

Evaluation of acid matrix effects in the determination of major elements in biomass by atomic absorption spectrometry from an environmentally friendly point of view

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Abstract The estimation of major element content in solid biofuels is required for prediction and prevention of eventual ash-related problems during combustion. These analyses have to be achieved with minimum impact on the environment. The quantitation of Al, Ca, Mg, Na, K, Fe, Si and Mn in biofuels was carried out according to EN 15290 using acid decomposition of solid samples followed by atomic absorption spectrometry (AAS). A microwave-assisted acid digestion with a HNO₃/H₂O₂/HF mixture was used, followed by HF complexation using H₃BO₃. Due to the presence of tetrafluoroboric acid complex in the digestion solution, matrix effects were noticed during elemental quantification by AAS. Standard addition calibration methods did not compensate for this matrix effect. Matrix effects that constrain an analytical response may be overcome by applying the procedure used for samples to the calibration standards using the same reagents. However, this entails using large amounts of toxic reagents. In this work, the fluoric–boric acid matrix matching was assessed statistically using one-way ANOVA tests. For the seven groups of nitric acid and reagent blank (HNO₃/H₂O₂/HF/H₃BO₃) mixtures used, ranging from 0 to 1 volume ratios, no significant differences were observed for Si, Al, Fe and Mn. The calculated *F* values were lower than the critical value, $F_{6,14} = 2.85$ ($p = 0.05$). However, for Ca, Mg, Na

and K, significant differences were observed. Tenfold dilution was used for samples where the mass fraction exceeded the analytical dynamic range of the AAS instrument. The calibration solutions were prepared using the reagent blanks in the same proportion thus decreasing the amount of acids used. The procedure was validated using SRM 1573a—tomato leaves—purchased from the National Institute of Standards and Technology. Target recoveries of (1 ± 0.1) were achieved.

Keywords Acid matrix matching evaluation · Major elements · Flame atomic absorption spectrometry · Traceability to SRM · Internal and external quality control · Measurement uncertainty · Assessment of acid matrix reagents consumption

Introduction

Over the last decade, thermochemical conversion of biomass, i.e. solid biofuels, has attained higher importance and is subject of extensive R&D, aiming to reduce CO₂ emission and diversification of fuel sources [1].

The behaviour of biomass ash during thermal conversion processes is strongly dependent on the biofuel mineral composition. The knowledge of mass fractions of major elements present in the biomass, namely Al, Ca, Mg, Na, K, Fe, Si and Mn, is essential to predict and to prevent operational ash-related problems [2].

The increasing use of biomass as a fuel enhances economic, environmental and social impact, leading to the standardization of solid biofuel characterization procedures. Standard technical specification (TS) for determination of major elements, CEN/TS 15290, was first published in 2006 by the European Committee for Standardization (CEN),

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