AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

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SPECTROGREEN

Multi-Element Analysis of AdBlue® (Urea AUS 32) Following ISO 22241-2 Using ICP-OES with Dual Side-On Interface Plasma Observation

Introduction

Since 1992, when the first emission standard Euro 1 was introduced, maximum limits for the emission of air pollutants such as carbon monoxide (CO) and nitrous oxides (NOx) were set for newly registered vehicles.
To meet the decreasing maximum NOx emission limits, new technologies primarily for diesel engines had to be developed.

The selective catalytic reduction (SCR) has proven effective to reduce the emission of NOx from diesel engines using an additional, finely dosed fluid. It is a synthetically produced aqueous solution of urea that is marketed under the name of AdBlue® and stored in an extra tank inside the vehicle [1]. Applying the SCR technology, AdBlue® is injected into the exhaust stream. The released ammonia reduces the nitrous oxides to nitrogen and water at the catalyst's surface [1].

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a method of choice for the analysis of AdBlue®, due to its multi-element determination capability, large linear dynamic range, sensitivity and robustness.

This report demonstrates that the SPECTROGREEN has all the required analytical capabilities in terms of sensitivity, precision and accuracy to perform the analysis of AdBlue® according to ISO 22241-2. The SPECTROGREEN with Dual Side-On Interface enables high precision, high stability and low detection limits.

AdBlue® is a 32.5% solution of urea in deionized water [1]. The quality of AdBlue® is very important for its use, therefore regulated in the ISO standards 22241-1 to 4. The contamination limits of certain elements are detailed in Table 1 [2].

This report describes the basic methodology for the analysis of AdBlue® following ISO 22241-2. It presents typical detection limits for required elements together with studies on precision and accuracy using spike recovery measurements and the analysis of a control sample.

Table 1: Specification for AdBlue® following ISO 22241

	Max. levels [mg/kg]
Al	0.5
Ca	0.5
Cu	0.2
Cr	0.2
Fe	0.5
K	0.5
Mg	0.5
Na	0.5
Ni	0.2
PO_4	0.5
Zn	0.2

Experimental

Instrumentation

All measurements were performed with the SPECTROGREEN ICP optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) with Dual Side-On plasma observation. It allows for an average factor 2 enhanced sensitivity compared to single radial plasma observation and achieves a sensitivity comparable to vertical torch dual view systems, while eliminating typical axial view interferences. In addition, it offers a high matrix compatibility, a large linear dynamic range and excellent precision without the need to change the plasma observation mode during analysis. The SPECTROGREEN features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique. Consisting of two hollow section cast shells, optimized small volume and 15 linear CMOS detectors, the wavelength range between 165 and 770 nm can be analyzed, allowing complete spectrum capture within 3s. Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later point in time.

The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the UV is achieved, allowing for the determination of non-metals as well as the use of prominent and interference free lines in this region. An air-cooled, 27.12 MHz, free running type LDMOS ICP-generator is installed, which ensures excellent stability of the forward power even in the case of rapidly changing sample loads.

All relevant ICP operating parameters are software controlled, allowing easy selection of the optimum operating conditions. For sample introduction, a Noordermeer nebulizer and a cyclonic spray chamber were used. Additionally, as recommended in the ISO Norm, humidification of the nebulizer gas was accomplished using an Elegra Dual Argon Humidifier (Glass Expansion, Melbourne, Australia). The ICP operating conditions are given in Table 2.

Table 2: Typical ICP operating conditions for the analysis of AdBlue®

Power	1200W
Observation Mode	Dual-Side-On
Coolant flow	14.0 L/min
Auxiliary flow	1 L/min
Nebulizer flow	0.90 L/min
Plasma Torch	Quartz, fixed, 1.8 mm Injector tube
Spray Chamber	Cyclonic
Nebulizer	Noordermeer
Sample aspiration rate	2 mL/min
Replicate read time	50 s per replicate

Sample Preparation

Following ISO 22241-2, a solution of 32.5% urea (Urea pa, Merck KGa, Darmstadt) in deionized water was prepared. This solution was diluted 1:1 (25 mL urea solution filled up to 50 mL), spiked with a multi-element standard (EPA 200.7, Bernd Kraft GmbH, Duisburg, Germany) and acidified with 5% (v/v) suprapure HNO3 (Merck, Darmstadt, Germany). As specified in ISO 22241-2, five standards with concentrations of: 0, 0.05, 0.2, 0.4 and 1 mg/L were prepared and used. The internal standard (y) was added to all sample and standard solutions.

Results and Discussion

Table 3 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [3]:

$$\mathbf{LOD = 3\ RSD_b\ c / 100\ SBR}$$

Where:

RSD_b: - relative standard deviation of 10 replicates of the blank (in %)

c: - concentration of the standard

SBR: - signal to background ratio

Table 3: Limits of detection for the selected elements and emission lines with Dual Side-On plasma observation in µg/kg, in the original material

Element	λ [nm]	LOD [µg/kg]
Al	396.152	22.0
Ca	396.847	1.0
Cr	267.716	2.0
Cu	324.754	4.0
Fe	259.941	1.5
K	766.491	87.0
Mg	279.553	0.1
Na	589.592	17.0
Ni	231.604	2.5
P	177.495	5.0
Zn	213.856	0.5

Accuracy and precision

Accuracy and precision of the method using the SPECTROGREEN with DSOI plasma observation were investigated analyzing a synthetic QC sample (n=10). As shown in Table 4, excellent recoveries in the range of 97% to 102% were achieved for all elements. An average precision of below 0.8 % RSD could be reached. The higher RSDs for some elements are likely caused by the decomposition of the sample matrix, since the acidified aqueous urea solution decomposes to carbon dioxide and ammonia. This matrix change, even though small, continuously changes the structure of the carbon background emission and thus leads to some instability.

Table 4: Results for the synthetic QC sample

Element	λ [nm]	QQC theoretical value [µg/l]	Measured conc. [µg/l]	Recovery [%]	RSD [%]
Al	396.152	100	99.8	100	0.8
Ca	396.847	100	96.6	97	1.4
Cr	267.716	100	99	99	0.5
Cu	324.754	100	98.7	99	0.5
Fe	259.941	100	100	100	1.0
K	766.491	500	494	99	2.2
Mg	279.553	100	100	100	0.6
Na	589.592	100	99.7	100	0.4
Ni	231.604	100	102	102	0.5
P	177.495	500	507	101	0.3
Zn	213.856	100	100	100	0.5

Additionally, the accuracy of the method was tested using spike recovery measurements. For this, one sample was spiked with 100 µg/L of the target elements. Excellent recoveries between 98 and 103% were found for all elements. The results obtained are presented in Table 5.

Table 5: Recoveries of a 100 µg/L spike

Element	λ [nm]	Measured sample conc. [µg/L]	Measured sample + spike conc. [µg/L]	Measured spike conc. [µg/L]	Spike set value conc. [µg/L]	Recovery [%]
Al	396.152	14.2	115	101	100	101
Ca	396.847	12.6	112	99	100	99
Cr	267.716	<DL	98	98	100	98
Cu	324.754	4.1	104	100	100	100
Fe	259.941	<DL	100	100	100	100
K	766.491	<DL	502	502	500	100
Mg	279.553	3.4	105	102	100	102
Na	589.592	41.4	143	102	100	102
Ni	231.604	3.4	104	101	100	101
P	177.495	5.3	520	515	500	103
Zn	213.856	1.8	101	99	100	99

Stability test

To further prove the robustness of the method, a 3.5h stability test was performed. The results are shown in Figure 1. Very good stabilities were achieved for the target elements over the investigated time.

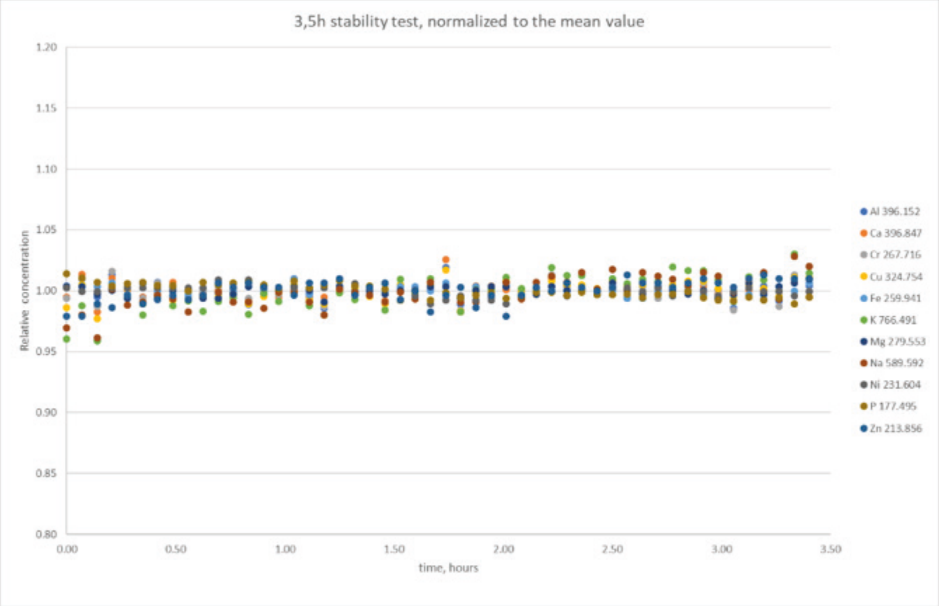

Figure 1: 3.5 h stability test

Conclusion

The SPECTROGREEN's unique radial Dual Side-On Interface (DSOI) technology represents a brand-new approach to the critical question of plasma view design. It provides about twice the sensitivity of conventional radial plasma-view instruments, reaching the sensitivity of vertical-torch dual-view designs, while avoiding their complexity.

The SPECTROGREEN is a powerful tool for the multi-element determination in aqueous urea solutions. Due to its sensitivity, the requirements of DIN ISO 22241-1 are easily fulfilled.

Using the DSOI interface, high sensitivity with good LODs were achieved for this application.

Additionally, excellent recoveries could be obtained for the analysis of a control sample, as well as for a spiked AdBlue® sample.

References

[1] https://www.vda.de/en/topics/innovation-and-technology/ad-blue/adBlue.html
[2] DIN ISO 22241-1
[3] P. W. J. M. Boumans, Spectrochim. Acta 46B, 431 (1991)

www.spectro.com

SPECTRO
AMETEK®

GERMANY
SPECTRO Analytical Instruments GmbH
Boschstrasse 10
D-47533 Kleve
Tel. +49.2821.892.0
spectro.sales@ametek.com

U.S.A.
SPECTRO Analytical Instruments Inc.
50 Fordham Rd
Wilmington 01887, MA
Tel. +1 800 548 5809
+1 201 642 3000
spectro-usa.sales@ametek.com

CHINA
AMETEK Commercial
Enterprise (Shanghai) CO., LTD.
Part A1, A4 2nd Floor Building No. 1 Plot Section
No. 526 Fute 3rd Road East; Pilot Free Trade Zone
200131 Shanghai
Tel. +86.400.022.7699
spectro-china.sales@ametek.com

Subsidiaries:
▶**FRANCE:** Tel. +33.1.3068.8970, spectro-france.sales@ametek.com ▶**GREAT BRITAIN:** Tel. +44.1162.462.950, spectro-uk.sales@ametek.com
▶**INDIA:** Tel. +91.22.6196.8200, sales.spectroindia@ametek.com ▶**ITALY:** Tel. +39.02.94693.1, spectro-italy.sales@ametek.com
▶**JAPAN:** Tel. +81.3.6809.2405, spectro-japan.info@ametek.co.jp ▶**SOUTH AFRICA:** Tel. +27.11.979.4241, spectro-za.sales@ametek.com

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