

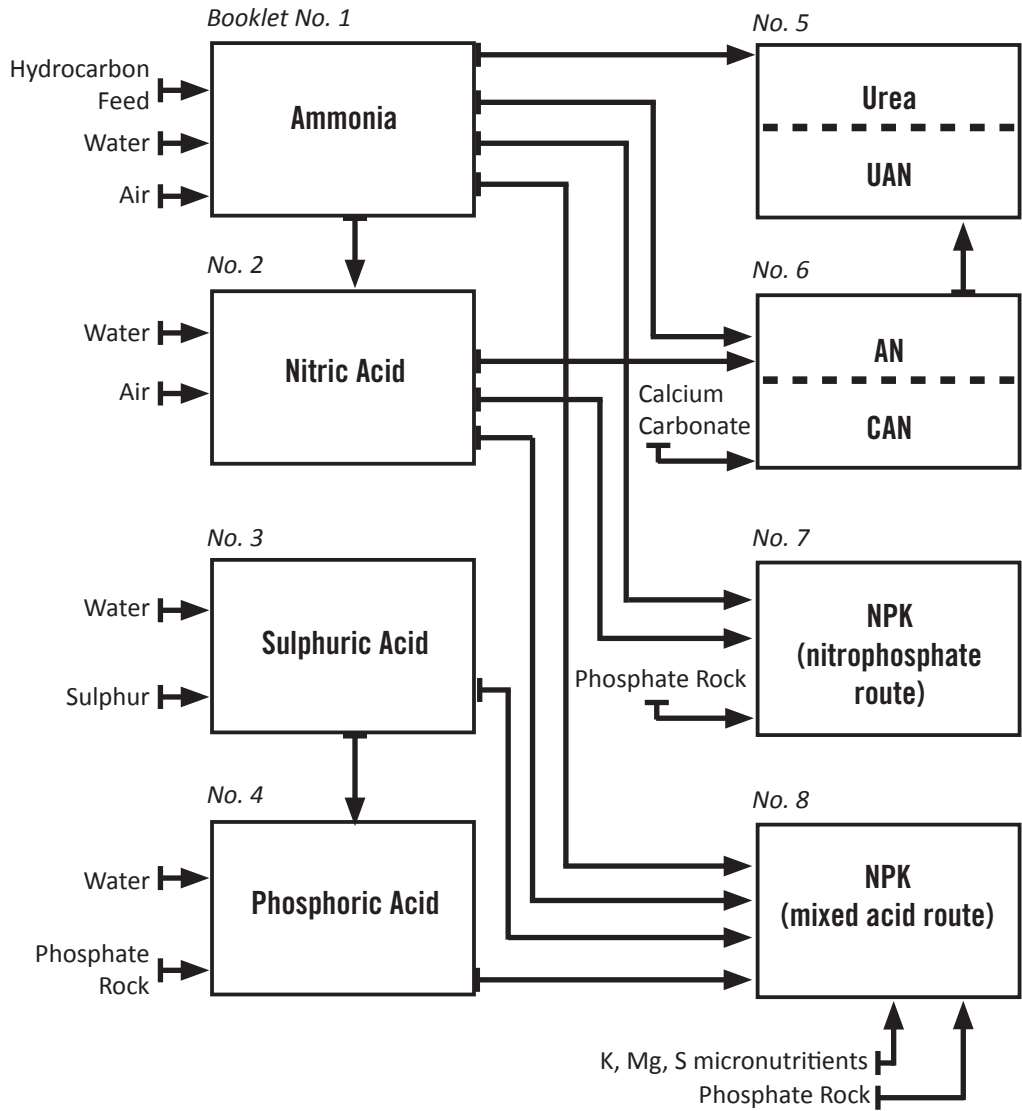








# Fertilizers Europe BAT Booklets



















































































Method	Potential Interferences	Comments
<b>Oxides of Nitrogen</b>		
Chemiluminescence	CO <sub>2</sub> , H <sub>2</sub> O and NH <sub>3</sub>	
<i>In-situ</i> NDIR	H <sub>2</sub> O and particulates	Interferences can be reduced by precise selection of the wavelength.
<b>Carbon Monoxide/Carbon Dioxide</b>		
Extractive NDIR	H <sub>2</sub> O and particulates	Straightforward conditioning
<i>In-situ</i> IR (fibre optics)	Other IR absorbing components, H <sub>2</sub> O, particulates, fibre optic losses	Reduced accuracy due to interferences.

## 2.4 Manual Methods

### 2.4.1 Sulphur dioxide

Standard methods rely on the solubility and acidic nature of the gas. An oxidising agent is generally used to convert the SO<sub>2</sub> to SO<sub>3</sub>. National standard methods include the use of hydrogen peroxide solution as the oxidising agent with titration against standard alkali or gravimetric analysis using barium chloride and hydrochloric acid to precipitate the sulphate. An alternative to this uses a sample collected in hydrogen peroxide solution and titration against barium perchlorate with thiorin as indicator. A method which draws the filtered gas through a standard solution of iodine in potassium iodide is also used. The unreacted iodine is determined by titration with sodium thiosulphate and the SO<sub>2</sub> calculated from the amount of iodine used to oxidise the SO<sub>2</sub>.

All the methods have errors associated with the interferences and the user should be knowledgeable about the method and its suitability.

### 2.4.2 Oxides of nitrogen

The instrumental methods given in 2.3 are preferred.

### 2.4.3 Carbon monoxide/carbon dioxide

These gases are generally measured by solution absorption into liquid reagents specific for each gas.







### 3. Emissions into Water

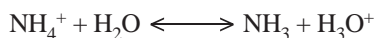
Whilst emissions into water are likely to be intermittent and of a low level, it is probable that any site operating an ammonia plant will have at least one overall consent for emissions into water and a requirement for plant monitoring. Typical monitoring methods may rely on flow proportioned sample collection or high frequency spot sampling and flow measurement. In either case the samples obtained may be analysed as follows:-

#### 3.1 Ammonia/Ammoniacal N

The spectrophotometric method for ammonia relies on the reaction in which monochloramine is reacted with phenol to form an indophenol blue compound. This method is particularly suitable for the determination of ammonia in cooling waters derived from saline sources (dock, estuarine or sea water) and may be used in continuous flow colorimetry.

Ion selective electrodes can also be used and are suitable for saline applications as well as pure water.

Note that free ammonia exists in equilibrium with  $\text{NH}_4^+$  as follows:-



and that the equilibrium depends on pH. The above method determines the  $\text{NH}_4^+$  ammonia. Free ammonia is particularly toxic to fish and should an incident occur, it may be more important to relate the  $\text{NH}_4^+$  result to free ammonia. Any suitable pH determination may be used and the free ammonia estimated as given in "Hampson B L, J Cons Int Explor, Mer, 1977,37, 11" and "Whitfield M, J Mar Biol. Ass UK, 1974,54, 562".

Manual laboratory based methods may be used for spot checks using Kjeldahl methods for the determination of organic and ammoniacal nitrogen in a mineralised sample.

#### 3.2 Methanol

The spectrophotometric method for methanol relies on the oxidation reactions of potassium permanganate under acid conditions to give formaldehyde. The formaldehyde is reacted with acetylacetone in the presence of excess ammonium salt, to form diacetyldihydrotoluidine. The method may be used in continuous flow colorimetry or gas chromatography.





## APPENDIX 2 GENERAL PRODUCT INFORMATION ON AMMONIA

### 1. Identification

Name	: Ammonia
Commonly used synonyms	: Liquid Ammonia
C.A.S. Registry number	: 7664-41-7
EINECS Number	: 231-635-3
EINECS Name	: Anhydrous Ammonia
Molecular formula	: NH <sub>3</sub>

### 2. Hazards to Man and the Environment

#### To man

Ammonia is toxic by inhalation and pulmonary oedema may occur up to 48 hours after severe exposure and could be fatal.

Vapours cause irritation and watering of eyes and in the presence of moisture, irritation of the skin.

Liquid ammonia splashes may produce severe burns to the skin and permanent damage to the eyes.

In enclosed spaces (eg vessels, closed workshops) ammonia vapour may be flammable/explosive.

#### To the environment

Ammonia is toxic to aquatic life.

### 3. Physical and Chemical Properties

Appearance	: Colourless liquefied gas
Odour	: Pungent, suffocating
pH water solution (1%)	: 11.7
Melting point (triple point)	: -77.7°C
Boiling point	: -33.4°C at 101.3kPa
Explosive limits	: 16-27% NH <sub>3</sub> by vol. in air at 0°C
Auto-ignition temperature	: 651°C
Vapour pressure	: 1013kPa at 25°C
Relative vapour density	: 0.6 (air =1)
Solubility in water	: 529g.l <sup>-1</sup> at 20°C
Solubility in organic solvents	: Soluble in alcohol, acetone, chloroform
Liquid density	: 0.6386g.cm <sup>-3</sup> (at 0°C, 101.3kPa)
Gas density	: 0.7714g.l <sup>-1</sup> (at 0°C, 101.3kPa)







Best Available Techniques Booklets were first issued by Fertilizers Europe in 1995. Second revised edition 2000.

1. Production of Ammonia
2. Production of Nitric Acid
3. Production of Sulphuric Acid (in collaboration with ESA)
4. Production of Phosphoric Acid
5. Production of Urea and Urea-Ammonium Nitrate
6. Production of Ammonium Nitrate and Calcium Ammonium Nitrate
7. Production of NPK Compound Fertilizers by Nitrophosphate Route
8. Production of NPK Compound Fertilizers by Mixed Acid Route



Avenue E. van Nieuwenhuysse 4/6  
B-1160, Brussels, Belgique  
Tel: +32 2 675 3550  
Fax: +32 2 675 3961  
main@fertilizerseurope.com

[www.fertilizerseurope.com](http://www.fertilizerseurope.com)

[twitter.com/FertilizersEuro](https://twitter.com/FertilizersEuro)



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