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Determination of Trace Elements in Aqueous Urea Solution (AUS 32) Diesel Exhaust Fluid by ICP-OES

Using an Agilent 5800 Radial View ICP-OES method in accordance with ISO 22241-2 standard

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Introduction

Poor ambient air quality in many towns and cities around the world is a major health concern. While different factors contribute to the problem, emissions from road transport are one of the biggest sources of pollutants. To reduce emissions from motor vehicles across India, the government will introduce and enforce new standards on 1 April 2020 (*1*). The Bharat Stage VI (BS-VI) standards, which supersede the existing BS-IV norms, are in line with the Euro VI standards that have already been adopted in many European countries.

To reduce emissions from diesel engines, especially nitrogen oxides (NOx), selective catalytic reduction (SCR) and exhaust gas recirculation (EGR) technologies are used. SCR requires a high-quality diesel exhaust fluid (DEF), also known as AUS 32 (aqueous urea solution), to treat exhaust gases and remove harmful pollutants, especially nitrogen dioxide (NO_2). AUS 32 consists of a high purity 32.5% solution of urea in water and is stored in its own tank in the car. Unlike fuel, AUS 32 is not

introduced into the engine but is injected into the flow of exhaust gases, where a chemical reaction converts NOx into harmless nitrogen and water.

The "AdBlue" trade name, which is registered by the German car manufacturers association (Verband der Automobilindustrie, VDA), is the best-known AUS 32 diesel exhaust fluid (*2*). VDA issues licenses to any manufacturers of AUS 32 wishing to use the trade name AdBlue. However, to maintain the quality of AdBlue, all licensees must adhere to ISO 22241 standards (*3*, *4*). The ISO 22241 guidelines also ensure that AUS 32 products comply with the requirements specified by engine manufacturers or government regulations. The maximum allowable concentrations for elemental impurities in AUS 32 per ISO-22241-1 quality requirements are given in Table 1 (*3*). The ISO 22241-2 test method for the determination of trace element content of AUS 32 uses ICP-OES (*4*).

Table 1. Specifications for elemental impurities in AUS 32 according to ISO-22241 quality requirements.

Specifications	Maximum Concentration (mg/kg)
Phosphate (PO$_4$)	0.5
Calcium	0.5
Iron	0.5
Copper	0.2
Zinc	0.2
Chromium	0.2
Nickel	0.2
Aluminum	0.5
Magnesium	0.5
Sodium	0.5
Potassium	0.5

To best support manufacturing quality standards, it is important that busy QC/QA testing laboratories maximize the productivity of their analytical workflows. For efficient elemental analysis, the Agilent 5800 ICP-OES uses enabling technologies such as IntelliQuant to provide detailed information on samples, and get the right results the first time. IntelliQuant captures data from the entire wavelength range as each sample is measured, then uses the data to calculate the approximate concentration of up to 70 elements in the sample. The extra information provided by IntelliQuant ensures that high-quality results are produced first time, without the need to remeasure samples or standards (*5*).

The 5800 ICP-OES uses a series of sensors together with the smart early maintenance feedback (EMF) feature to identify problems before they happen, maximizing instrument uptime and maintaining analytical performance. EMF can also be used to prompt maintenance after a specific parameter has been met, such as the number of samples measured or the time that the plasma has been turned on. As instrument performance is affected by different sample matrices, EMF can be set for specific sample types, so that more frequent instrument maintenance is carried out when measuring complex samples. By tracking actual instrument performance, maintenance can be scheduled at a convenient time for the analyst. A color-coding system shows which activities should be done immediately (red), and which are lower priority (green), as shown in Figure 1.
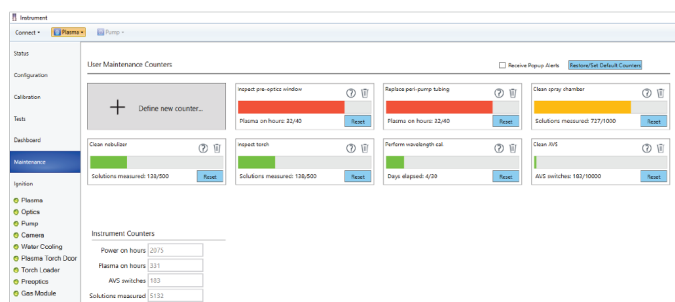

Figure 1. The EMF system monitors critical instrument parameters to maintain optimum analytical performance and reduce sample remeasurement.

In this study, an Agilent 5800 radial view (RV) ICP-OES was used to analyze AUS 32 diesel exhaust fluids according to the ISO-22241 standard test method.

Experimental

Instrumentation

An Agilent 5800 simultaneous RV ICP-OES was used for the analysis because of its tolerance of high levels of total dissolved solids (TDS). The sample introduction system consisted of a double-pass glass cyclonic spray chamber, a OneNeb series 2 nebulizer, and a 1.8 mm i.d. injector torch. An Agilent SPS 4 autosampler was used for the fast and automated delivery of the samples to the ICP-OES. The 5800 uses a solid-state RF (SSRF) system operating at 27 MHz to produce a robust plasma that is capable of excellent long-term analytical stability measurements of high TDS samples. The high speed (1 MHz) VistaChip III CCD detector enables fast warm up, fast analysis times, and high sensitivity. It also measures the full wavelength range from 167 to 785 nm simultaneously from a single entrance slit without the need for multiple detectors or slits. Instrument operating conditions used are listed in Table 2.

Table 2. Agilent 5800 RV ICP-OES instrument and method parameters.

Parameter	Setting
Read Time (s)	3
Replicates	3
Sample Uptake Delay (s)	12
Stabilization Time (s)	10
Rinse Time (s)	15
Pump Speed (rpm)	12
Fast Pump (rpm)	80
RF Power (kW)	1.40
Aux Flow (L/min)	1.0
Plasma Flow (L/min)	12.0
Nebulizer Flow (L/min)	0.7
Viewing Mode	Radial
Viewing Height (mm)	8
Sample Pump Tubing	White/white
Waste Pump Tubing	Blue/blue
Background Correction	Fitted

Preparation of sample and calibration standards

Working calibration standards for Al, Ca, Cr, Cu, Fe, K, Mg, Na, Ni, P, Zn were prepared in a urea matrix according to the ISO 22241-2 standard preparation procedure specified for ICP-OES. Agilent multi-element standards and a single element standard for phosphorus were used to prepare the calibration blank and standards. Standards were prepared from 0.3 to 5 ppm in a 1:1 diluted 32.5% aqueous urea solution, acidified with 5% HNO_3. Yttrium (10 ppm) was added as an internal standard (ISTD) to the blanks and standards. Linear calibrations were obtained for all analytes and wavelengths, with calibration coefficients greater than 0.999, as shown in Table 3. The intensity overlay graphs and calibration curves for Cr and Mg are shown in Figure 2.

The AUS 32 sample was obtained from a customer in North India. Because of more robust plasma conditions of the radial plasma configuration, the samples were prepared with a higher salt content, as specified in ISO 22241-2. Around 50 g of the sample was weighed into a 100 mL volumetric flask. 30 mL of water was added to the sample, followed by 5 mL of nitric acid. Yttrium (10 ppm) ISTD was added to the samples. The solution was made up to 100 mL using ultrapure water (UPW, Milli-Q 18.2 MΩ.cm) and mixed thoroughly. Two lots of spiked samples were prepared by spiking the samples with Al, Ca, Cr, Cu, Fe, K, Mg, Na, Ni, P, and Zn at 0.3 and 0.5 mg/kg.
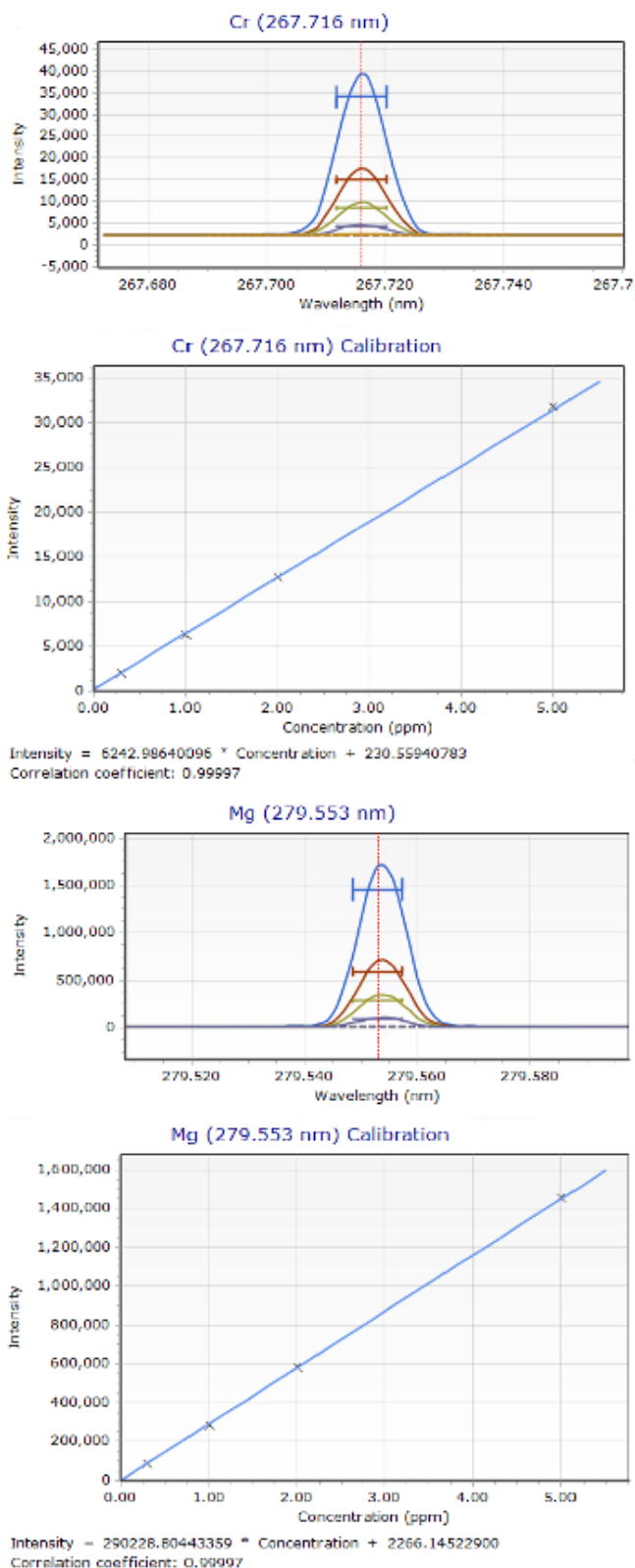

Intensity = 6242.98640096 * Concentration + 230.55940783
Correlation coefficient: 0.99997

Intensity = 290228.80443359 * Concentration + 2266.14522900
Correlation coefficient: 0.99997

Figure 2. Intensity overlay graphs and calibration curves for Cr 267.716 nm (top) and Mg 279.553 nm (bottom).

Results and discussion

Method detection limits (MDLs)

The method detection limits (MDLs) shown in Table 3 were based on three sigma of 10 replicate measurements of the blank AUS 32 solution diluted 1:1 in UPW. The MDLs are well below the maximum concentration levels specified in the ISO 22241-1 standard (Table 1).

Table 3. Method detection limits and calibration correlation coefficients.

Element	Wavelength (nm)	MDL (mg/kg)	Correlation Coefficient
Al	396.152	0.0204	0.99998
Ca	396.847	0.0020	0.99999
Cr	267.716	0.0034	0.99997
Cu	327.395	0.0053	0.99996
Fe	259.940	0.0019	0.99997
K	766.491	0.0263	0.99990
Mg	279.553	0.0004	0.99997
Na	589.592	0.0136	0.99995
Ni	231.604	0.0032	0.99996
P	213.618	0.0107	0.99986
Zn	213.857	0.0012	0.99995

Sample analysis

All the trace elements were measured in the AUS 32 sample using the 5800 RV ICP-OES. The sample was free from elemental impurities, as indicated by the results given in Table 4. All measured concentrations were below the MDL.

The spiked AUS 32 samples (spiked at 0.3 and 0.5 mg/kg) were also analyzed. All spike recoveries were between 90 to 110%, as shown in Table 4, indicating that the method can analyze the elements at these concentrations with good accuracy.

Long-term stability data

A long-term stability test was carried out by analyzing a solution of AUS 32 spiked at 0.5 mg/kg over four hours. The percent relative standard deviation (% RSD) for all elements was less than 2%, as shown in Table 5. The results show the robustness and precision of the method over the extended run. The radial view vertically oriented plasma of the 5800 RV ICP-OES and the SSRF system handle high TDS samples, such as AUS 32, with ease.

Sample analysis time

Sample-to-sample analysis time was only 52 seconds for all elements using the 5800 RV ICP-OES with SPS 4 autosampler. The fast analysis time and low gas consumption of the 5800 is due to a variety of technologies, including the high-speed VistaChip III CCD detector. The detector reads all wavelengths simultaneously, rather than bracketing high emission wavelengths and low emission wavelengths into separate sequential measurements like other simultaneous detectors. Considering all gas flows into the ICP-OES, not just the torch gas flows, the total argon consumption was less than 12 L per sample.

Table 4. Recovery results for AUS 32 samples spiked at two concentration levels.

Element and Wavelength (nm)	Measured Sample Conc (mg/kg)	Spiked Conc (mg/kg)	Measured Spiked Conc (mg/kg)	Recovery (%)	Spiked Conc (mg/kg)	Measured Spiked Conc (mg/kg)	Recovery (%)
Al 396.152	<MDL	0.300	0.308	103	0.500	0.506	101
Ca 396.847	<MDL	0.300	0.292	97	0.500	0.498	100
Cr 267.716	<MDL	0.300	0.302	101	0.500	0.502	100
Cu 327.395	<MDL	0.300	0.298	99	0.500	0.490	98
Fe 259.940	<MDL	0.300	0.302	101	0.500	0.500	100
K 766.491	<MDL	0.300	0.326	109	0.500	0.512	102
Mg 279.553	<MDL	0.300	0.300	100	0.500	0.496	99
Na 589.592	<MDL	0.300	0.310	103	0.500	0.514	103
Ni 231.604	<MDL	0.300	0.300	100	0.500	0.500	100
P 213.618	<MDL	0.300	0.306	102	0.500	0.502	100
Zn 213.857	<MDL	0.300	0.300	100	0.500	0.494	99

Table 5. Long-term stability results (% RSD) for an AUS 32 spiked sample analyzed over four hours.

Element	Wavelength	% RSD
Al	396.152	1.11
Ca	396.847	1.04
Cr	267.716	0.75
Cu	327.395	0.77
Fe	259.940	0.88
K	766.491	1.69
Mg	279.553	0.98
Na	589.592	1.41
Ni	231.604	0.36
P	213.618	1.12
Zn	213.857	0.98

Conclusion

The Agilent 5800 RV ICP-OES with SPS 4 autosampler was used for the determination of all elemental impurities in AUS 32 diesel exhaust fluid according to ISO 22241 standards. Following the sample preparation method specified in ISO 22241-2 for radial view ICP-OES, the MDLs for all elements were well below the maximum concentration levels specified in the ISO 22241-1 standard. The accuracy of the method was demonstrated by the excellent spike recovery test results of AUS 32 samples spiked at 0.3 and 0.5 mg/kg. The vertical plasma and robust 27 MHz SSRF system of the 5800 RV ICP-OES delivered excellent stability, with %RSD < 2% for all elements spiked into AUS 32 at 0.5 mg/kg.

For busy routine laboratories needing to maximize instrument performance, reduce operating costs, and minimize unplanned downtime, the 5800 ICP-OES offers several advantages. The fast analysis run time of only 52 s meant that less than 12 L of total argon was required per sample. Also, the EMF function allows analysts to manage any maintenance tasks in a planned, efficient, and preventive way, rather than having to disrupt the analysis to deal with a problem.

The quality control of the AUS 32 NOx reduction agent is vital in the drive to improve air quality in urban areas around the world. Reliable, robust, and fast QC is also important for manufacturers of AUS 32 wishing to use the AdBlue trade name. None of the elements determined in the AUS 32 sample was measured above the maximum concentration levels specified in the ISO 22241-1 standard.

References

1. Bharat Stage VI: Govt. Proposes BS VI Emission Norms For Quadricycles From April 1, 2020, https://www.news18.com/news/auto/govt-proposes-bs-vi-emission-norms-for-quadricycles-from-april-1-2020-2437349.html

2. Verband der Automobilindustrie, Information about VDA-trademark AdBlue, accessed March 2020, https://www.vda.de/en/topics/innovation-and-technology/ad-blue/AdBlue-brand-list-and-licensees-list.html

3. International Standard ISO 22241-1, Diesel engines — NOx reduction agent AUS 32 — Part 1: Quality requirements, accessed March 2020, https://www.iso.org/standard/66408.html

4. International Standard ISO 22241-2 Diesel engines—NOx reduction agent AUS 32—Part 2: Test methods, Second edition 2019-02, accessed March 2020, https://www.iso.org/standard/66409.html

5. Agilent IntelliQuant Software: For greater sample insight and simplified method development, Agilent publication, 5994-1516EN

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