Challenge
Analysis of trace elements in volatile organic matrices with high robustness, high resolution, and high sensitivity.

Solution
ICP-OES with a high-resolution optical system, highest sensitivity, and matrix tolerance to achieve lowest detection limits for trace element determination in ethanol fuel.

Intended audience
biofuel producers, analytical chemists, and quality-control laboratories involved in the elemental purity assessment of bioethanol and other renewable fuels.

Determination of elemental impurities in ethanol fuel according to standard methods with HR array ICP-OES

Introduction

Fossil fuels have been the main source of energy in industrial applications and transportation for decades. However, scarcity of resources coupled with increasing demand, environmental aspects, and economic and political issues require sustainable, easily accessible, cheap, and environment-friendly alternatives. Therefore, biofuels are becoming increasingly important for sustainable energy and climate policy due to their considerable potential to replace fossil fuels while reducing CO_2 remissions.
Besides biodiesel, bioethanol is one of the most important biofuels. Bioethanol is produced by alcoholic fermentation from sugar-rich biomass (e.g., sugar cane, sugar beets). Also starch-rich materials, such as corn, sorghum, or wheat can be used as a precursor, but therefore starch has to be converted in an additional enzymatic hydrolysis to sugar in advance. Since usage of food as feedstock material is controversial, the goal is their reduction/replacement by cellulose-rich biomass like straw, wood, or energy plants (switch grass). Like starch, cellulose also has to be hydrolyzed to sugar before fermentation takes place.
The resulting bioethanol is utilized as an alternative energy carrier for combustion engines (Otto engine) and in fuel cells. Utilization as pure fuel (E100) or blending component for fossil fuels, such as gasoline (E2, E5, E10, E15, E25, E50, E85) requires the highest purity of ethanol. Depending on the source material, production process, and transportation, ethanol can be contaminated with elemental impurities. Especially the presence of elements such as copper (Cu), iron (Fe), sodium (Na), phosphorus (P), and sulfur (S) must be controlled and must not exceed the product specific limit values (Table 1). Therefore, various international standards describe the analysis and tolerable limits of ethanol, such as ASTM D4806, EN 15376 and 15837, as well as in the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) Resolution No. 19/2015. For the control of such trace element impurities the high-resolution (HR)

inductively coupled plasma optical emission spectroscopy (ICP-OES) with its high sensitivity, and matrix tolerance enables to achieve lowest detection limits.

Organic matrices are one of the most challenging sample matrices to be analyzed by ICP techniques. The high load and carbon content of the organic matrix requires a robust sample introduction and plasma system, which reliably excites the samples within the ICP and does not suffer from carbon build-up within the torch system. For this challenge, the vertical geometry of the V-Shuttle torch and the powerful high-frequency generator in the PlasmaQuant 9200 have proven themselves, which is established by the direct analysis of undiluted ethanol.

Spectral interferences originating from the unspecific carbon background of the sample matrix are a major challenge to reliably measure trace concentrations of elements like copper (Cu) and phosphorus (P). To account for these interferences, classical ICP-OES needs to employ laborious calibration strategies such as standard addition calibration or to select alternative emission lines with less sensitivity, which compromises the achievable limits of detection (LOD). The high-resolution optical system of the PlasmaQuant 9200 Elite (2 pm @ 200 nm) in combination with the CSI software algorithm (correction of spectral interferences) avoid such compromises since the most sensitive emission lines remain interference-free and hence, available for measurement.

The methodology presented her analyzes ethanol samples following ASTM D4806 and EN 15837 methods. The use of primary emission lines throughout all investigated elements as well as the possibility to run undiluted samples allow for LODs in the lower µg/kg range and below on a routine basis.

Table 1: Limit concentrations of elemental impurities in ethanol according to international standards (1-3)

Element	ASTM D4806 [mg/kg]	ANP Resolution 19/2015 [mg/kg]	EN 15376 [mg/kg]
Cu	0.1	0.07	0.1
Fe	-	5	-
Na	-	2	-
P	-	-	0.15
S	30	-	10

Materials and methods

Samples and reagents

Three fortified ethanol samples, which are emulating different percentage levels of legal limit values, were submitted to the analysis. The following chemicals were used for the preparation of standards, blank, QC sample, and samples:

- Ethanol (≥ 99.9%, Emsure®, Merck)
- Subboiled distilled HNO_3
- Single and multi-element standards (Merck, Sigma-Aldrich)
- Deionized (DI) water (18.2 MΩ cm, PURELAB system, ELGA LabWater, High Wycombe, England)

Sample preparation

To match the ethanol matrix of the calibration standards, the ethanol samples were diluted with DI water and acidified with HNO_3 to give a final ethanol concentration of 90% (v/v) and acid concentration of 1% (v/v). Samples were spiked at levels (reflecting 10, 50, and 150% of limit values) as follows:

- 0.01, 0.05, and 0.15 mg/L for Cu
- 0.05, 2.5, and 7.5 mg/L for Fe
- 0.2, 1.0, and 3.0 mg/L for Na
- 0.015, 0.075, and 0.225 mg/L for P
- 1.0, 5.0, and 15 mg/L for S

Calibration

All multi-element stock solutions were made up using single element and multi-element standard solutions (Merck, Sigma-Aldrich, CPAchem, Inorganic Ventures). The working standards were prepared by serial volume/volume dilution in polypropylene tubes of the stock solutions using 90% (v/v) aqueous ethanol containing 1% (v/v) HNO_3 (for stabilization of analytes). The concentrations of the calibration standards were in accordance with EN 15837 and are listed in Table 2. The blank solution was prepared from 90% (v/v) aqueous ethanol containing 1% (v/v) HNO_3. According to EN 15837 a quality control (QC) sample should be measured after the calibration has been established and has to be prepared from a different stock solution. The spiked levels of the QC sample need to be set in accordance with the specification limits and are also shown in Table 2.

Table 2: Concentration (mg/L) of calibration and quality control (QC) standards

Element	Cu	Fe	Na	P	S
Blank	0	0	0	0	0
Std. 1	0.05	1.0	1.0	0.10	1.0
Std. 2	0.10	2.5	2.5	0.50	5.0
Std. 3	0.20	5.0	5.0	1.0	10
Std. 4	0.40	10	10	1.5	20
QC Std.	0.10	5.0	2.0	0.15	10

Instrument settings

The PlasmaQuant 9200 Elite ICP-OES, equipped with the organic sample introduction kit, was employed for this analysis. Just 10 minutes of warm up time was necessary prior to the sample analysis. No oxygen was inserted into the plasma and no tempered cyclonic spray chamber was used to run the analysis. An Teledyne CETAC ASX-560 autosampler was employed. The instrument parameters can be seen in Table 3.

Table 3: Instrument settings

Parameter	Settings 9100 Elite	Settings 9200 Elite
RF power	1450 W	
Plasma gas flow	15 L/min	10 L/min
Auxiliary gas flow	1.25 L/min	1.5 L/min
Nebulizer gas flow	0.45 mL/min	0.35 mL/min
Nebulizer	Borosilicate concentric nebulizer, 1 mL/min	
Spray chamber	Borosilicate cyclonic spray chamber with dip tube, 50 mL	
Outer tube/inner tube	Quartz/quartz	
Injector	Quartz, inner diameter 1 mm	
Pump tubing	PU (black, black)	
Sample pump rate	1 mL/min	
Fast mode	1 mL/min	
Read delay	90 s	
Rinse time	60 s	
Torch position*	-2 mm	-1 mm

* Spacing between injector and coil further suppresses carbon deposits on the injector tip

Method and evaluation parameters

In the EN 15837 method, analysis wavelengths are recommended as a standard. With the outstanding spectral resolution of the Analytik Jena PlasmaQuant 9200 Elite, each line can be chosen with no interference. In the device's ASpect PQ software, the automatic background correction (ABC) was utilized for data evaluation. The ABC function automatically fits in a global baseline to the whole spectral background concurrently throughout the sample analysis. Additionally, the CSI software tool was employed for certain elemental lines to remove background signals originating from the organic matrix. The evaluation parameters can be seen in Table 4.

Table 4: Method parameters

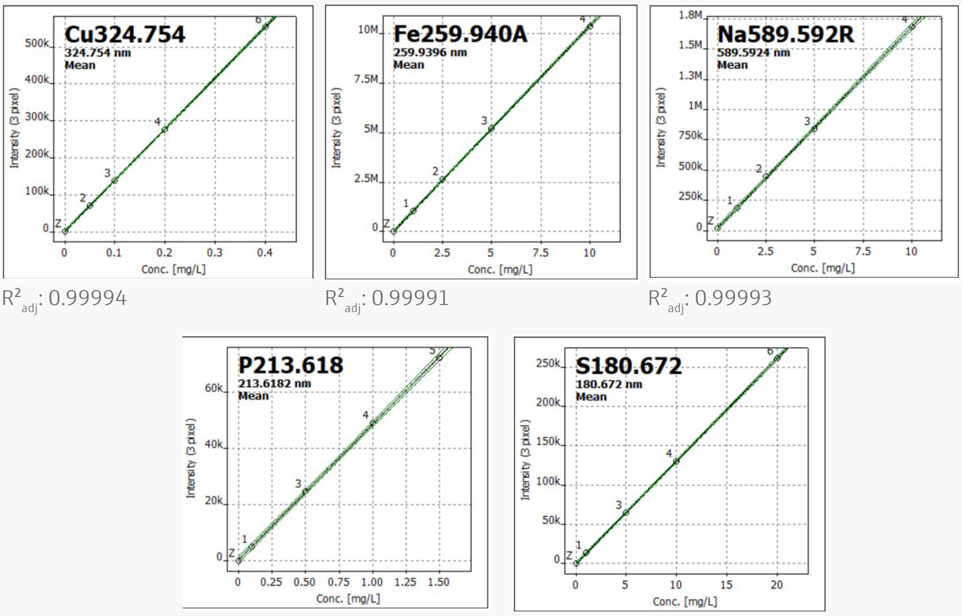
Element	Line [nm]	Plasma view	Integration mode	Replicates	Read time [s]	Evaluation		
						No. of pixel	Baseline fit	Correction
Cu	324.757	axial	peak	3	3	3	ABC[1]	-
Fe	259.940	axial	peak	3	3	3	ABC	-
Na	589.592	radial	peak	3	3	3	ABC	-
P	213.618	axial	peak	3	10	3	ABC	CSI[2]
S	180.672	axial	peak	3	3	3	ABC	CSI

[1] Automated Baseline Correction

[2] Mathematical correction of spectral interferences originating from organics

Results and discussion

Linear calibrations were obtained with a correlation coefficient greater than 0.9999 for all elements indicating excellent linearity across the calibration range. Calibration curves for the method are shown in Figure 1 together with the adjusted coefficient of correlation (R^2_{adj}).



R^2_{adj}: 0.99994

R^2_{adj}: 0.99991

R^2_{adj}: 0.99993

R^2_{adj}: 0.99995

R^2_{adj}: 0.99991

Figure 1: Calibration functions with achieved correlation coefficient

Figure 2 shows the recovery of the spiked ethanol samples. The spiked levels are equal to 10, 50, and 150% of the legal limits according to beforementioned international specifications (see Table 1) for ethanol fuel. All recoveries were within ± 10% indicating a good accuracy of the method overs the whole working range.

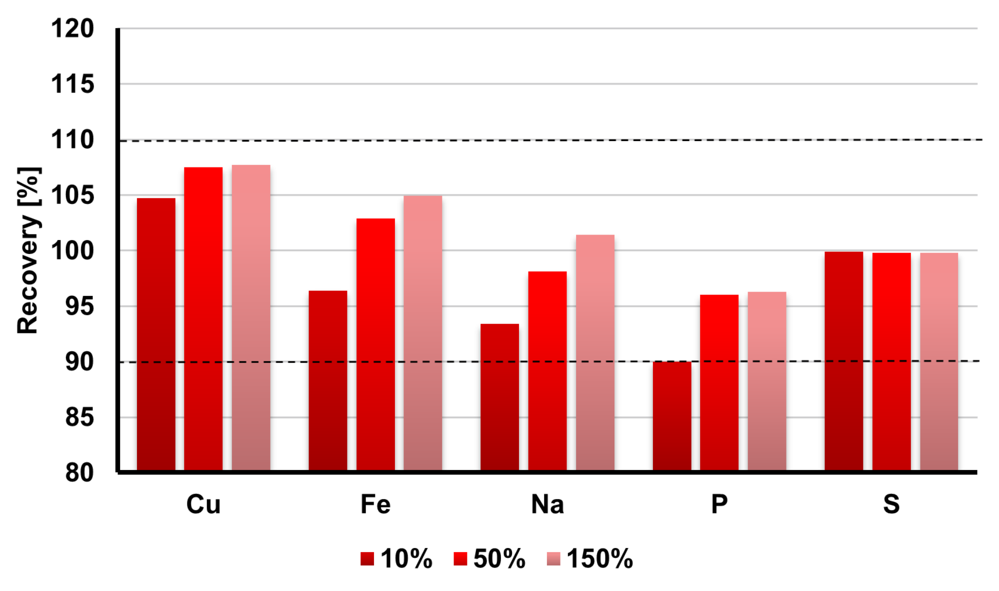


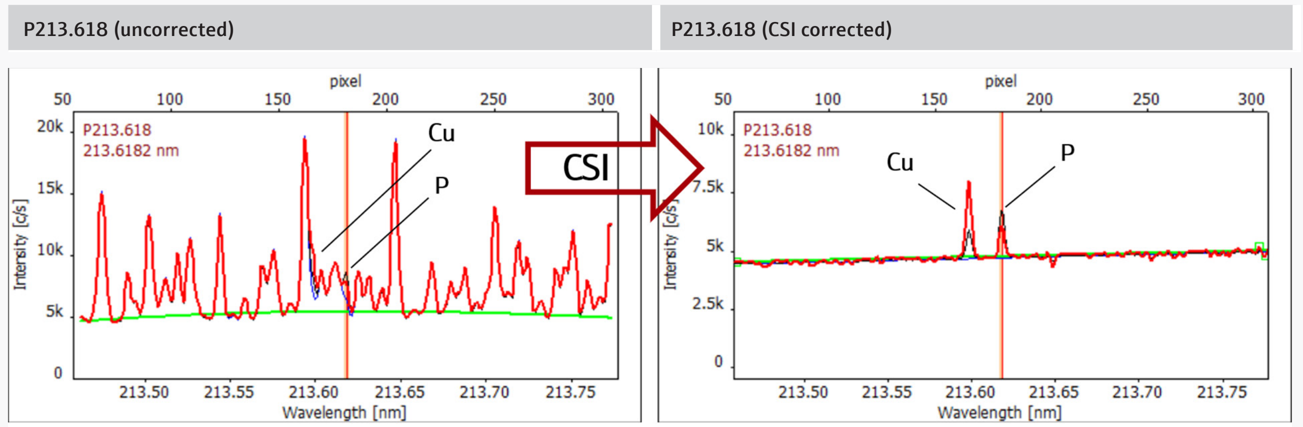
Figure 2: Recoveries of spiked ethanol samples, spike levels reflect 10, 50, and 150% of the legal limits

The excellent recoveries of the low spike levels are remarkable. Since 10% of the legal limits corresponds to a concentration of 10 and 15 µg/kg for copper (Cu) and phosphorus (P), respectively, the high performance capabilities of the PlasmaQuant 9200 Elite for such matrices is proven. The high-resolution optics in combination with the CSI software tool allow for an interference-free analysis of all investigated elements resulting in the lowest limits of detection (LOD). Table 5 shows selected wavelengths and achieved method detection limits (MDL). Instrument detection limits (IDL) were determined using three times standard deviation from eleven measurements of the calibration blank. The method detection limits, comprising the instrument detection limits and the sample preparation, were all in the lower µg/kg range.

Table 5: Method detection limits (MDL) for elemental lines

Element	Line [nm]	Observational view	MDL [µg/kg]
Cu	324.757	axial	0.14
Fe	259.940	axial	0.24
Na	589.592	radial	3.4
P	213.618	axial	2.3
S	180.672	axial	11.6

The CSI tool precisely removes background signals from the recorded sample spectrum resulting in a clean and simple to evaluate peak, which typically improves the signal-to-noise ratio and, consequently, accuracy and precision. Figure 3 shows the effectiveness of the CSI correction tool on the examples of phosphorus (P). On the left-hand side, as-recorded spectrum with significant contribution of background signals are displayed. Evaluating such a peak will result in a false quantification of the respective analyte. The corrected spectrum, as displayed on the right-hand side of Figure 3, shows an analyte peak that can be easily and reliably evaluated resulting in excellent accuracy and precision of the obtained results.



P213.618 (uncorrected)

P213.618 (CSI corrected)

Figure 3: Application advantage of high-resolution spectra and correction of spectral Interferences software tool (red: 50% sample, black: 100 µg/L Std., blue: Cal. 0, green: baseline correction).

To achieve consistent and precise results and reduce the need for recalibration or remeasurement of samples, the ICP-OES system must provide good long-term stability. Long-term stability was tested by hourly analysis of the QC sample. Between the QC measurements regular spiked ethanol samples were analyzed. Recovery values between 96% and 107% were achieved, which demonstrates the exceptional plasma robustness and superior performance of the PlasmaQuant 9200 Elite for organic matrices.

Table 6: Recoveries of quality control (QC) sample over a 4 hour time period

Element	Line [nm]	After calibration Recovery [%]	1 hour check Recovery [%]	2 hour check Recovery [%]	3 hour check Recovery [%]	4 hour check Recovery [%]
Cu	324.757	98.6	103.5	104.9	106.5	106.6
Fe	259.940	99.4	102.1	103.3	103.3	103.7
Na	589.592	97.2	97.0	97.9	98.6	99.3
P	213.618	95.9	95.9	96.6	95.6	99.0
S	180.672	100.8	101.5	103.7	104	103.2

Conclusion

The methodology presented here allows for a simple routine analysis of trace impurities in ethanol fuel by means of ICP-OES according to ASTM D4806 and EN 15837. Typical challenges when analyzing organic samples such as ethanol fuel are plasma instability, signal fluctuation due to carbon deposition, and matrix-based spectral interferences.
High accuracy and precision results are achieved by a uniform excitation of the undiluted ethanol samples using the high-frequency RF generator of the PlasmaQuant 9200 Elite. Carbon deposits on the glassware can be suppressed by using a vertical torch design, such as the unique V Shuttle Torch. Furthermore, an optimized torch position guarantees minimal soot formation and hence, excellent long-term stability of the measurements.
The high spectral resolution of the PlasmaQuant 9200 Elite of 2 pm @ 200 nm in combination with the CSI software tool ensure a sufficient separation of analyte and background signals. Thus, the unspecific background resulting from the high carbon content in ethanol is efficiently separated from analyte emission lines and spectral interferences are eliminated. It allows for the use of most sensitive emission lines and therefore guarantees the highest sensitivity for all investigated elements. Additionally, data evaluation is easily performed by automatically executed baseline and spectral corrections with the help of software tools like ABC and CSI. As a result, limits of detection in the range of 1 µg/L are achieved, which ensures the precise and accurate determination of the required limits, especially for critical elements such as copper (Cu) and phosphorus (P). It also allows ethanol manufacturers to push their specification limits to a new level, proving the superiority of their ethanol products.

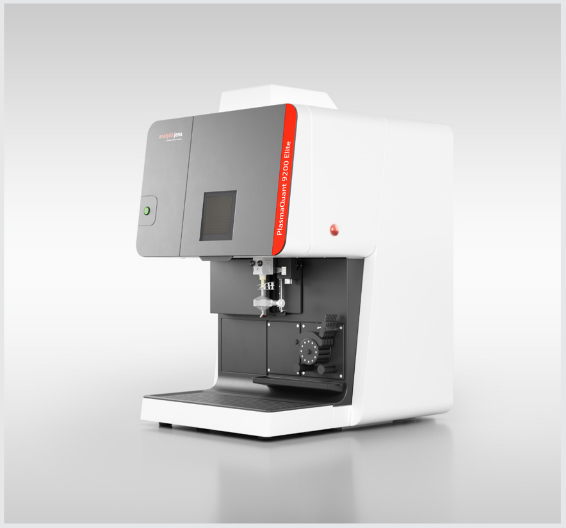


Figure 4: PlasmaQuant 9200 Elite

Recommended device configuration

Table 7: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9200 Elite	818-09201-2	High resolution ICP-OES
ORGANIC KIT for PlasmaQuant 9200	810-88562-0	Sample introduction kit for organic samples
PU pump tubing (black/black) for sample	418-13-410-528	Pump tubing for organic solvents (Kerosene, Ethanol)
PU tubing (red/red) for waste	418-13-410-529	Pump tubing for organic solvents (Kerosene, Ethanol)
Teledyne CETAC ASX-560	810-88015-0	Autosampler with integrated rinse function
ASX-560 Oil Upgrade Kit	418-88224-0	Organic resistant autosampler parts

References

[1] American Society for Testing and Materials – ASTM D4806 – Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel. 2021.

[2] Brazilian National Agency of Petroleum, Natural Gas and Biofuels, Resolution ANP Resolution number 19, 2015.

[3] European Standard – EN 15837 – Ethanol as a blending component for petrol - Determination of phosphorus, copper and sulfur content - Direct method by inductively coupled plasma optical emission spectrometry (ICP OES). 2010.

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