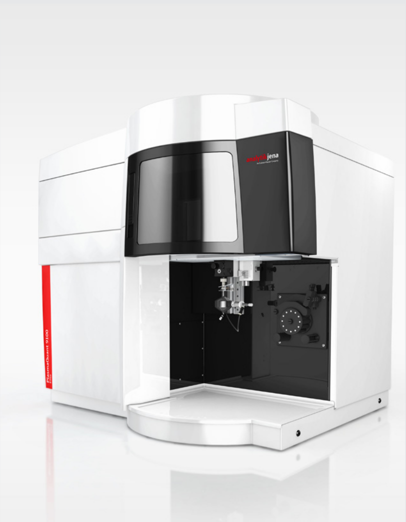

Challenge

Trace element analysis of impurities in high-purity urea featuring complex emission spectra originating from the sample matrix.

Solution

HR ICP-OES with industry leading high-resolution optical system and superior sensitivity and matrix tolerance to achieve lowest detection limits for trace element analysis in urea.

Detection of Trace Elements in Urea by HR ICP-OES

Introduction

Urea is an organic compound that plays an important role in biological metabolism processes. Besides its physiological properties, synthetically synthesized urea has become a very meaningful compound in the clinical, pharmaceutical, and chemical industries. It is a starting material for the synthesis of a large number of chemicals including hydrazine and melamine that are further used for the production of resins eventually used as building materials. In agriculture, urea is a preferred compound to be used as fertilizer because of its high nitrogen content.

Another application with constantly rising importance is its use as an active ingredient in exhaust gas treatment processes such as SNCR and SCR for environmental protection purposes. In these processes, ammonia or urea is injected to the exhaust gases of power plants (incineration plants, gas turbines, etc.), utility vehicles, and automobiles to reduce the emission of NOX gases to the environment by reaction to harmless products such as water and nitrogen.

Due to its manifold application areas (chemistry, food and agriculture, environment, etc.), the quality of urea and its products is highly regulated. For instance, the quality of urea as NOX reduction agent AUS 32 in diesel engines is regulated by ISO 22241. Here, maximum limits for calcium, iron, copper, zinc, chromium, nickel, aluminum, magnesium, sodium, potassium, and phosphorus (as phosphate) are in the range of 0.2 to 0.5 mg/kg. Nevertheless, the demands for other application areas might be more stringent, and QC laboratories aim towards lower matrix-specific limits of detection for specification analysis.

The proposed method for trace element detection is by ICP optical emission spectroscopy. For the product control of urea by ICP-OES, high precision and the lowest detection limits are desirable, yet the detectability of many trace elements is affected by signal suppression and drifting (matrix load) as well as by spectral interferences. The latter often require less sensitive alternative lines to be used. When using the High-Resolution Array ICP-OES, many of these analytical shortcomings can be avoided.

Here, the exceptionally high spectral resolution and sensitivity of the PlasmaQuant 9100 Elite by Analytik Jena offers a new analytical potential! It allows for an interference-free analysis of trace elements in a complicated matrix such as urea. Furthermore, the high plasma robustness of the high-frequency generator and the sample introduction system with its centerpiece, the V-Shuttle torch, allow for the analysis of high matrix samples with high accuracy and precision.

Within this study, the PlasmaQuant 9100 Elite was evaluated regarding the matrix specific detection limits for twenty commonly tested trace elements. Furthermore, the analysis of a QC control standard was included for method validation and long-term stability testing.

Materials and Methods

Samples and reagents

A high-purity urea sample was analyzed. A multi-element standard (Sigma Aldrich) spiked into high-purity urea was used for calibration and QC recovery testing.

Sample preparation

Here, a nitric acid solution of high-purity urea with a nominal matrix content of 130 g/L was prepared. Aliquots of the urea solution were spiked with 1 g/L multi element standard (Sigma Aldrich) to yield seven-point calibration curves in the range from 10 to 1000 µg/L. Various single element standards were used to test for spectral interferences.

Calibration

Table 1: Concentration of calibration standards

Element	Unit	Cal.0	Cal.1	Cal.2	Cal.3	Cal.4	Cal.5	Cal.6
Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Si, Tl, Zn	µg/L	0	10	50	100	200	500	1000
P	µg/L	0	100	500	1000	5000	10000	–

Instrumentation

For the analysis, a PlasmaQuant 9100 Elite equipped with Salt-Kit and ASPQ 3300 autosampler was used. The detailed system configuration is given in Table 2.

Table 2: Plasma configuration and set-up of the sample introduction system

Parameter	Specification
Power	1400 W
Plasma gas flow	15 L/min
Auxillary gas flow	0.5 L/min
Nebulizer gas flow	0.5 L/min
Nebulizer	Concentric nebulizer, borosilicate, 2.0 mL/min
Spray chamber	Cyclonic spray chamber, 50 mL, borosilicate
Outer tube/Inner tube	Quartz / Quartz
Injector	Quartz, 2 mm
Pump tubing	PVC
Sample pump rate	1.0 mL/min
Rinse/ Read delay	45 s
Autosampler	ASPQ 3300

Evaluation parameters

Table 3: Overview of method specific evaluation parameters

					Evaluation			
Element	Line [nm]	Plasma view	Integration mode	Read time [s]	No. of Pixel	Baseline fit	Polynomial degree	Correction
Al	396.152	axial	peak	3	3	ABC[1]	auto	–
Al	167.022	axial	peak	3	3	ABC	auto	–
As	188.979	axial	peak	10	3	ABC	auto	–
As	228.812	axial	peak	10	3	ABC	auto	–
Ba	455.403	axial	peak	3	3	ABC	auto	–
Ba	233.527	axial	peak	3	3	ABC	auto	–
Ca	396.847	axial	peak	3	3	ABC	auto	–
Ca	393.366	axial	peak	3	3	ABC	auto	–
Cd	214.441	axial	peak	3	3	ABC	auto	–
Cd	226.502	axial	peak	3	3	ABC	auto	–
Co	228.615	axial	peak	3	3	ABC	auto	–
Co	237.863	axial	peak	3	3	ABC	auto	–
Cr	205.552	axial	peak	3	3	ABC	auto	–
Cr	267.716	axial	peak	3	3	ABC	auto	–
Cu	324.754	axial	peak	3	3	ABC	auto	–

1 ... automatic baseline correction (ABC)

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of Pixel	Baseline fit	Polynomial degree	Correction
Fe	259.940	axial	peak	3	3	ABC	auto	–
Fe	238.204	axial	peak	3	3	ABC	auto	–
K	766.491	axial	peak	3	3	ABC	auto	–
K	769.897	axial	peak	3	3	ABC	auto	–
Mg	279.553	axial	peak	3	3	ABC	auto	–
Mg	285.213	axial	peak	3	3	ABC	auto	–
Mn	257.610	axial	peak	3	3	ABC	auto	–
Mn	259.372	axial	peak	3	3	ABC	auto	–
Mo	202.030	axial	peak	3	3	ABC	auto	–
Mo	281.615	axial	peak	3	3	ABC	auto	–
Na	589.592	radial	peak	3	3	ABC	auto	–
Na	588.995	radial	peak	3	3	static	auto	–
Ni	213.858	axial	peak	3	3	ABC	auto	–
Ni	221.648	axial	peak	3	3	ABC	auto	–
P	213.618	axial	peak	3	3	ABC	auto	–
P	214.914	axial	peak	3	3	ABC	auto	–
Pb	220.353	axial	peak	3	3	ABC	auto	–
Si	251.611	axial	peak	3	3	ABC	auto	–
Si	288.158	axial	peak	3	3	ABC	auto	–
Tl	190.796	axial	peak	3	3	ABC	auto	–
Zn	206.200	axial	peak	3	3	ABC	auto	–
Zn	213.856	axial	peak	3	3	ABC	auto	–

Results and Discussion

Using a high-resolution ICP-OES enables the interference-free analysis of trace elements as displayed in Table 4. Neither matrix based nor inter-element interferences were observed for the analysis of multiple lines of 20 typically measured trace elements. The investigation resulted in exceptional matrix-specific limits of detection in the low-ppb range (<20 µg/kg) for all investigated elements and lines. Method validation by measuring QC recovery of Cal.3 after 4 hours of constantly aspirating a 13% urea solution proves method robustness over a long term run, which is crucial for routine analysis. Recovery values between 97% and 104% were achieved.

Table 4: Overview of recovery values for CQ Cal.3 and achieved matrix specific limits of detection in 13% urea

Element	Line [nm]	Recovery QC Cal.3 [&]	Matrix specific LOD [mg/kg]
Al	396.152	100	0.010
Al	167.022	102	0.014
As	188.979	99.2	0.030
As	228.812	101	0.041
Ba	455.403	99.6	0.001
Ba	233.527	98.1	0.003

Element	**Line [nm]**	**Recovery QC Cal.3 [&]**	**Matrix specific LOD [mg/kg]**
Ca	396.847	100	0.006
Ca	393.366	99.9	0.004
Cd	214.441	98.0	0.002
Cd	226.502	97.7	0.002
Co	228.615	97.2	0.004
Co	237.863	98.0	0.011
Cr	205.552	100	0.011
Cr	267.716	97.2	0.005
Cu	324.754	100	0.004
Cu	327.396	101	0.011
Fe	259.940	102	0.014
Fe	238.204	99.3	0.022
K	766.491	97.4	0.018
K	769.897	106	0.016
Mg	279.553	100	0.001
Mg	285.213	100	0.003
Mn	257.610	100	0.0004
Mn	259.372	102	0.001
Mo	202.030	99.5	0.013
Mo	281.615	101	0.009
Na	589.592	103	0.014
Na	588.995	104	0.024
Ni	213.858	98.4	0.005
Ni	221.648	102	0.008
P	213.618	99.8	0.092
P	214.914	96.5	0.140
Pb	220.353	102	0.032
Si	251.611	101	0.016
Si	288.158	98.1	0.037
Tl	190.796	97.3	0.041
Zn	206.200	97.7	0.003
Zn	213.856	99.4	0.004

Conclusion

The yearly production of urea is amongst the highest of all synthetically produced chemicals, because of its versatile application in many industries. Urea contributes to food production as fertilizer, protects the environment as an ingredient of exhaust cleaning systems, and is used as starting material for the production of materials used every day. Therefore, the quality requirements for urea are high, which translates into a demanding task for quality-control labs on a daily basis.

While conventional ICP-OES systems struggle due to analytical challenges such as matrix bases spectral interferences and plasma robustness for matrix-rich samples, the PlasmaQuant 9100 Elite masters this demanding application without effort. Features such as the high-frequency generator and V-Shuttle torch allow for great plasma robustness in terms of short- and long-term stability. QC recovery values of 100% ± 4% are achieved after 4 hours of constantly running 13% urea samples. This high robustness allows for less dilution of the samples and therefore the possibility to reach lower limits of detection. In combination with the exceptionally high resolution, most sensitive lines can be used and compromises on line selection are not needed.

The PlasmaQuant 9100 Elite is able to achieve matrix dependent limits of detection which are about 100 times lower than the requirements of ISO 22241. The combination of high analytical performance and ease of use and data handling (automatic background correction) make the PlasmaQuant 9100 Elite the ideal tool for QC labs of the chemical industry.

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