

Challenge

Direct analysis of beer exhibiting a high amount of total dissolved solids as well as volatile alcoholic components

Solution

HR ICP-OES with exceptional matrix tolerance towards complex matrices, high sensitivity and industry leading high-resolution optical system for interference-free detection of metals with high precision and accuracy

Direct Analysis of Beer by HR ICP-OES

Introduction

Beer is traditionally brewed from water, malted barley and hop. Often yeast is added during the fermentation process. Other base ingredients such as rice, wheat or corn are also used to brew beers of a huge variety with a wide range of different tastes. Since the brewing ingredients affect the taste and quality of the final beer, their quality is of highest importance. Metal contamination originating from the raw materials or the brewing process itself can adversely affect the final quality of the beer.

Copper contamination originating from the brewing kettle and increased iron contents may result in an unwanted metallic taste. Iron significantly contributes to the characteristics of the froth, which is important especially in regions where beer is traditionally served in a glass. Other elements to be monitored in beer and its precursors are sodium, zinc, manganese and calcium. Similar to iron, calcium affects the froth of the beer. Since calcium or zinc salts (CaSO_4 , ZnSO_4) are added intentionally as a pH buffer, their final concentration needs to be adjusted.

Monitoring metallic contents in final beer products as well as in precursors of the brewing process by the use of inductively coupled plasma optical emission spectroscopy (ICP-OES) demonstrates a routine task of quality control laboratories in the brewing industry. The main focus is on highly precise and accurate measurements with minimum sample preparation and data evaluation efforts.

Major challenges in the analysis of beer are the varying contents of alcohol (typically 4–6% (v/v)), the high amount of total dissolved solids (TDS) and the carbon dioxide (CO_2) contents. CO_2 causes unsteady sample introduction and thus poor precision of the obtained results. Therefore it must be removed before the analysis.

Running high TDS samples in combination with moderate amounts of alcoholic components additionally requires a highly robust sample introduction and plasma system to avoid poor precision due to plasma-based signal fluctuation. To account for these effects, many ICP-OES systems require dilution of the samples. The resulting dilution factors eventually compromise limits of detection (LOD), which is a limitation for trace elemental analysis.

The presented methodology describes a direct analysis of beer for calcium, sodium, copper, zinc, manganese and iron contents by the use of a high-resolution ICP-OES, the PlasmaQuant 9100 Elite. The exceptionally high resolution allows for interference-free analysis of all investigated analytes in the demanding matrix of undiluted beer samples. The dedicated introduction kit for high matrix samples combined with the robust plasma of the high-frequency generator enables precise and accurate measurements of demanding matrices with LODs in the sub-ppb range.

Materials and Methods

Samples and reagents

Sample preparation

Beer samples were divided into two aliquots in order to investigate different sample degassing methodologies:

- sonication (20 min)
- pass-through of argon stream (60 min)

The obtained samples were acidified with nitric acid (65%, p.a.)

Calibration

Ethanol (GC grade) was added to the standards in order to perform a matrix-matched calibration. The standards were prepared from single element standard solutions (1000 mg/L). Yttrium and gallium were used as internal standards. Table 1 summarizes the used calibration levels.

Table 1: Concentration of calibration standards

Element	Unit	Cal.0	Cal.1	Cal.2	Cal.3
Ca	mg/L	0	10	25	50
Cu	mg/L	0	0.05	0.10	0.25
Fe	mg/L	0	0.01	0.025	0.05
Na	mg/L	0	5.0	10	25
Mn	mg/L	0	0.025	0.05	0.10
Zn	mg/L	0	0.01	0.025	0.05

Instrumentation

Instrument settings

For the analysis a PlasmaQuant 9100 Elite equipped with a sample introduction kit tailored to high matrix samples and an ASPQ 3300 autosampler was used. The detailed system configuration is shown in Table 2.

Table 2: Configuration of the PlasmaQuant 9100 Elite equipped with Salt kit

Parameter	Settings	Parameter	Settings
Power	1300 W	Injector	2 mm, Quartz
Plasma gas flow	14 L/min	Outer tube/Inner tube	Quartz/Quartz
Auxillary gas flow	0.5 L/min	Pump tubing	PVC (0.76 mm ID) black/black
Nebulizer gas flow	0.6 L/min	Sample pump rate	1.0 mL/min
Nebulizer	Concentric nebulizer seaspray (2.0 mL/min)	Rinse/Read delay	45 s
Spray chamber	Cyclonic spray chamber with dip tube, 50 mL	Auto sampler	Yes

Evaluation parameters

Table 3: Overview of method-specific evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of Pixel	Baseline fit	Polynomial degree	Correction
Ca	315.887	radial	peak	3.0	3	ABC ¹	auto	Y ² (radial)
Ca	317.933	radial	peak	3.0	3	ABC	auto	Y (radial)
Cu	324.933	axial	peak	3.0	3	ABC	auto	Ga ³ (axial)
Cu	327.396	axial	peak	3.0	3	ABC	auto	Ga (axial)
Fe	238.204	axial	peak	3.0	3	ABC	auto	Y (axial)
Fe	259.940	radial	peak	3.0	3	ABC	auto	Y (axial)
Na	588.995	radial	peak	3.0	3	ABC	auto	Ga (radial)
Na	589.592	radial	peak	3.0	3	ABC	auto	Ga (radial)
Mn	257.610	axial	peak	3.0	3	ABC	auto	Y (axial)
Mn	260.568	axial	peak	3.0	3	ABC	auto	Y (axial)
Zn	202.548	axial	peak	3.0	3	static	auto	Y (axial)
Zn	213.856	axial	peak	3.0	3	ABC	auto	Ga (axial)

¹ Automatic Baseline Correction

² Y 371.030

³ Ga 294.364

Results and Discussion

Prior to the analysis, the samples were degassed using the approaches of degassing by a an argon stream (60 min) and sonication (20 min). Since the differences of the obtained concentrations and precision values (RSD) are negligible, sonication demonstrates the more practical sample preparation technique due to the shorter processing times and its straightforward approach to process multiple samples at the same time.

Table 4 displays the as-recorded spectra of a beer sample for copper at 327.396 nm and zinc at 202.548 nm including their spectral surrounding. It can be seen that lines which are amongst the most sensitive ones for the respective element are base-line separated from their spectral vicinity and hence interference-free.

Verification of the obtained results was performed via multi-line evaluation of each analyte. The evaluation of two lines for each element shows excellent accuracy with deviations of less than 3% for each line pair. Furthermore, excellent precision of RSD values far below 1% and QC recoveries within $\pm 5\%$ were achieved. All results are summarized in Table 5.

Table 4: Collection of high-resolution spectral data and applicability of the CSI tool

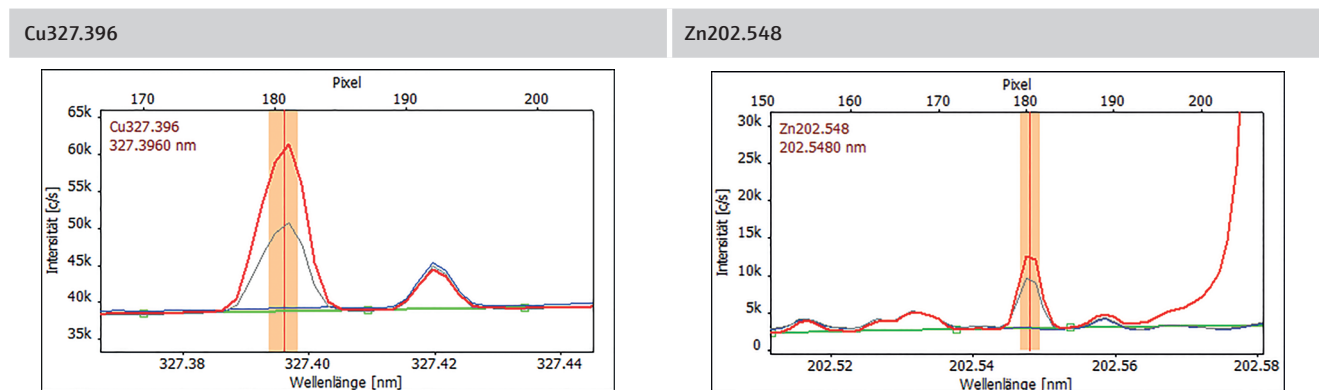


Table 5: Overview of the results for a representative beer sample

Element	Line [nm]	Ar gas stream		Sonication		LOD ¹ [µg/L]	Recovery [%]
		Concentration [mg L ⁻¹]	RSD [%]	Concentration [mg L ⁻¹]	RSD [%]		
Ca	315.887	38.8	0.3	38.3	0.8	0.80	99
Ca	317.933	38.7	0.7	38.4	0.7	1.01	99
Cu	324.933	0.110	0.8	0.108	0.9	0.25	105
Cu	327.396	0.110	0.6	0.111	0.6	0.84	103
Fe	238.204	0.021	2.1	0.024	5.8	0.07	96
Fe	259.940	0.021	0.4	0.023	0.3	0.05	95
Na	588.995	19.9	0.5	20.6	0.3	4.51	103
Na	589.592	19.8	0.6	20.5	0.9	4.80	103
Mn	257.610	0.064	0.3	0.065	0.4	0.02	98
Mn	260.568	0.064	0.6	0.065	0.4	0.03	99
Zn	202.548	0.018	0.2	0.018	0.1	0.06	95
Zn	213.856	0.018	4.9	0.019	1.8	0.14	105

¹ Matrix-specific detection limit obtained from 3σ of SD for QC matrix blank

Conclusion

The analysis of beer for trace and major levels of metals represents a routine task in quality control laboratories. The focus is on achieving highly accurate and precise results with a robust and reliable methodology. This application note describes a straightforward approach starting at the sample preparation routine of degassing the samples. Within this study, degassing via sonication proved to be the most convenient approach due to a rather short processing time and the ability to process many samples in parallel.

Sample dilution is an often required approach to reduce the matrix load within the plasma and hence to obtain sufficient accuracy and precision of the results. The PlasmaQuant 9100 Elite allows for a direct measurement of undiluted beer samples, which minimizes sample preparation efforts, reduces the risk of contamination and enables lowest limits of detection. The analysis of high TDS samples such as neat beer greatly benefits from a vertical torch concept in combination with a powerful RF generator to ensure long term stability of the measurements as well as reliable excitation of the samples. Here the PlasmaQuant 9100 Elite offers the unique V-shuttle torch, which ensures easy handling and maintenance and exceptionally long-term stability for the analysis of demanding samples. Excellent method robustness with RSD values well below 1% was achieved by the instruments High-Frequency Generator and the use of a sample introduction kit specific to the analysis of matrix-rich samples.

Due to the high spectral resolution (2 pm @ 200 nm) of the PlasmaQuant 9100 Elite, an interference-free analysis of all investigated elements is possible. Thus time-consuming data analysis of multi-line evaluation becomes obsolete. The PlasmaQuant 9100 Elite delivers results of highest confidence by single line evaluation in a routine task such as the analysis of beer. The PlasmaQuant 9100 Elite executes this analytical task with high matrix samples including varying concentrations of ethanol in a precise and robust manner and achieves low limits of detection in the sub-ppb range. At the same time major levels can be quantified from one measurement by exploiting the wide working range of the DualView Plus plasma observation modes. Single-line evaluation and the absence of sample dilution reduce analysis time significantly. The PlasmaQuant 9100 Elite therefore is the ideal instrument for the analysis of metals in beer samples.

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