SPOTLIGHT feature

Refractometry & Polarimetry

NO_X Reduction – How to Meet the Performance Emission Standards for Diesel Engines

Precise concentration measurements of urea solutions by using a refractometer

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Nitrogen oxide (NO_X) is a general term for different oxides of nitrogen. They are poisonous and irritate the human respiratory system. Nitrogen oxides also cause environmental pollution, for example when being part of smog or forming acid rain.

The main source of nitrogen oxide in the atmosphere is the combustion of diesel fuel in diesel engines. In order to protect human health and the environment the reduction of the NO_X emissions caused by diesel engines is an important challenge for vehicle manufacturers worldwide. In order to meet vehicle emission performance standards, a selective catalytic reduction (SCR) of the NO_X to nitrogen by injecting urea solutions into the exhaust is used for decreasing nitrogen oxides in diesel fuel exhausts.

The content of the urea solutions needs to be precisely measured to achieve an optimum reduction of nitrogen oxide in the diesel exhaust. The determination of the urea content is described in the revised ISO 22241-2: 2019 standard, Annex C.

Read on to find out how a refractometer is used for urea concentration measurement.

The process of selective catalytic reduction

Selective catalytic reduction is used to convert NO_X into nitrogen and water by using a urea solution and a suitable catalyst.

In the first step urea is injected into the exhaust pipeline, where it is thermally decomposed to ammonia and carbon dioxide:

$$(NH_2)_2\,CO + H_2O \rightarrow 2\,NH_3 + CO_2$$

In the second step the selective catalytic reaction takes place, in which the ammonia reacts with the NOx and oxygen to nitrogen and water, e.g:

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$

$$2\,NH_3 + NO + NO_2 \rightarrow 2\,N_2 + 3\,H_2O$$

With this SCR process the NO_X in diesel exhaust can be reduced by up to 90%. The products N_2 and H_2O released through the exhaust are harmless and will not cause any damages to the environment.

For best conversion, the stoichiometric rate between the NOx and urea solution needs to be correct. This requires an exact knowledge of the urea concentration in the injected urea solution. If the ratio is wrong, the NOx emission could be increased and/or damages to the SCR catalyst may occur. Therefore, quality control of the urea solution needs to be very strict. The test methods for aqueous urea solutions with a urea content of 32% (AUS 32) are given in ISO 22241-2 (2019).

Technical requirements for the refractometer according to ISO 22241-2 (2019)

ISO 22241-2 (2019) is the international standard for the measurement of aqueous urea solutions (AUS 32) used for diesel engines. Synonyms for these urea solutions are AdBlue (registered trademark of the German Automotive Industry), DEF (Diesel Exhaust Fluid), and ARLA (Agente Redutor Liquido de Óxido de Nitrogênio Automotivo). Annex C of ISO 22241-2 describes the determination of the refractive index and urea content in the range of 30% to 35%.

ISO 22241 requirements for the refractometer to be used for urea content measurement:

Wavelength [nm]	589.3
Measuring range [nD]	1.33000 – 1.39000
Resolution [nD]	0.00001
Temperature control [°C]	20 ± 0.1°C
Certified reference material (CRM)	Traceable to a national measurement institute with an uncertainty of ±0.00005 nD

According to ISO 22241-2 a weekly control of the refractometer by using water and a verified CRM has to be carried out with a maximum allowed deviation of 0.00005 nD from the certified refractive index value. If the deviation is higher, the instrument needs to be readjusted. If the refractometer cannot be adjusted within the prescribed limits, the instrument cannot be used for this application anymore.

Figure 1: Abbemat 3200 refractometer from Anton Paar

From the measured refractive index the urea content wU has to be calculated according to the formula given in C.6. of ISO 22241-2:

$w_U = (-742.747\,88 \times (n_D^{20})^2 + 2\,669.653\,61 \times (n_D^{20}) - 2\,238.799\,1) - B$

where

n_D^{20} is the refractive index measured at 20 °C and

B is the Biuret mass fraction (%), which has to be determined photometrically according to Annex E of the ISO standard.

The required repeatability and reproducibility are as follows:

Property	**Repeatability r**	**Reproducibility R**
Urea content (mass fraction, in %)	0.154	0.211
Refractive index nD20	0.000 25	0.000 33

The fulfilment of this quality parameter has to be ensured throughout the entire distribution chain from production over transport and bottling to the final use in the diesel engine.

Urea content measurements with an Abbemat refractometer

Abbemat refractometers from Anton Paar fulfil the requirements of the latest ISO 22241-2 standard. They come with internal temperature control with an accuracy of 0.03°C to ensure the correct measuring temperature and thus a very high accuracy in refractive index measurement of ±0.00002 nD. There is no need to use an external water bath which would cause additional costs and maintenance.

Temperature is an important influencing factor on the measuring result and wrong temperature measurements lead to wrong refractive index results. Therefore, the measured temperature – or, more exactly, the prism surface temperature of the refractometer – must be correct. In order to check and adjust the prism surface temperature of Abbemat refractometers Anton Paar offers the patented Abbemat T-Check which allows precise checking and, if required, adjustment of the temperature sensor. This ensures precise refractive index measurements for years.

Automatic measurements with Abbemat refractometers are operator-independent and cannot be manipulated.

A configurable check reminder function makes sure that weekly or monthly checks will be performed. These checks are recorded and the check history can be reviewed at any time. If an adjustment is required, a user-guided adjustment procedure ensures the proper and precise adjustment of the instrument with water and the CRM. All adjustment data will be automatically stored on the instrument for later review (adjustment history). The configurable user management of Abbemat refractometers ensures that only authorised personnel is allowed to perform adjustments.

Abbemat refractometers from Anton Paar are delivered with a ready-to-use method in accordance with the latest ISO 22241-2 standard for urea concentration measurements in the range between 30% and 35%. Operators enter the previously determined Biuret mass fraction directly into the refractometer and Abbemat automatically calculates and displays the urea concentration accordingly. The results are recorded and can be printed in the form of a configurable report or transferred to a PC for further use.

In addition to the urea content measurement according to ISO 22241-2, further urea methods are available on the Abbemat refractometers: One urea method is based on the CRC Handbook of Chemistry and Physics, 96 Edition: This method is valid at a measuring temperature of 20°C and offers a urea concentration range between 0 % and 46%. The accuracy of this method is up to 0.11 g/100 g solution.

Anton Paar additionally developed a urea method that is valid for a temperature range from 10°C to 85°C and a urea concentration range from 0 g to 60 g/100 g solution. The accuracy of this method is 0.56 g/100 g.

Benefits of precise urea concentration measurements

A very strict and precise control of the urea concentration is required to meet governmental regulations, for example Euro 6 standards. Furthermore, a correctly prepared urea solution avoids damages and extends the lifetime of the SCR catalyst. The use of precise urea solutions reduces the exhaust NO_X emissions by up to 90 %. Further, the fuel consumption can be cut down by approx. 5 %. Another benefit is the biodegradability of urea.

Summary

NO_X in diesel exhaust is one of the main polluting gases worldwide and causes several health- and environmental issues. In order to reduce the NO_X in the exhaust the selective catalytic reduction using a well-defined urea solution is widely in place to fulfil the latest governmental regulations. The measurement of the exact urea content is essential - technically, economically, and ecologically - to reduce the NO_X in the best way possible. The measurement of the urea concentration is defined in the International Standard ISO 22241-2 (2019).

Abbemat refractometers from Anton Paar fulfil the requirements of these standards and come with useful features to ensure a fast, precise, and reliable measurement of the urea content.