Challenge
Accurately determining major and minor elemental compositions in solid biofuels to ensure compliance with ISO 16967 and 16968 standards.

Solution
A rapid ICP-MS methodology using PlasmaQuant MS that combines ISO 16967 and ISO 16968, enabling efficient analysis of major and minor elements while reducing costs and increasing throughput.

Intended audience
Biofuel producers, environmental labs, and researchers in chemicals and materials analysis.

Determination of major and minor elements in solid biofuels according to ISO 16967 and 16968 using ICP-MS

Introduction

The increasing global demand for renewable energy has positioned solid biofuels—such as wood, straw, and agricultural residues—as key contributors to sustainable energy production. These materials, whether natural or partially processed, are widely used in power generation and heating applications. However, their elemental composition plays a critical role in determining combustion efficiency, environmental impact, and overall fuel quality.

Accurate elemental analysis is essential for stakeholders across the bioenergy value chain, including fuel producers, power plant operators, equipment manufacturers, and regulatory bodies. Major elements like calcium, silicon, potassium, sodium, and iron influence ash formation, slagging, fouling, and corrosion in combustion systems. Meanwhile, minor and trace elements—such as arsenic, cadmium, chromium, mercury, and lead—can pose serious environmental and health risks when released during combustion. Regulatory frameworks increasingly impose strict limits on these elements, especially in residential and small-scale applications.

While traditional techniques such as AAS, ED-XRF, and ICP-OES are commonly used for elemental analysis, they often fall short in providing simultaneous, multi-element detection in accordance with ISO 16967 and ISO 16968 standards [1,2]. This gap highlights the need for more efficient, standardized, and reliable analytical solutions.

This application note introduces the PlasmaQuant MS from Analytik Jena as a powerful tool for the simultaneous determination of major and minor elements in solid biofuels. The method integrates both ISO 16967 and ISO 16968 into a single workflow, significantly improving throughput, reducing operational costs, and ensuring compliance with international standards. Validation is performed using

certified reference materials (CRMs) such as BCR 482, NIST 1575a, and NIST 2790, ensuring analytical accuracy and traceability.

The application note is designed for analytical laboratories engaged in solid biofuels characterization—such as quality control labs, research institutions, regulatory bodies, and commercial testing facilities—and offers practical guidance that is accessible even to those with limited experience in biomass analysis. While it emphasizes ISO-compliant methods and certified reference materials (CRMs), the workflows and principles outlined are broadly applicable to the elemental analysis of diverse biomass materials and adaptable to various laboratory environments. By supporting the reliable implementation of standardized methods, the note contributes to quality assurance, regulatory compliance, and the advancement of sustainable practices in the expanding solid biofuels sector.

Materials and methods

Instrument settings

Sample digestion was performed using a closed-vessel microwave-assisted digestion system (SpeedWave XPERT) with PM60 digestion vessels, ensuring complete decomposition of solid biofuel matrices under controlled temperature and pressure conditions. This method minimizes contamination and volatilization losses, particularly for volatile or trace elements.

Elemental analysis was conducted using the PlasmaQuant MS, equipped with integrated collision/reaction cell (iCRC) technology to effectively eliminate polyatomic interferences—especially those affecting first-row transition metals—using helium and hydrogen as collision/reaction gases, respectively. This ensures high accuracy and low detection limits, even in complex biomass matrices.

The Inductively Coupled Mass Spectrometer (ICP-MS) system was coupled with a CETAC ASX-560 autosampler and a CETAC ASXPress Plus injection valve, enabling high-throughput, automated sample introduction. An inert PFA sample introduction kit was used, featuring a Scott-type spray chamber with Peltier cooling and a PFA nebulizer, providing excellent chemical resistance and signal stability. Although H_3BO_3 was used to complex residual HF from digestion, the inert kit was selected not only for HF resistance but also due to the need for accurate silicon quantification, a major element in biomass ash.

All analyses were performed in a routine laboratory environment, not under cleanroom conditions, demonstrating the method's robustness and suitability for standard operational settings.

In total, 49 elements were determined in the solid biofuel samples. This includes the 9 major, and 13 minor elements specified in ISO 16967 and ISO 16968, as well as a broader suite of elements such as rare earth elements (REEs) and other trace metals. This extended scope provides a more comprehensive elemental profile, supporting advanced research, regulatory compliance, and quality control.

Instrument operating parameters, including plasma conditions, gas flows, and iCRC settings, are summarized in Table 1.

Table 1: Instrument settings – PlasmaQuant MS.

Parameter	Specification
Plasma gas flow	9.0 L/min
Auxiliary gas flow	1.50 L/min
Sheath gas flow	0.00 L/min
Nebulizer gas flow	0.95 L/min
Sampling depth	5.5 mm
Plasma RF power	1.40 kW
Rump rate	20 rpm – black/black PVC pump tubing (<1mL/min)

Parameter	Specification	
Stabilization delay	10 s	
iCRC gas setting	He 120 mL/min	^{31}P, ^{44}Ca, ^{49}Ti, ^{89}Y, ^{114}Cd, and REE
	He 150 mL/min	^{27}Al, ^{45}Sc, ^{51}V, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, and ^{66}Zn
	No Gas	^{23}Na, ^{25}Mg, ^{39}K, ^{85}Rb, ^{86}Sr, ^{98}Mo, ^{107}Ag, ^{118}Sn, ^{121}Sb, ^{133}Cs, ^{137}Ba, ^{182}W, ^{202}Hg, ^{205}Tl, $^{206+207+208}$Pb, ^{232}Th, and ^{238}U
	H_2 100 mL/min	^{52}Cr, ^{57}Fe, and ^{75}As
	H_2 200 mL/min + boost (4V)	^{28}Si and ^{78}Se
Dwell time	10 ms (No gas), 30 ms (He), and 50 ms (H_2)	
Scan per replicate	20 (peak hopping, 1pt/peak)	
No. of replicates	3	
Sample uptake time	0 s – ASXPress Plus sample introduction system used	
Internal standards	^{6}Li, ^{103}Rh, ^{115}In, ^{193}Ir, and ^{209}Bi at 25 µg/L, interpolate correction	

Samples and reagents

For the digestion of solid biofuel CRMs, the following high-purity reagents were used to ensure trace-level accuracy and minimize contamination:

- Deionized water (>18.2 MΩ·cm, Millipore Milli-Q)
- Nitric acid (HNO_3, 69%, sub-boiled, Analytik Jena GmbH+Co. KG)
- Hydrogen peroxide (H_2O_2, 30%, for trace analysis, Supelco Suprapur®)
- Hydrofluoric acid (HF, 48%, ROTIPURAN® Supra quality)
- Boric acid (H_3BO_3, 99.9999%, Supelco Suprapur®)

These reagents were selected for their ultra-trace purity, suitable for multi-elemental analysis by ICP-MS, especially when targeting both major and trace elements in complex biomass matrices.

Sample preparation

For method validation, three CRMs of solid biofuels were prepared in quadruplicate:

- NIST 1575a and NIST 2790 (National Institute of Standards & Technology, USA)
- BCR 482 (Joint Research Centre, Geel, Belgium)

Each CRM was weighed (0.25 g, dried and sieved) and transferred into pre-cleaned PM60 digestion vessels of the SpeedWave XPERT microwave-assisted digestion system. A two-step digestion protocol was applied, as detailed in Table 2, to ensure complete matrix decomposition and compatibility with ICP-MS analysis.

Table 2: Digestion methods parameters used by SpeedWave XPERT microwave digestion system.

Parameter	Specification
Sample amount	0.25 g dried and sieved
H_2O	Few drops
H_2O_2	2 mL
HNO_3	5 mL
HF	0.5 mL
Au	500 µg/L
Vessel	PM60
Temp. / ramp / hold	200°C / 15 min / 20 min at 1200 W
Cooling / Time	Room / 30 min
Boric acid	10 mL of 4% (w/v)
Temp. / ramp / hold	170°C / 5 min / 10 min at 1000 W
Cooling / time	Room / 30 min
Final volume	Fill up to 50 mL with DI H_2O
ICP-MS prior dilution	1:10, 1:5 and 1:2 with DI H_2O

Following digestion, samples were diluted to a final volume of 50 mL polypropylene (PP) tubes (Sarstedt, Germany) with deionized water. Prior to ICP-MS analysis, the digests were further diluted 1:2, 1:5 1:10 with deionized water. The final acid concentrations after digestion and dilution were approximately:

- 1% (v/v) HNO_3
- 0.2% (v/v) HF
- 0.008% (w/v) H_3BO_3

The boric acid addition effectively neutralized residual HF, protecting the instrument and enabling accurate quantification of elements such as silicon. The total dissolved solids (TDS) in the final diluted solutions ranged from 0.07% to 0.13%, well within the PlasmaQuant MS's routine handling capacity (up to 0.3% TDS) without requiring aerosol dilution.

To assess recovery and matrix effects, each CRM digest was also spiked post-digestion with a multi-element solution. Final spike concentrations ranged from 0.5 to 2500 ppb, depending on the expected concentration range of each target element.

Calibration

Standard solutions for external calibration were matrix-matched using 1% (v/v) HNO_3 by appropriate dilution in 50 mL polypropylene (PP) tubes (Sarstedt, Germany). There was no need to add HF to the standards because any HF remaining after the digestion would be neutralized by H_3BO_3. Single element solutions (CertiPUR® 1000 mg/L, in 2-3% HNO_3) for As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V, Zn, Se, Sr, Sn, Ag, Tl, Ba, Cs, Rb, Th, W, and U, and single element solution (CertiPUR® 10 000 mg/L, in 2-3% HNO_3) for Al, Ca, Fe, K, Mg, Na, P, Si, and Ti; for REE, a Rare Earth element mix for ICP was used (TraceCERT®, 16 elements, 50 mg/L in 2-3% HNO_3) were used to prepare seven-point concentration curve as follow:

- 0.05 up to 5 µg/L for As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Sb, V, Se, Sn, Ag, Tl, Cs, Th, W, U, and REE
- 0.25 up to 25 µg/L for Rb;
- 0.05 up to 50 µg/L for Ti, Pb, and Sr ;
- 1 up to 100 µg/L for Na, Zn, and Ba;
- 2 up to 200 µg/L for Fe;
- 5 up to 500 µg/L for Mn;
- 10 up to 1000 µg/L for Al, Mg, P, and Si;
- 50 up to 5000 µg/L for Ca and K

Excellent linearity was achieved for major, minor, and trace elements, as indicated by the four representative calibration curves shown in Figure 1. In all cases, the R value exceeded the method requirement and was greater than 0.9996.

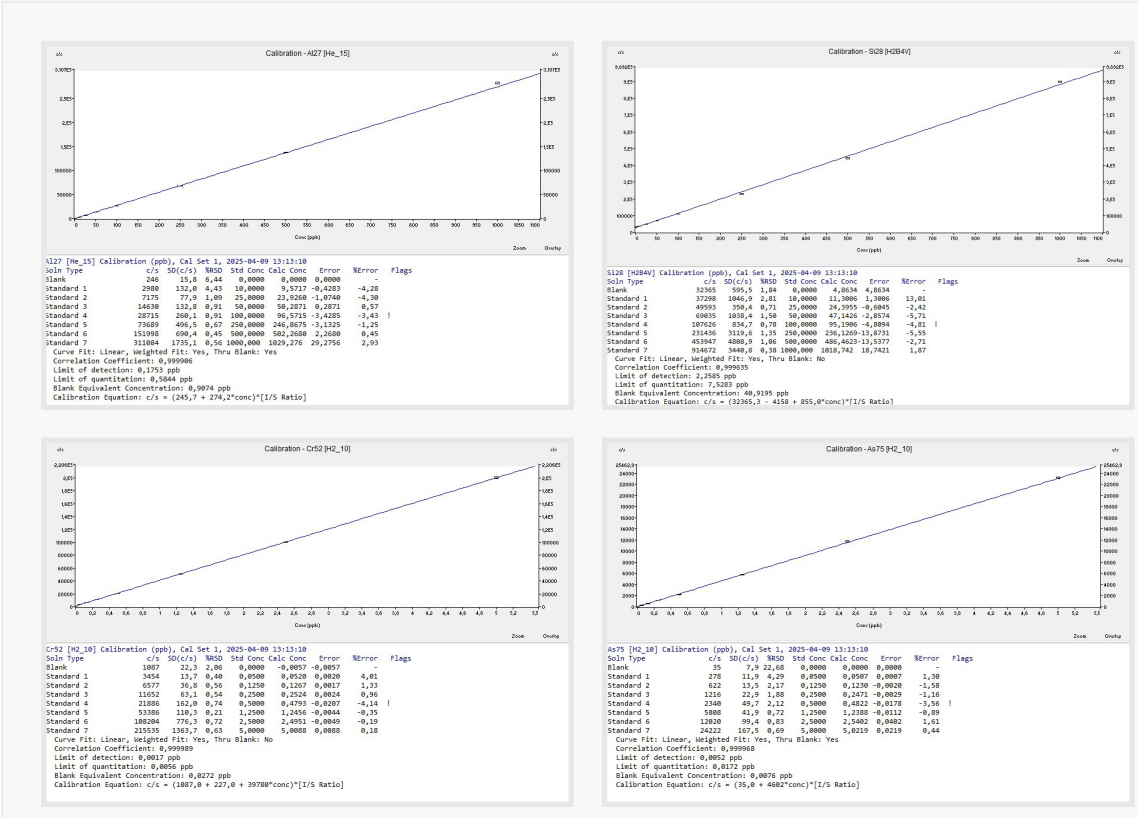

Figure 1: Calibration graphs for some investigated major, minor, and trace elements.

Evaluation

Addressing polyatomic interferences in ICP-MS analysis of solid biofuels

Accurate quantification of elements in complex matrices such as solid biofuels using ICP-MS is often hindered by polyatomic interferences. These interferences occur when matrix components, plasma gases, or digestion reagents combine to form molecular ions with the same mass-to-charge ratio (m/z) as the analyte of interest.

In this study, three CRMs were used to represent a broad range of biomass and environmental matrices:

- BCR 482 – Lichen
- NIST 1575a – Pine Needles
- NIST 2790 – Hardwood Biomass

These CRMs contain significant levels of major elements such as Ca, K, Na, Mg, Al, Fe, P, Cl, and S, which are known to form problematic polyatomic species. Examples of common interferences include:

- $ArCl^+$ → interferes with As^+ (m/z 75) and Se^+ (m/z 78)
- CaO^+, $CaOH^+$, FeO^+ → interfere with Fe, Mn, and Cr
- PO^+, NO^+, CO^+ → affect P, Si, and V
- Ar_2^+, Cl_2^+ → contribute to Se interferences
- NaO^+, KO^+, AlO^+ → impact alkali and alkaline earth metals

Mitigation strategy using iCRC and boost technology

To overcome these interferences, the PlasmaQuant MS was operated using a multi-mode gas strategy via its integrated Collision/Reaction Cell (iCRC). The following gas modes were applied:

- Helium (He) mode: Reduces kinetic energy of larger polyatomic ions through collision-induced dissociation. Effective for oxide and hydroxide interferences (e.g., CaO^+, FeO^+).
- Hydrogen (H_2) mode: Reacts chemically with interfering species such as $ArCl^+$ and Ar_2^+. Particularly useful for As, Se, and Cr.
- Boosted H_2 mode (H_2B4V): Combines maximum hydrogen flow with Boost technology—a patented enhancement applied to the skimmer cone—to improve sensitivity for elements like Si and Se, which are prone to severe interferences.
- No gas (NG) mode: Used for elements with minimal interference or where direct measurement is optimal.

The iCRC is uniquely integrated into the skimmer cone, positioned before the ion optics. This design enables signal recovery and retuning after collision/reaction processes, ensuring high sensitivity and precision—an exclusive feature of the PlasmaQuant MS.

Measurement protocol and data acquisition

To ensure optimal performance, five gas mode conditions were applied during each measurement cycle:

- Helium at 120 mL/min
- Helium at 150 mL/min
- No gas (standard mode)
- Hydrogen at 100 mL/min
- Hydrogen at 200 mL/min + Boost (4 V)

Each condition was paired with specific isotopes, and all five modes were executed sequentially within a single measurement, with 10-second switching intervals between modes.

For data acquisition:

- Three replicate averages were calculated from 20 scans each
- A final average and standard deviation were computed
- Total analysis time per sample (including rinsing and uptake): ~5 minutes
- 49 elements and 5 internal standards were measured per sample

Results and Discussion

Digested blank solutions and method detection limits

To account for potential contamination from reagents and vessels, digested blank solutions were prepared using the same procedure as the sample digestions. This included identical volumes of the acid mixture and application of the same microwave-assisted digestion program used for the solid biofuel CRM samples.

The concentrations of Mg, Al, Si, P, Ca, Fe, and Zn detected in the procedural blanks were subtracted from the corresponding values measured in the CRM solutions. These elements were specifically corrected due to their presence in the blank at levels that could significantly impact the accuracy of the results—primarily due to trace contamination from the high-purity reagents.

Method Detection Limits (MDLs) were determined following a full calibration sequence. The MDLs, presented in Table 3, were calculated as ten times the standard deviation of the procedural blank measurements (n = 14), treated as samples throughout the analytical sequence. The resulting values were then multiplied by the dilution factor (1000) to reflect the final sample concentrations.

Table 3: MDL of metals in solid biofuels samples obtained by PQMS after microwave-assisted digestion of samples in closed-vessels.

Element	MDL (mg/kg)	Element	MDL (mg/kg)	Element	MDL (mg/kg)
Na	0.002	As	0.00005	Eu	0.00005
Mg	0.001	Se	0.00005	Gd	0.00005
Al	0.004	Rb	0.0006	Tb	0.00005
Si	0.02	Sr	0.0005	Dy	0.00005
P	0.04	Y	0.00005	Ho	0.00005
K	0.06	Mo	0.00005	Er	0.00005
Ca	0.08	Ag	0.00005	Tm	0.00005
Sc	0.00005	Cd	0.00005	Yb	0.00005
Ti	0.005	Sn	0.00005	Lu	0.00005
V	0.00005	Sb	0.00005	W	0.0008
Cr	0.00005	Cs	0.00005	Hg	0.00005
Mn	0.007	Ba	0.003	Tl	0.00005
Fe	0.002	La	0.00005	Pb	0.0005
Co	0.00005	Ce	0.00005	Th	0.00005
Ni	0.0005	Pr	0.00005	U	0.00005
Cu	0.00005	Nd	0.00005		
Zn	0.001	Sm	0.00005		

Spike recoveries, CRM recoveries, and Precision

Tables 4a, 4b, and 4c present the results for 49 major, minor, and trace elements determined in the three Solid Biofuels CRMs analyzed. These tables include spike recoveries, mean recovery concentrations compared to certified values, and precision data. The certificates of analysis provide both certified and reference values for various elements. To gain a comprehensive understanding of the matrix components, additional information of the remained quantification elements has also been included.

Three different spike levels (e.g., same concentrations as Calibration Standard 4, 5 and 6) were added to the microwave-digested samples, based on the concentration levels observed in the original materials. As expected, some spikes did not align with the concentration ranges of specific elements, so only the appropriate spike concentrations that corresponded to the expected levels are presented.

The overall spike recoveries ranged from 81% to 127%, with a mean recovery of 105 ± 7% (n = 147). For the certified values, the recovery of the four replicate digestions of the three Solid Biofuels CRMs ranged from 88% to 105%, with relative standard deviations (RSDs) of less than 10% for the majority of results. However, some minor issues were observed, primarily related to the very low concentrations of Se (NIST 2790) and Hg (NIST 1575a).

Table 4a: Metals and semi-metals concentration, recoveries, precision, Z-score, and spike recoveries achieved in the BCR 482 – Lichen after microwave-assisted digestion (n=4). Legend: * Non-certified values

Isotope	Certified value ± U (mg/kg)	Measured Conc. (mg/kg)	RSD	Recovery (%)	Z-score	Spike Recovery (%)
Al	1103 ± 24	1121	9.1	102	0.8	107
Cr	4.12 ± 0.15	3.8	5.5	93	-1.9	102
Ni	2.47 ± 0.07	2.5	5.2	103	1.0	122
Cu	7.03 ± 0.19	7.0	4.3	100	0.0	109
Zn	100.6 ± 2.2	95	2.5	95	-2.4	107
As	0.85 ± 0.07	0.78	2.5	92	-0.9	100
Cd	0.56 ± 0.02	0.52	4.3	94	-1.8	104
Hg	0.48 ± 0.02	0.48	7.4	100	0.0	98
Pb	40.9 ± 1.4	39	3.6	94	-1.7	119
Additional Information						
Na*	-	4.7	17.3	-	-	105
Mg*	-	485	11.1	-	-	97
Si*	-	2124	7.7	-	-	109
P*	-	567	6.9	-	-	103
K*	-	3811	11.3	-	-	102
Ca*	-	1944	8.6	-	-	99
Sc*	-	0.19	7.7	-	-	102
Ti*	-	65	7.8	-	-	113
V*	-	3.2	8.6	-	-	97
Mn*	-	30	9.2	-	-	116
Fe*	-	716	8.0	-	-	81
Co*	-	0.31	8.5	-	-	114
Se*	-	0.46	13.9	-	-	97
Rb*	-	8.7	7.3	-	-	106
Sr*	-	9.3	7.4	-	-	105
Y*	-	0.49	7.7	-	-	110
Mo*	-	0.41	6.5	-	-	114
Ag*	-	0.061	7.6	-	-	104
Sn*	-	1.6	7.7	-	-	112
Sb*	-	0.32	8.2	-	-	114
Cs*	-	0.23	8.4	-	-	108
Ba*	-	13	10.2	-	-	107

Isotope	Certified value ± U (mg/kg)	Measured Conc. (mg/kg)	RSD	Recovery (%)	Z-score	Spike Recovery (%)
La*	-	0.75	9.5	-	-	106
Ce*	-	1.5	9.0	-	-	112
Pr*	-	0.17	8.0	-	-	106
Nd*	-	0.65	8.7	-	-	109
Sm*	-	0.13	7.6	-	-	107
Eu*	-	0.026	15.1	-	-	108
Gd*	-	0.11	8.3	-	-	112
Tb*	-	0.016	12.7	-	-	109
Dy*	-	0.094	6.6	-	-	115
Ho*	-	0.023	12.0	-	-	110
Er*	-	0.050	12.9	-	-	112
Tm*	-	0.007	20.9	-	-	113
Yb*	-	0.042	11.7	-	-	113
Lu*	-	0.006	20.8	-	-	113
W*	-	0.23	11.0	-	-	102
Tl*	-	0.050	9.8	-	-	108
Th*	-	0.21	9.4	-	-	127
U*	-	0.059	9.2	-	-	112

Table 4b: Metals and semi-metals concentration, recoveries, precision, Z-score, and spike recoveries achieved in the NIST 1575a – Pine Needles after microwave-assisted digestion (n=4). Legend: * Non-certified values

Isotope	Certified value ± U (mg/kg)	Measured Conc. (mg/kg)	RSD	Recovery (%)	Z-score	Spike Recovery (%)
Na*	63 ± 1*	62	10.3	99	-0.7	102
Mg*	1060 ± 170*	1030	6.8	97	-0.2	99
Al	580 ± 30	522	9.2	90	-1.9	102
P	1070 ± 80	963	6.4	90	-1.3	105
K	4170 ± 70	4110	7.8	99	-0.9	110
Ca	2500 ± 100	2249	6.4	90	-2.5	109
Sc*	0.0101 ± 0.0003*	0.010	47.0	98	-0.7	102
Mn*	488 ± 12*	471	7.0	97	-1.4	110
Fe	46 ± 2	42	4.3	92	-1.8	99
Co*	0.061 ± 0.002*	0.058	1.7	95	-1.4	105
Ni*	1.47 ± 0.1*	1.5	8.1	99	-0.1	103
Cu	2.8 ± 0.2	2.6	4,2	93	-1.0	104

Isotope	Certified value ± U (mg/kg)	Measured Conc. (mg/kg)	RSD	Recovery (%)	Z-score	Spike Recovery (%)
Zn	38 ± 2	34	4.1	90	-1.9	97
As*	0.039 ± 0.002*	0.039	9.1	100	0.0	102
Se*	0.099 ± 0.004*	0.105	6.9	106	1.5	92
Rb	16.5 ± 0.9	16	7.5	95	-1.0	92
Cd	0.233 ± 0.004	0.23	7.5	98	-0.9	103
Cs*	0.283 ± 0.009*	0.27	4.0	94	-1.8	100
Ba	6.0 ± 0.2	6.0	11.6	100	0.0	97
Hg	0.0399 ± 0.0007	0.04	31.2	101	0.4	100
Pb*	0.167 ± 0.015*	0.15	7.9	92	-0.9	100
Additional Information						
Si*	-	2012	7.7	-	-	96
Ti*	-	6.5	14.3	-	-	100
V*	-	0.11	20.7	-	-	99
Cr*		0.35	13.9			107
Sr*	-	5.8	8.9	-	-	98
Y*	-	0.033	14.3	-	-	114
Mo*	-	0.019	33.2	-	-	102
Ag*	-	0.016	41.0	-	-	99
Sn*	-	0.11	20.5	-	-	97
Sb*	-	0.011	22.2	-	-	104
La*	-	0.043	16.0	-	-	105
Ce*	-	0.09	15.4	-	-	108
Pr*	-	0.010	13.4	-	-	108
Nd*	-	0.040	18.4	-	-	106
Sm*	-	0.007	25.8	-	-	105
Eu*	-	0.0009	40.7	-	-	106
Gd*	-	0.004	70.1	-	-	113
Tb*	-	<0.00005	-	-	-	115
Dy*	-	0.006	14.1	-	-	118
Ho*	-	0.004	21.0	-	-	115
Er*	-	0.003	23.5	-	-	117
Tm*	-	0.0001	-	-	-	115
Yb*	-	0.002	28.8	-	-	116
Lu*	-	<0.00005	-	-	-	119

Isotope	Certified value ± U (mg/kg)	Measured Conc. (mg/kg)	RSD	Recovery (%)	Z-score	Spike Recovery (%)
W*	-	0.013	94.4	-	-	99
Tl*	-	0.017	11.8	-	-	102
Th*	-	0.013	17.2	-	-	112
U*	-	0.004	16.9	-	-	103

Table 4c: Metals and semi-metals concentration, recoveries, precision, Z-score, and spike recoveries achieved in the NIST 2790 – Hardwood Biomass after microwave-assisted digestion (n=4). Legend: * Non-certified values

Isotope	Certified value ± U (mg/kg)	Measured Conc. (mg/kg)	RSD	Recovery (%)	Z-score	Spike Recovery (%)
Na	26 ± 5.3	26	13.7	102	0.1	101
Mg	189 ± 11	194	10.0	102	0.4	100
Al*	92.06 ± 0.89*	92	8.3	100	0.2	98
K	1040 ± 130	1045	4.9	100	0.0	109
Sc*	0.0111 ± 0.0004*	0.0102	5.5	92	-2.3	100
V	0.243 ± 0.011	0.24	4.3	97	-0.6	97
Cr	1.59 ± 0.15	1.55	4.0	97	-0.3	101
Mn	52.4 ± 1.9	53	2.2	100	0.1	108
Fe	82.9 ± 5.5	77	10.5	93	-1.1	104
Co	0.098 ± 0.012	0.100	5.1	102	0.2	104
Cu*	1.545 ± 0.03*	1.59	4.9	103	1.4	112
Zn	9.26 ± 0.9	8.3	6.2	90	-1.0	104
As	0.0335 ± 0.0089	0.033	9.7	99	0.0	105
Se	0.0102 ± 0.0023	0.010	45.3	97	-0.1	97
Rb*	3.11 ± 0.099*	2.9	4.7	94	-1.9	111
Sb*	0.0397 ± 0.0016*	0.040	5.8	101	0.2	108
Cs	0.0199 ± 0.0010	0.019	7.8	96	-0.7	102
La*	0.643 ± 0.063*	0.58	13.4	89	-1.1	103
Ce*	0.5523 ± 0.0098*	0.52	14.4	95	-3.1	103
Sm*	0.0507 ± 0.0052*	0.042	6.2	84	-1.6	103
W*	0.225 ± 0.029*	0.26	4.8	116	1.2	107
Hg	0.01323 ± 0.0002	0.014	17.8	102	1.4	103
Th*	0.0146 ± 0.0005*	0.014	11.6	94	-1.7	120
Additional Information						
Si*	-	268	9.2	-	-	92
P*	-	43	20.0	-	-	101

Isotope	Certified value ± U (mg/kg)	Measured Conc. (mg/kg)	RSD	Recovery (%)	Z-score	Spike Recovery (%)
Ca*	-	1377	10.3	-	-	103
Ti*	-	12	9.9	-	-	101
Ni*	-	1.05	5.5	-	-	106
Sr*	-	11.79	7.7	-	-	98
Y*	-	0.15	6.6	-	-	105
Mo*	-	0.70	7.1	-	-	109
Ag*	-	0.0090	9.7	-	-	100
Cd*	-	0.039	13.6	-	-	103
Sn*	-	0.21	15.7	-	-	104
Ba*	-	21	7.7	-	-	101
Pr*	-	0.076	10.4	-	-	102
Nd*	-	0.26	11.8	-	-	104
Eu*	-	0.0094	9.1	-	-	103
Gd*	-	0.039	11.1	-	-	104
Tb*	-	0.0045	13.6	-	-	104
Dy*	-	0.027	6.3	-	-	104
Ho*	-	0.009	14.7	-	-	103
Er*	-	0.011	10.1	-	-	105
Tm*	-	0.0009	38.0	-	-	104
Yb*	-	0.008	17.1	-	-	106
Lu*	-	0.0007	40.3	-	-	107
Tl*	-	0.0020	18.3	-	-	105
Th*	-	0.99	7.8	-	-	106
U*	-	0.0044	15.5	-	-	109

Internal Standards stability

A total of 70 solutions were analyzed over a 6-hour period to assess internal standard (ISTD) signal stability. The internal standards used in this study were ^{6}Li, ^{103}Rh, ^{115}In, ^{193}Ir, and ^{209}Bi. As shown in Figure 2, all ISTD recoveries remained within ±30%, with the majority falling within ±20%. This indicates excellent matrix tolerance of the PlasmaQuant MS system, achieved without the need for aerosol dilution. The ISTD signals exhibited minimal variation between samples throughout the analytical sequence, and no significant matrix deposition was observed on the instrument interface over the course of the run.

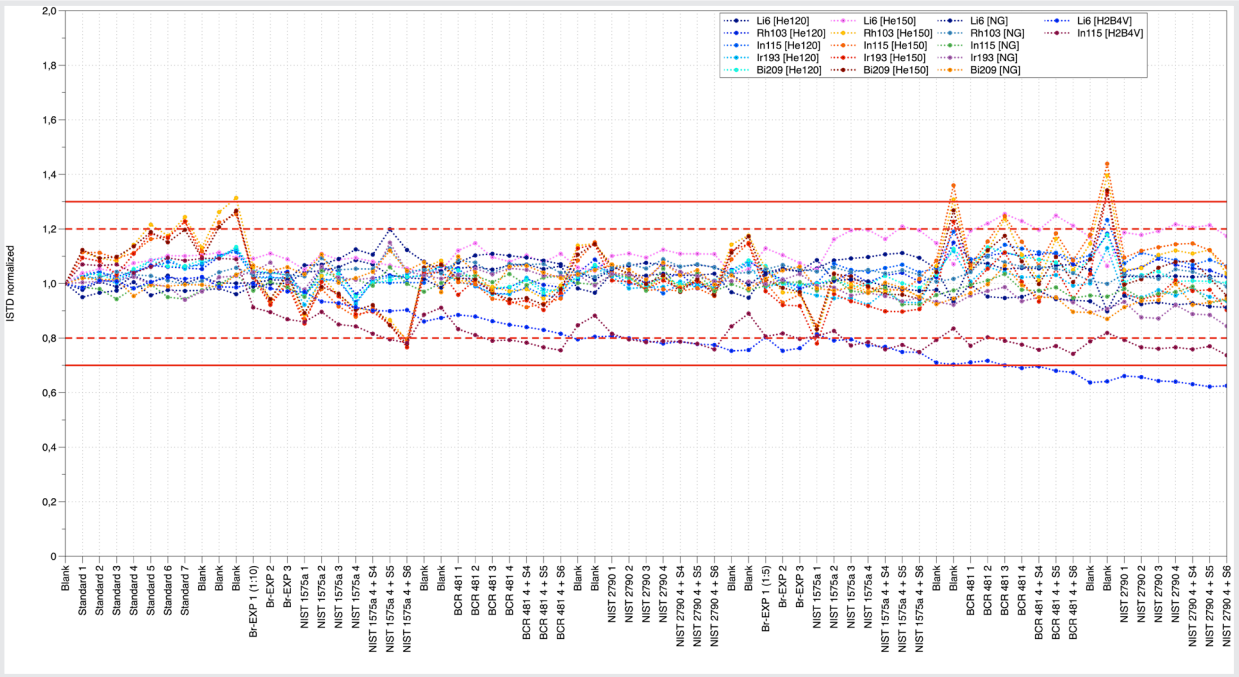

Figure 2: Internal standards stability during the analysis of a total of 70 solutions measured over a 6h run. ISTD for all samples have been normalized to the calibration blank.

Summary

According to ISO 16968, minor elements present in solid biofuels can pose environmental concerns, as certain energy crops are known to accumulate potentially harmful elements such as cadmium. In this study, the method demonstrated good accuracy in quantifying major, minor, and trace elements in solid biofuel certified reference materials (CRMs), as evidenced by the CRM recoveries obtained using a single 10-fold dilution. This streamlined approach not only simplifies the analytical workflow but also plays a critical role in enhancing the calorific and heating values of biomass and identifying minor elements that may impact fuel quality—addressing key factors in sustainable and efficient bioenergy production.

The optimized microwave digestion sample preparation method, utilizing closed vessels, proved effective for digesting solid biofuel matrices and ensuring accurate measurement of a wide range of elements.

This method allows for the measurement of both major and minor elements and provides an extended analysis of 49 elements in a single analytical run, offering a comprehensive understanding of the solid biofuel composition. This saves time, reduces running costs, and improves throughput compared to the separate procedures outlined in ISO 16967 and ISO 16968, which only require the measurement of major and minor elements.

Carefully controlled liquid dilution enabled accurate and precise elemental analysis without compromising MDLs, thanks to the high sensitivity of the PQMS. This approach allowed for reliable quantification of trace elements at the parts-per-trillion (ppt) level—such as Hg, a key environmental concern—without requiring additional techniques like Cold Vapor, which are often recommended

Figure 3: PlasmaQuant MS

in CRM certificates. While the standard PQMS model is capable of achieving these low detection limits, the PlasmaQuant MS Elite model is also available for laboratories requiring even greater sensitivity.

Overall, the combination of the PlasmaQuant MS and the optimized sample preparation method supports robust, routine analysis of solid biofuels. The system delivers efficient and accurate quantification across a wide range of elements and concentrations, making it a powerful tool for evaluating ash behavior during thermal conversion, predicting issues like sintering and melting, and ensuring compliance with quality and sustainability standards in bioenergy production.

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant MS	818-08010-2	PlasmaQuant MS is ideally suited for the elemental analysis of solid biofuels in line with ISO 16967 and ISO 16968. Its robust plasma and high sensitivity ensure accurate results even in complex matrices, making it the perfect tool for quality control and research in bioenergy applications.
Teledyne-Cetac ASX-560 autosampler	810-88015-0	The Teledyne CETAC Technologies ASX-560, next generation autosampler with integrated rinse function is sleek and durable by design.
Cetac ASXPress Plus (or equivalent)	810-88017-0	The ASXPress Plus is a Rapid Sample Introduction Accessory which reduces autosampler movement, sample uptake, stabilization, and rinse times, significantly cutting down sample run times.

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