Mg	1.00	mass%	Mg-KA	14.1213	0.0124
3	Al	0.257	mass%	Al-KA	11.7941	0.0180
4	Si	8.28	mass%	Si-KA	428.0166	0.0256
5	P	1.54	mass%	P -KA	167.8904	0.0268
6	S	0.750	mass%	S -KA	74.4712	0.0341
7	Cl	1.09	mass%	Cl-KA	29.4381	0.0460
8	K	16.4	mass%	K -KA	618.4663	0.1005
9	Ca	3.33	mass%	Ca-KA	69.3785	0.0647
10	Ti	0.0281	mass%	Ti-KA	0.3017	0.1014
11	Cr	0.0048	mass%	Cr-KA	0.1541	0.1615
12	Mn	0.0849	mass%	Mn-KA	4.6077	0.2023
13	Fe	0.188	mass%	Fe-KA	16.4715	0.2527
14	Cu	0.0030	mass%	Cu-KA	0.6922	0.4670
15	Zn	0.0188	mass%	Zn-KA	5.9886	0.5693
16	Br	0.0023	mass%	Br-KA	1.8073	1.3974
17	Rb	0.0052	mass%	Rb-KA	5.3619	1.9070
18	Sr	0.0155	mass%	Sr-KA	17.9304	2.2029
19	Zr	0.0028	mass%	Zr-KA	7.8754	2.8805
20	Ba	0.0553	mass%	Ba-LA	0.1792	0.1001
21	C	66.8	mass%			

SQX Calculation Result

Sample : wood ash ES 1
Application : F-U_Solid_N_001
Binder : Wax

Sample type : Oxide Powder
Ratio : 0.2796
Sample film corr. :
File : ash WC btl.05

Date analyzed : MAR/24/2023 13:11
Balance : C
Matching library :
Impurity corr. :

No.	Component	Result	Unit	El. line	Intensity	Analyzing depth
1	Na	0.252	mass%	Na-KA	1.0756	0.0072
2	Mg	2.27	mass%	Mg-KA	30.2361	0.0113
3	Al	0.311	mass%	Al-KA	13.1718	0.0161
4	Si	1.54	mass%	Si-KA	75.8266	0.0232
5	P	1.13	mass%	P -KA	147.9779	0.0307
6	S	0.275	mass%	S -KA	33.1359	0.0395
7	Cl	0.125	mass%	Cl-KA	4.2459	0.0539
8	K	3.57	mass%	K -KA	190.7740	0.1202
9	Ca	20.7	mass%	Ca-KA	784.3003	0.1218
10	Ti	0.0762	mass%	Ti-KA	0.7312	0.0866
11	Mn	0.299	mass%	Mn-KA	14.4074	0.1723
12	Fe	0.554	mass%	Fe-KA	43.0090	0.2151
13	Cu	0.0092	mass%	Cu-KA	1.8607	0.3867
14	Zn	0.0237	mass%	Zn-KA	6.4988	0.4707
15	Rb	0.0077	mass%	Rb-KA	6.5956	1.5558
16	Sr	0.0385	mass%	Sr-KA	37.8558	1.7949
17	Ba	0.0675	mass%	Ba-KA	5.7967	14.1591
18	W	0.0072	mass%	W -LA	0.5784	0.4475
19	C	68.8	mass%			

Preliminary results

Method: EASY SCAN

TABLE 1

	K (%)	Mg (%)	Na (%)	Fe (%)
assigned vaule for wood ash	**8.20**	**2.64**	**0.32**	**0.91**
ash wood btl.02	3.57	2.27	0.252	0.554
assigned vaule for wood ash	**17.01**	**2.49**	**0.17**	**0.36**
ash straw btl.07	16.40	1.00	0.15	0.19
ash straw btl.04	15.97	1.00	0.34	0.18
verdo	12.88	1.19	0.22	0.39

for SQX Calculation:
Sample type: oxide powder
Component type: metal
Balance: C

EASY SCAN method - easy scan method with original instrument settings. After the analysis in the SQX Calculation option, the concentrations were recalculated with the following parameters:
Sample type: oxide powder
Component type: metal
Balance: C

Method: EASY SCAN as Qualitative method

TABLE 2

	K (%)	Mg (%)	Na (%)	Fe (%)
assigned vaule for wood ash	**8.20**	**2.64**	**0.32**	**0.91**
ash wood btl.02	3.55	2.18	0.27	0.55
assigned vaule for wood ash	**17.01**	**2.49**	**0.17**	**0.36**
ash straw btl.07	15.07	0.94	0.16	0.17

EASY SCAN as Qualitative method - modified easy scan analysis in which changes were made in the form of selection of elements of interest. Thus, Mg, Ca, K, Na, Fe, and C were chosen as balance.

Method: Quantitative method

TABLE 3

	K (%)	Mg (%)	Na (%)	Fe (%)
assigned vaule for wood ash	**8.20**	**2.64**	**0.32**	**0.91**
ash wood btl.02	11.99	4.17	0.33	0.83
assigned vaule for wood ash	**17.01**	**2.49**	**0.17**	**0.36**
ash straw btl.07	38.61	2.05	0.23	0.32
ash straw btl.04	39.36	2.07	0.12	0.33

Quantitative method - the method was set up using prepared tablets for samples ash wood btl.02 and ash straw btl.07 to which the values for the elements of interest were assigned by MPAES method.

Preliminary results

- SAMPLE PREPARATION

- Optimization of sample preparation is still being done. When preparing the tablets, we started with weights of 5.5 g of sample and 1.5 g of wax. After conducted analysis, we came to the conclusion that the tablet can be made with approx. 7 g of sample and 1 g of wax, and that as such it meets the required conditions in terms of stability and texture.
- Another segment of great interest during sample preparation refers to the pressure exerted on the sample and the container in order to obtain a tablet. Since wax is used as a binder, too much pressure causes the wax (and thus the sample) to squeeze out of the container.
- The first tablets were made under a pressure of 85 kN, while the last one was made under a pressure of 110 kN.
- During the conduction of these analyses, it turned out that the biggest problem is the proper preparation of the samples. During preparation, the first problem occurs when homogenizing the samples. The preparation is done in mortar, where mass loss and sample contamination are very likely.
- Another problem is the comminution of the homogenized sample. During homogenization, "sticking" of the sample occurs. Such a sample is very difficult to pulverize without an adequate mill or some auxiliary apparatus that would serve for that purpose. Such sample is very difficult to transfer into an aluminum cup, where a large amount of air remains in it, which, even after preparing the tablet, expands during heating in the element.

Preliminary results

- The plan for the next period includes:

- Preparation of (at least) two new tablets with a sample mass of 7 g and a wax mass of 1 g using a pressure of min. 130 kN.

- After preparing the tablets, set up a "new method" using the tablets, and analyze the control samples for verification.

- To conduct an experiment to determine how the results are affected by the implementation of the method with background optimization and adjustment of the PHA value. For this purpose, it is necessary to prepare at least three tablets of each sample (straw and wood) from which we would analyze a maximum of two elements per tablet (to reduce the possibility of tablet melting).

Questions?

Thank you for your attention