Trace and major elements analysis of alternative solid fuels by means of ICP-MS: comparison with AAS and XRF results [†]

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Abstract: This work offers a comprehensive examination of ICP-MS as a higher level analytical method compared to Atomic Absorption Spectrometry (AAS) and X-ray Fluorescence (XRF). Comparisons between ICP-MS average mean difference and AAS were made with the determination of the concentration of trace elements in the same solid alternative fuel samples, while comparisons between ICP-MS and XRF were made by the determination of the concentration of major elements in the same solid alternative fuel samples, resulting in the superiority of the method. The results of the Relative Mean Differences (RDMs) between ICP-MS (7.56%) and XRF (9.42%) regarding the concentration of major elements compared with the reference values in solid biofuel samples while the RDMs for the Solid Recovered Fuel samples were 8.9% for ICP-MS and 12.27% for the XRF. The same procedure was followed for the determination of concentration for trace elements with ICP-MS and AAS, leading to the results for solid biofuel samples (average % RMD_{ICP-MS} = 12.77 and RMD_{AAS} = 13.9) while for SRF samples (average % RMD_{ICP-MS} = 10.02 and RMD_{AAS} = 11.10) in relation to the reference values. While acknowledging that the initial cost and complexity of operation may deter some from adopting ICP-MS, the study asserts that the advantages of enhanced precision, sensitivity, and speed of analysis validate the investment. Hence, ICP-MS is an extremely important laboratory tool used in modern physics and chemistry and has a wide range of applications: biological materials, high purity reagents and metals, atomic nuclear materials, geological samples and food.

Keywords: ICP-MS, AAS, XRF, Biomass, SRF.

1. Introduction

Alternative solid fuels are solid substances, other than conventional coal or petroleum-based fuels, that can be used as an alternative energy source, often derived from renewable or waste sources. Alternative fuels can be organic or inorganic components in solid, liquid or high viscosity forms. Typical materials used as alternative fuels range from tyres, wood, plastics, used oils, paints, resins, adhesives, solvents, sludges, animal waste and other organic waste, resulting in a variety of matrices and concentration ranges in samples of "unknown" nature [1]. As global energy demands rise, so does the urgency to transition away from conventional fossil fuels. Solid alternative fuels represent a category of energy sources, and can help alleviate this dependence. Due to the huge variety of materials that exist in the category of solid fuels, the determination the elemental competition of chemical compounds and their composites is crucial. This can be achieved with ele-

mental analysis. Understanding the composition of solid fuels is an essential as information is provided on the efficiency, environmental impact of each fuel [2,3]. 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). The Inductively Coupled Plasma Mass Spectrometry (ICP-MS) lies among the most dominant techniques for rapid spectroscopic multi-element analysis as a result of a set of attributes such as low detection limits (often parts per billion or trillion), a wide linear dynamic range and high precision. It was made a comparison between ICP-MS and AAS with the determination of the concentration of trace elements in the same solid alternative fuel samples, while comparison between ICP-MS and XRF is made by the determination of the concentration of major elements in the same Solid Recovered Fuels.

The results showed that the analysis using ICP-MS were more accurate and precise compared to AAS and XRF. Furthermore, it was showed that the ICP-MS analysis was contacted in a shorter time frame in relation to AAS. The aim of this study was to demonstrate the superiority of measurements using this specific instrument.

2. Materials and Methods

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. 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). This technique is also relatively free from interferences which, if do exist, can be easily removed [4].

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. There are two basic sample cells for atomization used in AAS: the flame burner and the electrothermal heating. The amount of the absorbed light is dependent on element concentration in the sample. If there is a sufficient amount of the element of interest in the sample, the flame cell (FAAS) can be used. This is a rapid technique and very simple to use. Its sensitivity is typically in the parts per million (ppm) range. For trace analysis, electrothermal heating (ETAAS), also known as graphite furnace (GFAAS), can be used instead of a flame burner to increase the sensitivity. ETAAS requires more skill and is less rapid, but has lower detection limits and is more suitable for low concentrations of the element in the sample [5].

X-ray fluorescence analysis (XRF) is one of the most universal techniques to deal with such a variety of samples. It is capable of handling solids, liquids, pastes, loose powders or granules with minimal or no sample preparation. Depending on the accuracy and concentration limits needed to adhere to the environmental regulations or kiln equilibrium, it is possible to measure the samples using XRF without the need for sample preparation or dilution techniques. This technique is also used when controlling the transfer of some elements into clinker. XRF also covers a wide range of elements (from boron to uranium in solids and from sodium to uranium in liquids) and can detect their presence down to sub ppm levels depending on the analysis time and instrument conditions. There are two types of XRF instruments: Wavelength Dispersive XRF (WDXFR) and Energy Dispersive XRF (EDXRF). While WDXRF instruments are used in central laboratories for more accurate and precise measurements across the periodic table, EDXRF instruments provide more flexible sample handling and quicker screening for medium to heavy elements [6].

2.1. Process Description

In order to investigate the analyses technique of our newly acquired ICP-MS equipment, tests of elemental analysis were performed in reference materials of alternative solid fuels. A palm kernel sample was used as solid biofuel and a Municipal Solid Wastes (MSW) one as Solid Recovered Fuel (SRF), both being interlaboratory test samples. Along with the ICP-MS tests, WDXRF and GFAAS tests were performed in order to compare results in terms of accuracy and sensitivity. Major elements concentration in samples ash was determined by ICP/MS and WDXRF, while trace elements content in the fuels was measured by ICP-MS and GFAAS.

Both analysis samples were prepared and analysed according standard methods. ISO 14780 [7] was employed for the solid biofuel preparation, ISO/TS 16996 & EN ISO 16967 [8,9] for the major elements determination in its ash and EN ISO 16968 [10] for the trace elements in the fuel. The respective standard methods for the SRF sample are EN 15443, EN ISO 22940 & EN 15410 and EN 15411 [11-14]. Both samples were comminuted to fine powder of less than 0.5 mm nominal top size. WDXRF determination was made in fused bed specimens, while fuels digestion prior to ICP and AAS measurements was implemented with the same procedure for both instruments, utilising a microwave furnace.

A more detailed description regarding the preparation of this kind of samples as mentioned above is: on a sample table, the reduction in size of initial samples is carried out with the help of quartering spatulas. Subsequently, the total moisture procedure is followed. Finally, the sample is quartered again, and the analysis sample is taken after grinding and sieving. The mass of the test sample must be at least 300 g. Then, for the calculation of moisture, the total weight loss during drying is considered in relation to the total distributed weight of the sample. The result constitutes a measurement. The sample is placed in an oven which operates at a temperature of 105 ± 2°C. It is heated until the mass of the sample remains constant. The mass of the sample is considered stable when, with new heating in the oven at a temperature of 105 ± 2°C for up to 60 minutes, the change in mass (new loss) does not exceed 0.2% of the original mass. The total drying time required depends on the size of the sample grains, the rate at which air circulates in the oven, and the thickness of the layer. The maximum total drying time of a sample should not exceed 24 hours to avoid the loss of volatile materials. The drying time for different materials is determined based on experience from similar experiments.

After this preparation regarding the WDXRF analysis, eight grams of the sample with a particle size <200μm are mixed with two grams of wax (cereox bm-0002-1 binder for XRF) to create a pellet. The mixed sample is then placed in a manual press (vaneox 15/25T press) and pressed at 20 tons for 60 seconds. This pellet is ready for the analysis.

For the AAS and ICP-MS analysis the samples have to undergo through the procedure of dissolution as presented: the required mass of the sample is mixed with H_2O_2 (30%), HNO_3 (65%) and HF (40%). This mixture is sealed in a Teflon vessel and heated with a temperature program in a microwave oven. This is followed by neutralization of HF with H_3BO_3. The neutralization is again carried out in a known temperature program in the microwave oven. In order to avoid the contamination of the total suspended solids in AAS and ICP-MS instruments, filtration and centrifugation are crucial. The final solution is ready for analysis.

For each analytical instrument, the Relative Mean Difference (RMD) between mean measured values and reported ones of each element is calculated and reported as percentage of RMD:

$$\%RMD_{DEV} = |\, Xi_{DEV} - Xi_{ref} \,| \,/\, Xi_{ref} \qquad (1)$$

where i stands for each measured element

       DEV stands for each utilised analytical instrument (ICP-MS, GFAAS, WDXRF)

       Xi_{DEV} is the measured concentration of the i element using the DEV equipment

       Xi_{ref} is the reference (reported) value of the i element

The average of all percentages of relative mean differences are then presented for each utilised analytical instrument.

3. Results

In Table 1 are shown the reported (reference) values (%) of six major elements in the ash of the reference materials (biofuel and SRF). The results for these elements of the samples ash measured with the instrument of WDXRF and of ICP-MS are also shown. Furthermore, in this Table the relative mean differences (%) for both techniques are also given. Finally, a comparison between the average RMDs for both measurements is shown.

Table 1. Major elements in the ash of reference materials (% w/w)

Element	Reference values	WDXRF results	ICP-MS results	WDXRF % RMD	ICP-MS % RMD
Solid biofuel RM (palm kernel)					
Na	0.21	0.26	0.23	23.81	9.52
Mg	6.96	7.02	6.51	0.86	6.47
Al	1.05	1.12	0.98	6.67	6.67
K	15.96	15.69	15.24	1.69	4.51
Ca	8.24	8.53	8.28	3.52	0.49
Fe	1.75	2.10	2.06	20.00	17.71
average %RMD	-	-	-	9.42	7.56
Solid recovered fuel RM (MSW)					
Na	1.46	1.46	1.59	0	8.90
Mg	1.54	1.7	1.34	10.39	12.99
Al	9.08	9.63	7.71	6.06	15.09
K	0.57	0.69	0.60	21.05	5.26
Ca	21.43	25.14	20.41	17.31	4.76
Fe	2.66	3.16	2.83	18.80	6.39
average %RMD	-	-	-	12.27	8.90

In Table 2 are shown the reported values (ppm) for seven trace elements for both fuels. The next two columns present the values of the same elements measured with GFAAS and ICP-MS instruments. The two RMDs of each technique are also presented in the last two columns. A comparison between the average RMDs of the measurements is also given.

Table 2. Trace elements in reference material fuels (ppm)

Element	Reference values	GFAAS results	ICP-MS results	GFAAS % RMD	ICP-MS % RMD
Solid biofuel RM (palm kernel)					
Cd	0.026	0.021	0.02	19.23	10.54
Cr	7.84	9.70	6.67	23.72	14.92
Cu	23.25	27.95	23.51	20.22	1.14
Mn	236	234.25	268	0.74	13.56
Ni	4.39	4.11	4.78	6.38	8.86
Pb	0.61	0.74	0.73	21.31	19.67
Zn	41.66	39.30	50.29	5.66	20.70
average %RMD	-	-	-	13.90	12.77
Solid recovered fuel RM (MSW)					
Cd	1.35	1.53	1.30	13.33	3.87
Cr	78.1	78.10	66.39	0.00	14.99
Cu	133.1	145	120.58	8.94	9.41
Mn	45.3	55	54.16	21.41	19.56
Ni	16.64	19.10	18.15	14.78	9.06
Pb	35.37	29.86	32.07	15.58	9.34
Zn	264.7	275	275	3.67	3.89

average %RMD	-	-	-	11.10	10.02

In Table 3 are shown results (ppm) for additional trace elements, in both reference materials, measured by ICP-MS in a single run which are not measured in GFAAS.

Table 3. Additional elements measured in the ICP-MS single run

Element	ICP-MS (ppm)
Solid biofuel RM	
Ti	1081
V	1.92
Co	4.35
As	2.71
Sb	94.7
Ag	1.42
Ba	46.5
Ce	1.49
Tl	0.01
Solid recovered fuel RM	
Ti	14.5
V	0.68
Co	0.14
As	0.72
Ag	0.01
Ba	3.23
Ce	0.20
Tl	0.01

4. Discussion and Conclusions

Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Atomic Absorption Spectroscopy (AAS), and X-ray Fluorescence (XRF) are analytical techniques employed in the analysis of elements in various matrices, including solid alternative fuels.

XRF provides rapid, simultaneous multi-element determinations and is non-destructive It's especially useful for major elemental analysis. The accuracy of this technique can be excellent, especially with calibration standards that closely match the matrix of the sample. XRF is less sensitive than ICP-MS for many trace elements. Surface homogeneity of the sample and particle size can affect the results.

AAS measures one element at a time, making it a bit slower than ICP-MS for multi-element analysis. Flame AAS is commonly used for major and minor elements, while graphite furnace AAS can detect trace levels. This technique offers good accuracy and precision for many elements, especially at the concentration levels typically found in alternative fuels. It's limited to the analysis of metals and some metalloids. Also, AAS may have matrix interferences, and certain elements may require special lamps or conditions for analysis.

ICP-MS provides rapid multi-element determinations with the capability to detect elements at extremely low concentrations (in the ppb or even ppt range). This technique offers high accuracy and precision, especially for trace elements. Isotopic analysis is also possible. Some potential interferences may arise from overlapping isotopic masses. Matrix interferences, double-ion species, or polyatomic species can sometimes affect accuracy. With collision/reaction cells, many of these interferences can be mitigated. elements.

4.1. Results Discussion

As presented in the tables 1 and 2, the results of the elemental analysis of biofuels and SRFs using the techniques that mentioned above shows a satisfactory accuracy compared to the reference values. The results of the detection of major and trace elements using WDXRF and GFAAS are expected to be close to the reported values since these techniques are applied constantly in the laboratory. The use of the newly acquired instrument (ICP-MS) even though it has not been extensively tested compared to the other two instruments showed that its results have better proximity to the reference values. Comparing each element individually, it is observed that in most elements (major and especially trace) the measured values are closer to the reference values compared to XRF and AAS. The high sensitivity of the instrument, combined with its complexity, requires further specialization of the analysts, the highest purity in reagents and also laboratory conditions (clean room) in which the measurement is conducted. When these challenges are achieved this instrument can provide greater accuracy in each measurement. Furthermore, the high productivity of the instrument allows for a large volume of samples to be processed. Observing the results, we conclude that ICP-MS will become a very powerful analytical tool for characterizing various solid fuels in a region transitioning from lignite to new more environmentally fuels.

In conclusion, the optimal technique often depends on the specific requirements of the analysis (e.g., elements of interest, required detection limits, available sample preparation facilities, and budget). In many labs working on solid alternative fuels, a combination of these techniques might be employed to leverage the strengths of each.

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