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ANNEX IV

Activity-specific monitoring methodologies related to installations (Article 20(2))

16. DETERMINATION OF NITROUS OXIDE (N₂O) EMISSIONS FROM NITRIC ACID, ADIPIC ACID, CAPROLACTAM, GLYOXAL AND GLYOXYLIC ACID PRODUCTION AS LISTED IN ANNEX I TO DIRECTIVE 2003/87/EC

A. Scope

Each operator shall consider for each activity from which N₂O emissions result, all sources emitting N₂O from production processes, including where N₂O emissions from production are channelled through any abatement equipment. This includes any of the following:

- (a) nitric acid production – N₂O emissions from the catalytic oxidation of ammonia and/or from the NO_x/N₂O abatement units;
- (b) adipic acid production – N₂O emissions including from the oxidation reaction, any direct process venting and/or any emissions control equipment;
- (c) glyoxal and glyoxylic acid production – N₂O emissions including from the process reactions, any direct process venting and/or any emissions control equipment;
- (d) caprolactam production – N₂O emissions including from the process reactions, any direct process venting and/or any emissions control equipment.

These provisions shall not apply to any N₂O emissions from the combustion of fuels.

B. Determination of N₂O emissions

B.1. Annual N₂O emissions

The operator shall monitor emissions of N₂O from nitric acid production using continuous emissions measurement. The operator shall monitor emissions of N₂O from adipic acid, caprolactam, glyoxal and glyoxylic acid production using a measurement-based methodology for abated emissions and a calculation-based method (based on a mass balance methodology) for temporary occurrences of unabated emissions.

For each emission source where continuous emissions measurement is applied, the operator shall consider the total annual emissions to be the sum of all hourly emissions using equation 1 given in section 3 of Annex VIII.

B.2. Hourly N₂O emissions

The operator shall calculate annual average hourly N₂O emissions for each source where continuous emission measurement is applied using equation 2 given in section 3 of Annex VIII.

The operator shall determine hourly N₂O concentrations in the flue gas from each emission source using a measurement-based methodology at a representative point, after the NO_x/N₂O abatement equipment, where abatement is used. The operator shall apply techniques capable of measuring N₂O concentrations of all emission sources during both abated and unabated conditions. Where uncertainties increase during such periods, the operator shall take them into account in the uncertainty assessment.

The operator shall adjust all measurements to a dry gas basis where required and report them consistently.

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B.3. Determination of flue gas flow

The operator shall use the methods for monitoring flue gas flow set out in Article 43(5) of this Regulation for measuring the flue gas flow for N₂O emissions monitoring. For nitric acid production, the operator shall apply the method in accordance with point (a) of Article 43(5) unless it is technically not feasible. In that case and upon approval by the competent authority, the operator shall apply an alternative method, including by a mass balance methodology based on significant parameters such as ammonia input load, or determination of flow by continuous emissions flow measurement.

The flue gas flow shall be calculated in accordance with the following formula:

$$V_{\text{flue gas flow}} [\text{Nm}^3/\text{h}] = V_{\text{air}} * (1 - O_{2, \text{air}}) / (1 - O_{2, \text{flue gas}})$$

Where:

V_{air}	= Total input air flow in Nm ³ /h at standard conditions;
$O_{2, \text{air}}$	= Volume fraction of O ₂ in dry air [= 0,2095];
$O_{2, \text{flue gas}}$	= Volume fraction of O ₂ in the flue gas.

The V_{air} shall be calculated as the sum of all air flows entering the nitric acid production unit.

The operator shall apply the following formula, unless stated otherwise in its monitoring plan:

$$V_{\text{air}} = V_{\text{prim}} + V_{\text{sec}} + V_{\text{seal}}$$

Where:

V_{prim}	= Primary input air flow in Nm ³ /h at standard conditions;
V_{sec}	= Secondary input air flow in Nm ³ /h at standard conditions;
V_{seal}	= Seal input air flow in Nm ³ /h at standard conditions.

The operator shall determine V_{prim} by continuous flow measurement before the mixing with ammonia takes place. The operator shall determine V_{sec} by continuous flow measurement, including where the measurement is before the heat recovery unit. For V_{seal} the operator shall consider the purged airflow within the nitric acid production process.

For input air streams accounting for cumulatively less than 2,5 % of the total air flow, the competent authority may accept estimation methods for the determination of that air flow rate proposed by the operator based on industry best practices.

The operator shall provide evidence through measurements under normal operating conditions that the flue gas flow measured is sufficiently homogeneous to allow for the proposed measurement method. Where non-homogeneous flow is confirmed through these measurements, the operator shall take that into account when determining appropriate monitoring methods and when calculating the uncertainty in the N₂O emissions.

The operator shall adjust all measurements to a dry gas basis and report them consistently.

B.4. Oxygen (O₂) concentrations

The operator shall measure the oxygen concentrations in the flue gas where necessary for calculating the flue gas flow in accordance with subsection B.3 of this section of Annex IV. In doing so, the operator shall comply with the requirements for concentration measurements within Article 41(1) and (2). In determining the uncertainty of N₂O emissions, the operator shall take the uncertainty of O₂ concentration measurements into account.

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The operator shall adjust all measurements to a dry gas basis where required and report them consistently.

B.5. *Calculation of N₂O emissions*

For specific periods of unabated emissions of N₂O from adipic acid, caprolactam, glyoxal and glyoxylic acid production, including unabated emissions from venting for safety reasons and when abatement plant fails, and where continuous emissions monitoring of N₂O is technically not feasible, the operator shall subject to the approval of the specific methodology by the competent authority calculate N₂O emissions using a mass balance methodology. For this purpose the overall uncertainty shall be similar to the result of applying the tier requirements of Article 41(1) and (2). The operator shall base the calculation method on the maximum potential emission rate of N₂O from the chemical reaction taking place at the time and the period of the emission.

The operator shall take the uncertainty in any calculated emissions for a specific emission source into account in determining the annual average hourly uncertainty for the emission source.

B.6. *Determination of activity production rates*

Production rates shall be calculated using daily production reports and hours of operation.

B.7. *Sampling rates*

Valid hourly averages or averages for shorter reference periods shall be calculated in accordance with Article 44 for:

- (a) concentration of N₂O in the flue gas;
- (b) total flue gas flow where this is measured directly and where required;
- (c) all gas flows and oxygen concentrations necessary to determine the total flue gas flow indirectly.

C. **Determination of annual CO₂ equivalent – CO_{2(e)}**

The operator shall convert the total annual N₂O emissions from all emissions sources, measured in tonnes to three decimal places, to annual CO_{2(e)} in rounded tonnes, using the following formula and the GWP values in Annex VI section 3:

$$\text{CO}_{2(e)} [\text{t}] = \text{N}_2\text{O}_{\text{annual}} [\text{t}] \times \text{GWP}_{\text{N}_2\text{O}}$$

Where:

$\text{N}_2\text{O}_{\text{annual}}$ = total annual N₂O emissions, calculated according to equation 1 given in section 3 of Annex VIII.

The total annual CO_{2(e)} generated by all emission sources and any direct CO₂ emissions from other emission sources included under the greenhouse gas permit shall be added to the total annual CO₂ emissions generated by the installation and shall be used for reporting and surrendering allowances.

Total annual emissions of N₂O shall be reported in tonnes to three decimal places and as CO_{2(e)} in rounded tonnes.

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Changes and effects yet to be applied to :

- Regulation amendment to earlier affecting provision S.I. 2020/1265, Sch. 4 by [S.I. 2020/1557 art. 35\(3\)-\(8\)](#)
- Regulation amendment to earlier affecting provision S.I. 2020/1265, Sch. 4 by [S.I. 2021/1455 art. 22\(2\)-\(9\)](#)
- Regulation amendment to earlier affecting provision S.I. 2020/1265, Sch. 4 by [S.I. 2022/1173 art. 13](#)
- Regulation amendment to earlier affecting provision S.I. 2020/1265, Sch. 4 by [S.I. 2023/850 art. 8\(2\)](#)
- Regulation amendment to earlier affecting provision S.I. 2020/1265, Sch. 7 para. 13 by [S.I. 2022/1173 art. 17\(3\)](#)
- Regulation modified by [S.I. 2020/1265 art. 24Sch. 4](#)
- Regulation modified by [S.I. 2020/1265 Sch. 7 para. 13](#)
- Regulation modified by 2019 c. 1, s. 77(4) (as substituted) by [2020 c. 14 Sch. 12 para. 7\(3\)](#)
- Regulation power to amend conferred by 2019 c. 1, ss. 76, 77 (as amended) by [2020 c. 14 Sch. 12 para. 4\(4\)\(b\)\(i\)7\(2\)\(b\)](#)
- Regulation power to amend conferred by 2019 c. 1, ss. 76, 77 (as amended) by [2020 c. 14 Sch. 12 para. 5\(b\)7\(2\)\(b\)](#)
- Regulation restricted by [S.I. 2020/1265 Sch. 8 para. 5\(3\)](#)