N_2O-Measurement Methods

Nitrous Oxide/Laughing Gas

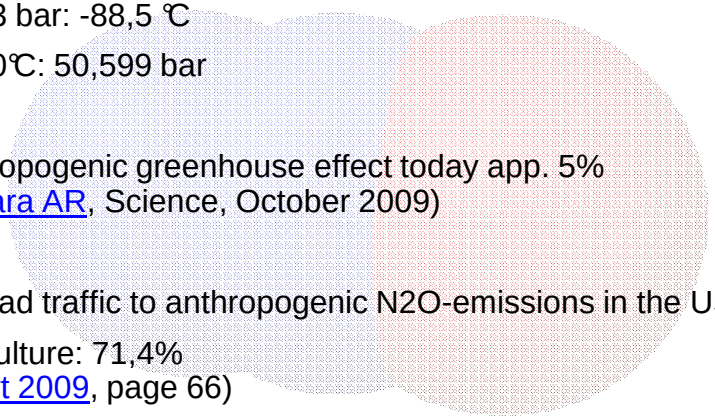
Molar mass: 44,013 kg/kmol

Gas density at 0℃ and 1,013 bar: 1,9781 kg/m³

Gas density in relation to air: 1,5299

Boiling point at 1,013 bar: -88,5 ℃

Vapor pressure at 20℃: 50,599 bar



Contribution to anthropogenic greenhouse effect today app. 5%
(Source: Ravishankara AR, Science, October 2009)

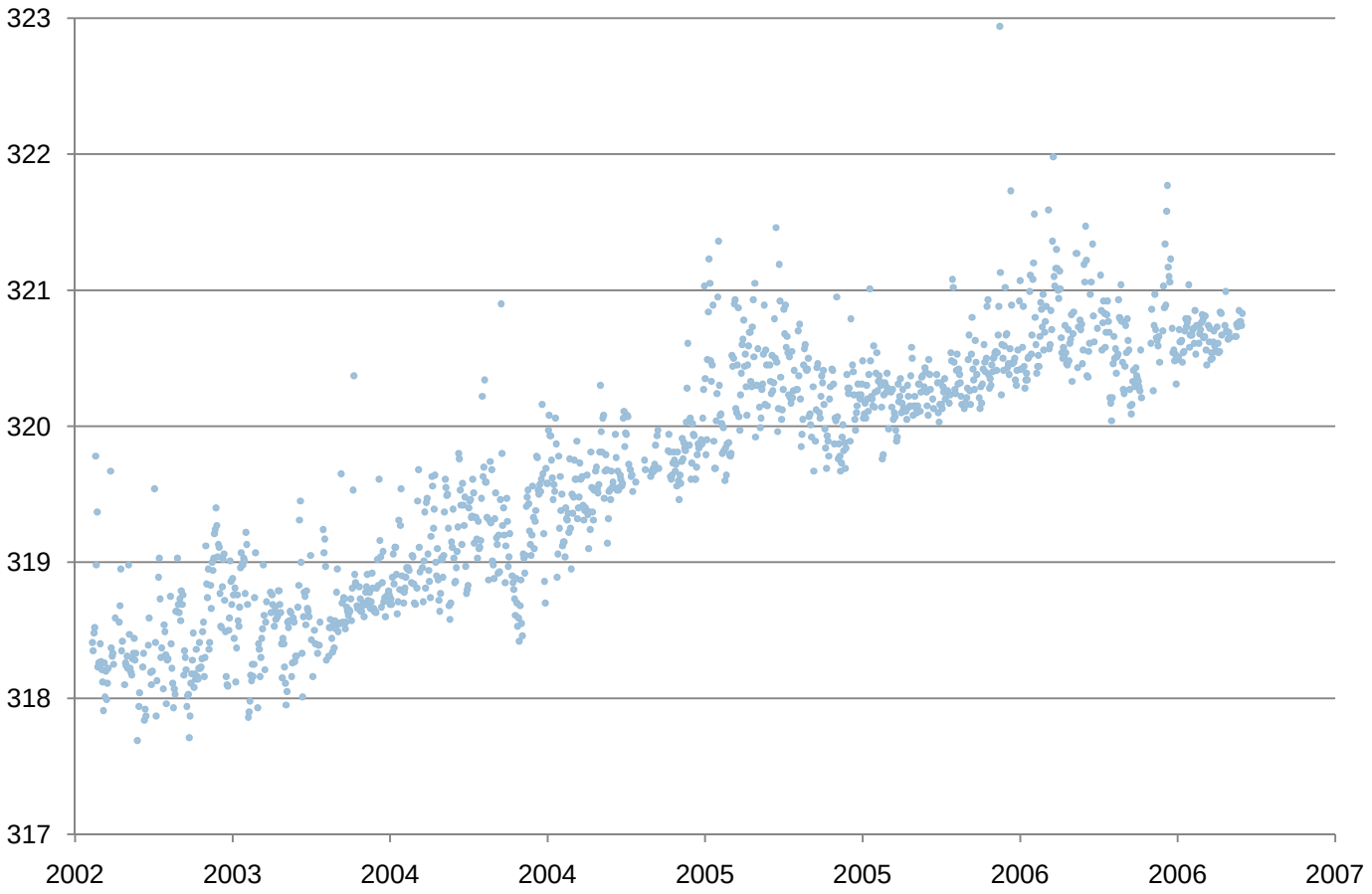
Contribution of on road traffic to anthropogenic N2O-emissions in the US 2007: 9,7%

Contribution of agriculture: 71,4%
(Source: EPA-Report 2009, page 66)

→ Contribution of N2O from on road traffic to anthropogenic greenhouse effect <0,5%!

N_2O-Measurement Methods

N_2O in ambient



Measurement station of German Umweltbundesamt at Schneefernerhaus/Zugspitze

N_2O-Measurement Methods

Definitions

- **LoD (Limit of Detection)**
  The LoD is the smallest quantity that can be reliably (99%) distingushed from zero
  DIN32645 / Skoog&Leary „Principles of Instrumental Analysis“: LoD = avg. (blank) + 3 x std. dev. (blank)

- **LoQ (Limit of Quantification)**
  Das LoQ is the smallest quantity at which two different concentrations can be distinguished reliably.
  DIN32645: LoQ= 3 x LoD or LoQ=10 x std. dev. (blank)
  Skoog&Leary „Principles of Instrumental Analysis“: LoQ=10 x std. dev. (blank)

- **Interpretation of the Values according DIN32645**

Result	**Interpretation**	**further Information**
x < LoD	Not measured	< 2 x LoD
LoD <= x < LoQ	measured	
LoQ <= x	Sufficient	Within confidence region

N_2O-Measurement Methods

Requirements for a reliable measurement method

- actual emission limit for N_2O: 0,010 g/mi
- measurement from bag → non or quasi continuous measurement is sufficient
- For a reliable measurement of air bag LoQ has to be at 300ppb (typicall background concentration)
  → LoD has to be in the order of 30 ppb
- No or little cross interference at typical bag concentrations:

2,5% CO2	20ppm THC
2,5% H2O	5ppm CH4
200ppm CO	5ppm NOx

- an offset of 0,1ppm in the measurement of te air bag results in a 30% error at limit level

N_2O-Measurement Methods

EPA-legislation allows four types of analyzers for N_2O:

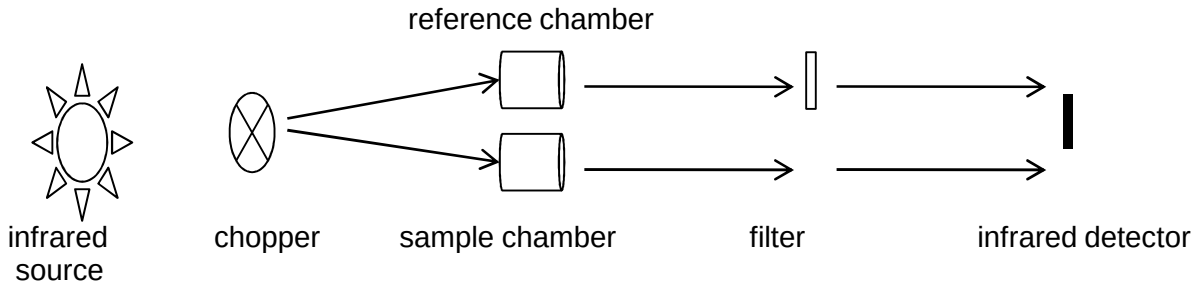
(Source: § 86.167-12 N2O measurement devices)

	Range	LoD	Resolution	Rising time (T_{10}-T_{90})	Sample rate	Cross sensitivity
NDIR	> 10ppm	0,3ppm				CO, CO_2, H_2O
FTIR		0,05ppm				
Photoacoustic analyzer		0,03ppm			0,05-0,2Hz	CO, CO_2, H_2O
Gas chromatography analyzer				-	-	
QCL analyzer*	100-10000ppm	0,20-10ppm	0,01ppm	<2s (planned <1s)	10Hz	
Mass Spectrometer*	Not applicable due to massive CO_2 interference					CO_2

*QCL-analyzer and mass spectrometer are not mentioned in EPA-legislation

N_2O-Measurement Methods

NDIR

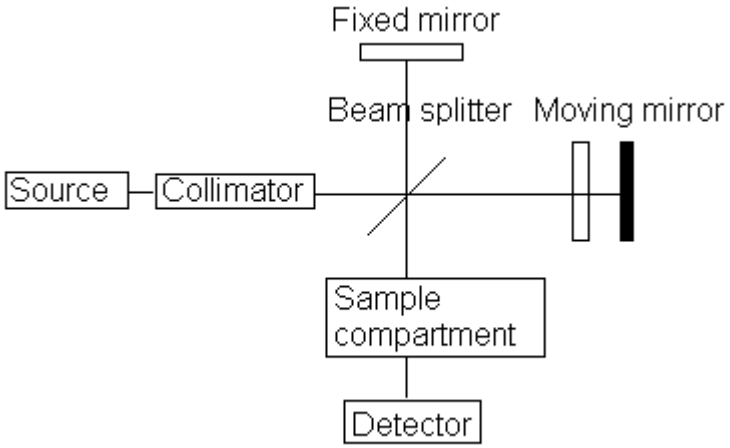


The main components are an infrared source, a sample chamber or light tube, a wavelength filter, and the infrared detector. The gas is pumped into the sample chamber, and gas concentration is measured electro-optically by its absorption of a specific wavelength in the infrared (IR). The IR light is directed through the sample chamber towards the detector. In parallel there is an other chamber with an enclosed reference gas, typically nitrogen. The detector has an optical filter in front of it that eliminates all light except the wavelength that the selected gas molecules can absorb. Ideally other gas molecules do not absorb light at this wavelength, and do not affect the amount of light reaching the detector.

Advantages	Disadvantages	Cross Sensitivity
• Standard method • Simple operation • Simple integration into existing benches	• High cross sensitivities • Mathematical correction necessary • LoD not sufficient	CO2 H2O CO (NO, HC, SO2)

N_2O-Measurement Methods

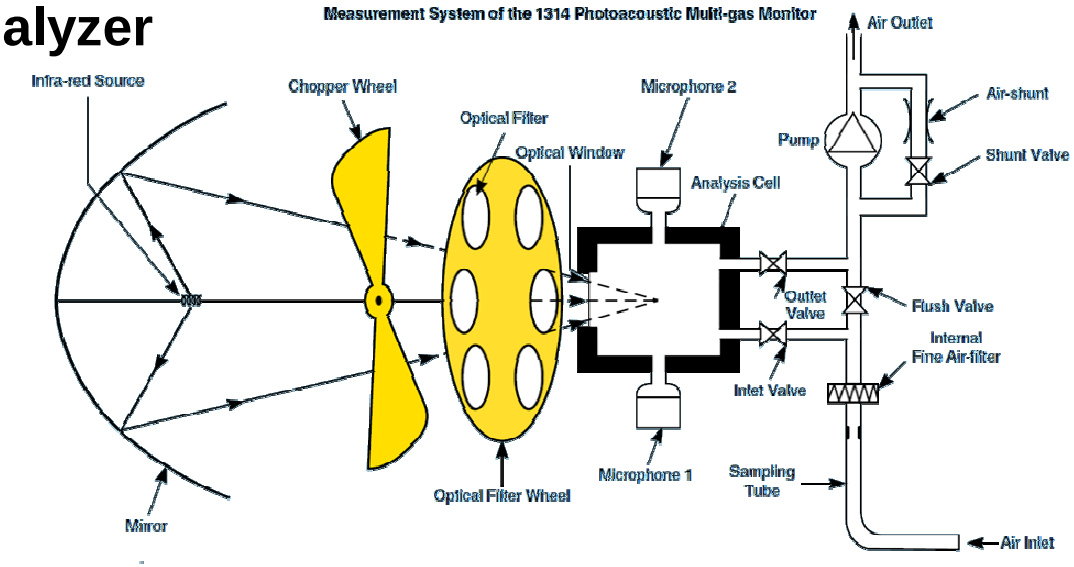
FTIR



Advantages	Disadvantages	Querempfindlichkeit
• Theoretically high LoD • Less cross interference as compared to NDIR	• Limited experience with bag measurement • Needs liquid nitrogen	Limited experience in the range below 1 ppm

N_2O-Measurement Methods

Photoacoustic analyzer

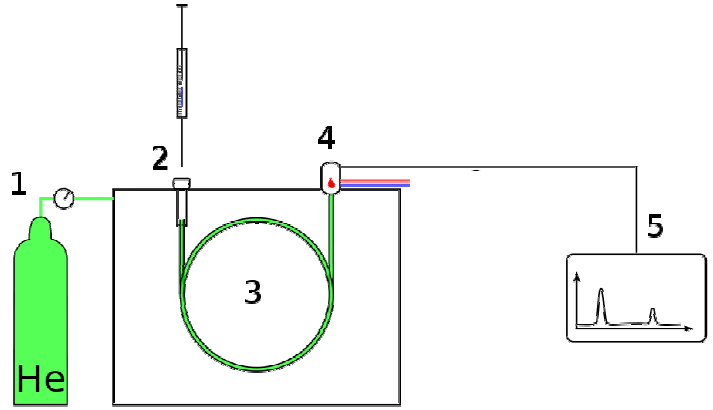


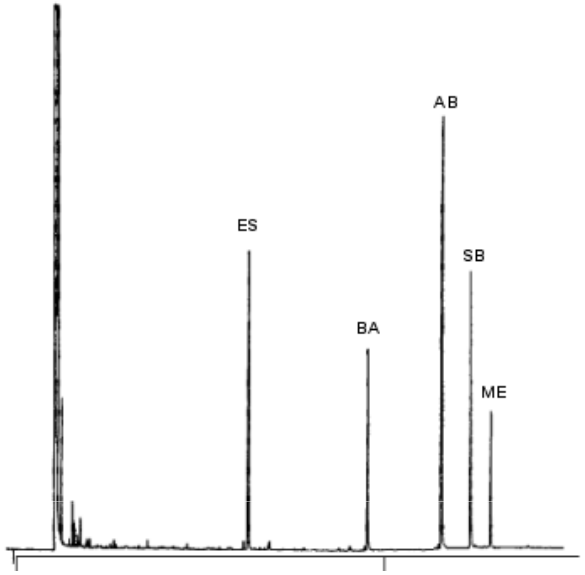
Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy (particularly of light) on matter by means of acoustic detection.
Photoacoustic spectroscopy has become a powerful technique to study concentrations of gases at the part per billion levels.

Advantages	Disadvantages	Cross Sensitivity
• LoD is sufficient	• High cross sensitivities • Slow • Mathematical correction necessary • Limited experience • Stability seems not suffucient	CO2 H2O CO

N_2O-Measurement Methods

Gas chromatography analyzer (GC)



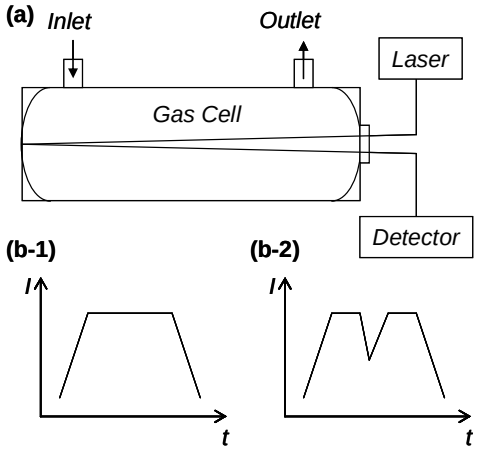


Advantages	Disadvantages	Cross Sensitivity
• Low LoD • No cross sensitivities	• No devices for use in analyzer bench available • Sample has to be brought to lab • Slow	-

N_2O-Measurement Methods

Quantum cascade laser analyzer

Sample gas is fed into the gas cell and a laser pulse irradiates into the gas cell. The laser radiation emitted as continuous pulse is detected after a multiple reflection between two mirrors in the gas cell. From it's inherent design and control, the wavelength of QCL radiation slightly varies with time therefore it is possible to scan the constant width of the wavelength in a particular region. If there is no gas component in the cell which absorbs within the predetermined scanning wavelength band, a time resolved spectrum as shown in Figure 1(b-1) is observed. On the other hand, when there is a gas component which offers absorption in the band, a time resolved spectrum as shown in Figure 1(b-2) is observed. According to the Beer-Lambert law, absorbance is proportional to the concentration of gas. So, the gas concentration can be obtained from the absorption spectrum with a predetermined correlation (source: Horiba)



Advantages	Disadvantages	Cross Sensitivity
• Fast	• No experience	• not known