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Industrial

Sensitive and robust multi-element analysis in bioethanol by ICP-OES

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Keywords

iCAP PRO Series, ICP-OES, alternate fuels, biofuel, ethanol, organics

Objective

To develop a robust and sensitive analytical method for the determination of various analytes including copper, phosphorus, sulfur, and other critical elemental contaminants by direct aspiration of ethanol using ICP-OES

Introduction

Global efforts to decarbonize transportation and reduce reliance on petroleum have accelerated the adoption of ethanol as a blend stock in gasoline (e.g., E10–E85). Produced primarily from biomass such as sugarcane and corn, ethanol supports cleaner combustion and improved engine efficiency. As production volumes grow and regional blend mandates evolve, consistent fuel quality—especially the control of trace elemental contaminants—becomes critical for engine durability, emissions compliance, and refinery throughput.

Elemental impurities may enter bioethanol at multiple points: from feedstock and fermentation residues, corrosion and wear of processing equipment, contact with storage/transfer infrastructure, water ingress, or the addition of denaturants and additives. Even at low concentrations, impurities of elements such as copper, iron, phosphorous, or sulfur (or other transition metals) can catalyze oxidation, promote gum formation, increase corrosivity, poison after treatment catalysts, and impair injector performance. Consequently, international and national product specifications—including ASTM D4806 (denatured fuel ethanol), ASTM D5798 (E85), IS 15464:2004, and Brazil's ANP Resolution 19/2015—define limits and recommended practices for analysis.

Inductively coupled plasma–optical emission spectroscopy (ICP-OES) is well suited to this task because it enables simultaneous multi element quantification across a wide dynamic range with high sample throughput. However, direct aspiration of volatile organic solvents, such as ethanol, presents practical challenges: elevated solvent load can destabilize the plasma, increase background, and promote carbon deposition on the injector and torch unless the sample introduction system and operating conditions are optimized.

This application note describes a direct analysis workflow on the Thermo Scientific™ iCAP™ PRO X ICP-OES Duo (Figure 1), using a Peltier cooled spray chamber (IsoMist™ XR Peltier-cooled spray chamber at 0 °C, Figure 2) to stabilize aerosol generation in neat ethanol. The method targets a comprehensive analyte panel relevant to regulatory specifications and refinery/plant quality control needs, and it evaluates analytical figures of merit—linearity, method detection limits, accuracy, and long term robustness—under routine conditions. The goal is to provide a sensitive, reproducible procedure that laboratories can implement quickly to verify compliance and safeguard process performance when qualifying bioethanol for blending.

Experimental

In this study, an iCAP PRO X ICP-OES Duo instrument was used for the simultaneous determination of 25 analytes in ethanol. The instrument was operated in axial Intelligent Full Range (iFR) mode, enabling full-spectrum acquisition with optimized dynamic range in a single measurement and supporting efficient multi-element analysis.

Direct analysis of ethanol was possible thanks to the use of the IsoMist™ XR Peltier-cooled spray chamber[1] (Glass Expansion, Melbourne, Australia), operated at 0 °C. Cooling the spray chamber reduces solvent vapor pressure and solvent loading on the plasma, improves plasma stability, and minimizes carbon-related effects such as injector fouling and elevated background emission. The IsoMist XR is a compact, Peltier-driven temperature-controlled spray chamber that integrates seamlessly with the Thermo Scientific™ iCAP™ PRO Series ICP-OES Systems. It incorporates the proven Twister™ cyclonic spray chamber design, delivering rapid washout and consistently high analytical performance. IsoMist XR operation is controlled through a simple, single-screen software interface that enables straightforward temperature adjustment and monitoring. When installed on the iCAP PRO Series ICP-OES, the IsoMist XR fits entirely within the instrument's sample introduction compartment, preserving valuable laboratory bench space while enhancing stability and robustness during routine analysis. This configuration allows volatile organic matrices, such as ethanol, to be analyzed directly without extensive dilution or additional sample preparation.

Further components of the sample introduction system included a concentric glass nebulizer, organic-resistant pump tubing, a quartz torch, and a 1.0 mm internal diameter quartz injector. Instrumental parameters, including RF power and gas flows, were optimized to ensure stable operation throughout the analysis. A summary of the sample introduction components and operating conditions is provided in Table 1.

Figure 1. iCAP PRO X ICP-OES Duo instrument.

Figure 2. IsoMist XR programmable temperature-controlled cyclonic spray chamber.

Table 1. Instrument configuration and operating parameters.

Parameter	Value
Spray chamber	IsoMist XR, cooled at 0 °C
Nebulizer	Glass concentric
Pump tubing	Sample uptake: Tygon™ orange/white (organic sample uptake tubing) Drain: Tygon™ white/white (organic sample drain tubing)
Center tube	1.0 mm quartz (organic)
Torch	Quartz
Pump speed	45 rpm
Flush pump speed	45 rpm
Nebulizer gas flow	0.40 L/min
Auxiliary gas flow	1.5 L/min
Coolant gas flow	14.5 L/min
Plasma RF power	1,350 W
Number of replicates	3

Sample and standard preparation

To determine key analytical figures, such as linearity and range, instrument detection limits (IDLs), and correlation coefficients, calibration plots were generated using five calibration standards and a blank. All standards were prepared using commercially available ethanol, which was acidified to contain 0.1% HNO_3 and was also used as calibration blank. Aqueous stock solutions of target analytes were diluted gravimetrically to prepare calibration standards with a separate set of calibration standards being prepared for sulfur. The list of analytes and their respective concentrations in calibration standards are given in Table 2. The ethanol samples prepared in a similar manner were analyzed as technical replicates during long term stability study.

Table 2. List of target elements and their concentrations in the calibration standards (mg·L^{-1}).

Elements	STD 1	STD 2	STD 3	STD 4	STD 5
Li, B, Na, Mg, Al, Si, P, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Mo, Ag, Cd, Ba, Tl, Pb, Bi	0.005	0.02	0.05	0.25	1
S	0.1	0.5	1	5	NA

Results and discussion

Calibration linearity and instrument detection limits

Instrument detection limits and correlation coefficients for all analytes as well as the wavelength used are given in Table 3. Instrument detection limits were calculated based on the standard deviation of 10 replicate measurements of the calibration blank and the slope of the calibration curve for each analyte. Excellent detection limits and linearity were achieved for all the analytes measured. In this case, since all samples were analyzed directly without any sample preparation or any upfront dilution performed prior to analysis, the instrument detection limits achieved also represent the method detection limits (MDLs).

Method accuracy

To determine the method accuracy, a batch of ethanol samples was spiked at two different concentration levels. These two spiked solutions consisted of a low concentration spike (0.05 mg·L^{-1} of other analytes and 0.1 mg·L^{-1} of sulfur) and a high concentration spike (0.1 mg·L^{-1} of other analytes and 0.5 mg·L^{-1} of sulfur). These spiked solutions were prepared in triplicate at each concentration level to determine accuracy and precision of the analytical method.

Table 3. List of analytes, wavelengths, correlation coefficients, and method detection limits (mg·L^{-1}).

Element	Wavelength (nm)	R^2	MDL (mg·L^{-1})	Element	Wavelength (nm)	R^2	MDL (mg·L^{-1})
Ag	338.289	0.9999	0.004	**Mg**	279.553	0.9999	0.001
Al	396.152	>0.9999	0.002	**Mn**	257.610	>0.9999	0.001
B	208.959	0.9985	0.004	**Mo**	202.030	0.9998	0.002
Ba	493.409	0.9999	0.001	**Na**	588.995	0.9988	0.011
Bi	223.061	0.9999	0.004	**Ni**	221.647	0.9999	0.001
Ca	393.366	0.9996	0.001	**P**	177.495	0.9998	0.010
Cd	226.502	>0.9999	0.001	**Pb**	220.353	>0.9999	0.004
Co	228.616	>0.9999	0.001	**S**	182.034	0.9998	0.103
Cr	267.716	>0.9999	0.001	**Si**	251.611	0.9997	0.004
Cu	324.754	0.9995	0.001	**Sr**	407.771	>0.9999	0.001
Fe	259.940	>0.9999	0.002	**Tl**	190.856	0.9997	0.008
K	766.490	0.9981	0.001	**V**	292.402	0.9960	0.003
Li	670.784	0.9999	0.001	**Zn**	213.856	0.9998	0.001

Figure 3 summarizes the average accuracy (n=3) calculated for all analytes in each spiked level. The average accuracy was found to be within 90%–110% for all analytes in both concentrations with relative standard deviation (%RSD) of less than 5%. The data obtained in this study indicates that the developed method delivers accurate and precise data even at low concentration levels.

System robustness – QC and internal standard recovery

Although ICP-OES is well recognized for its robustness and tolerance towards challenging matrices, it is essential to demonstrate that the developed method delivers accurate and precise results over extended analytical sequences, particularly when analyzing volatile organic matrices such as ethanol. In the context of fuel quality control, consistent quantification of elemental constituents is critical, as analytical data are often used to support compliance verification and process monitoring.

To verify that the developed methodology is suitable for extended analytical sequences, a robustness study was performed, mimicking a typical sequence in an analytical testing laboratory. A quality control (QC) check, containing defined concentrations (STD 3) of all target analytes, was analyzed every 20 samples during a continuous three-hour analytical run, alongside 50 unknown ethanol samples. Periodic measurement of the QC solution ensured data validity and verified stable plasma conditions, correct function of the sample introduction system, and absence of matrix-related drift over time. The results obtained from these QC measurements are summarized in Figure 4.

Across the entire run, recovery for all analytes remained within the range of 90%–110%, demonstrating consistent instrument response and effective control of matrix effects during prolonged operation. These results confirm that the selected instrumental setup and operating conditions provide stable and reproducible performance, supporting accurate and precise determination of trace elemental impurities in ethanol samples during long analytical batches typical of routine quality control workflows.

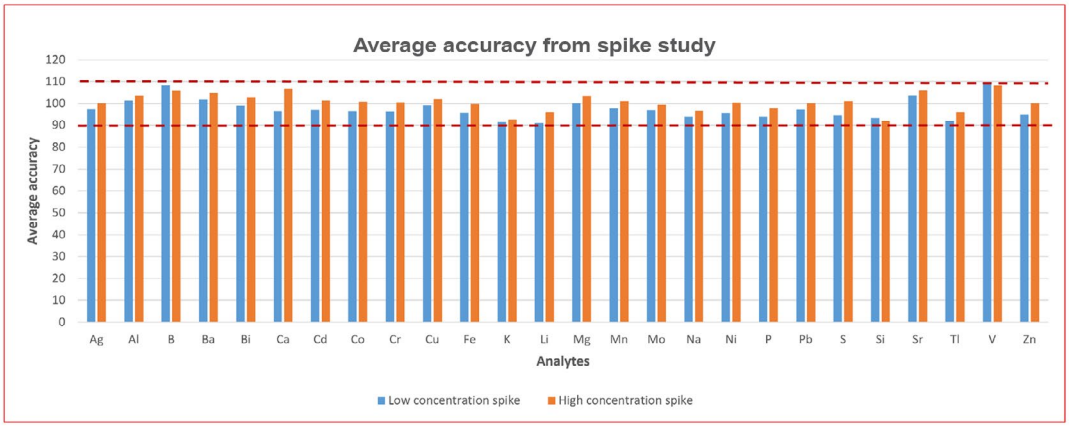

Figure 3. Average recovery observed for all analytes in spiked solutions.

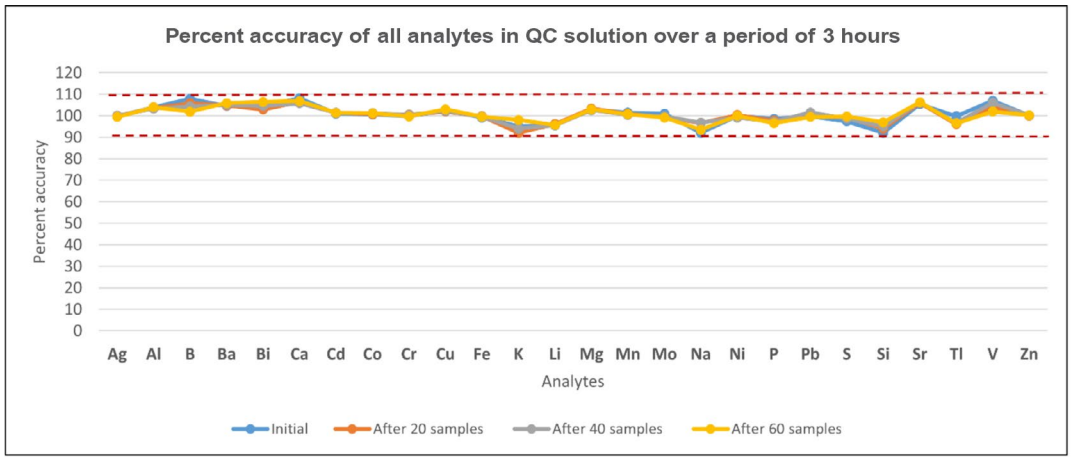

Figure 4. Percent accuracy of all analytes observed in periodically measured QC solution.

Long-term method robustness was further evaluated by monitoring the response of the internal standard, as a key indicator of instrument stability during continuous analysis. Consistent response over time is a key indicator, reflecting the combined effects of plasma conditions, sample introduction performance, and potential matrix-induced suppression or enhancement.

For this purpose, all measured solutions, including blank, standards, samples, and QCs, were spiked with yttrium at a concentration of 10 mg·L^{-1}. The response was monitored relative to the calibration blank throughout the analytical sequence. The resulting response is highlighted in Figure 5, once again supporting the reliability of the method for routine analysis of ethanol samples.

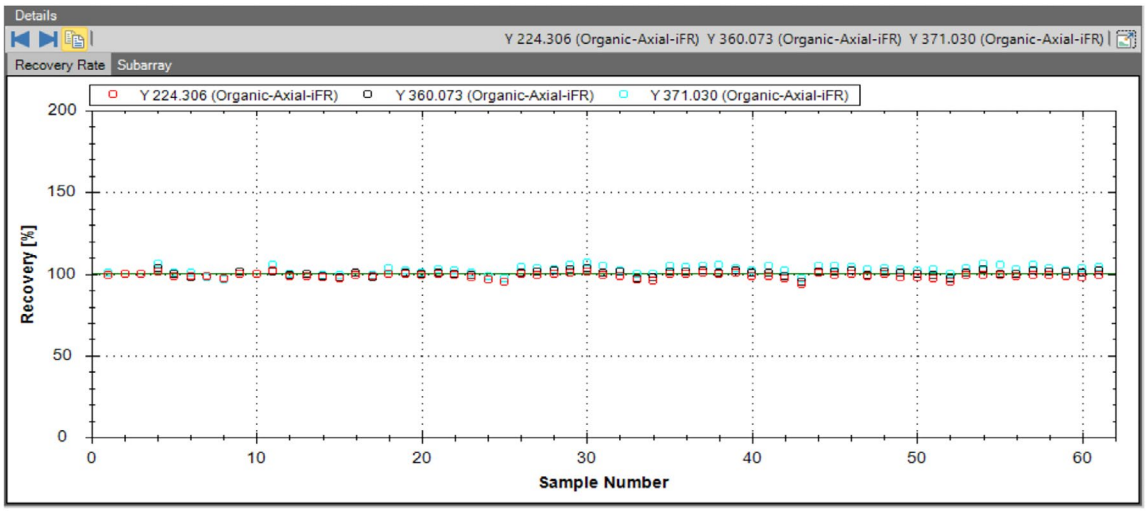

Figure 5. Internal standard response observed during a long analytical batch of over five hours.

Conclusion

This work establishes a streamlined and reliable ICP-OES methodology for direct elemental analysis of bioethanol, designed to meet regulatory and operational demands. The following conclusions highlight the key performance advantages and practical benefits for analytical laboratories.

- A robust and sensitive ICP-OES method was successfully developed for the direct multi-element analysis of ethanol using the iCAP PRO X ICP-OES Duo, eliminating the need for sample dilution or matrix conversion while meeting the requirements of relevant fuel quality standards.
- Excellent analytical performance was demonstrated for a broad suite of 25 elemental analytes, with good linearity, low method detection limits, and accurate recoveries at concentrations well below regulatory specification limits for critical impurities.
- The use of a Peltier-cooled spray chamber and organic-compatible sample introduction system enabled stable plasma operation during continuous ethanol aspiration, minimizing solvent loading effects and ensuring consistent analytical response.
- Long-term robustness was confirmed through periodic QC measurements and stable internal standard recoveries during extended analytical sequences, demonstrating the suitability of the method for routine, high-throughput quality control of bioethanol samples.
- The proposed method can also be extended to other water-miscible sample types with similar boiling point ranges, for example, isopropyl alcohol or methanol.

Reference

1. Thermo Fisher Scientific Product Spotlight 44370: Temperature controlled sample introduction for ICP-OES using the IsoMist XR

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