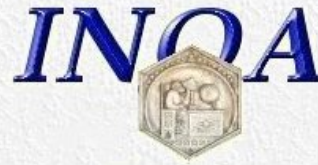


F
Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

F
Institut für Meteorologie und
Klimaforschung



Winter College on Optics in Environmental Science

February 2-13, 2009 - Trieste, Italy

Atmospheric Monitoring with Tunable Diode Lasers

Peter Werle

Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology, Germany

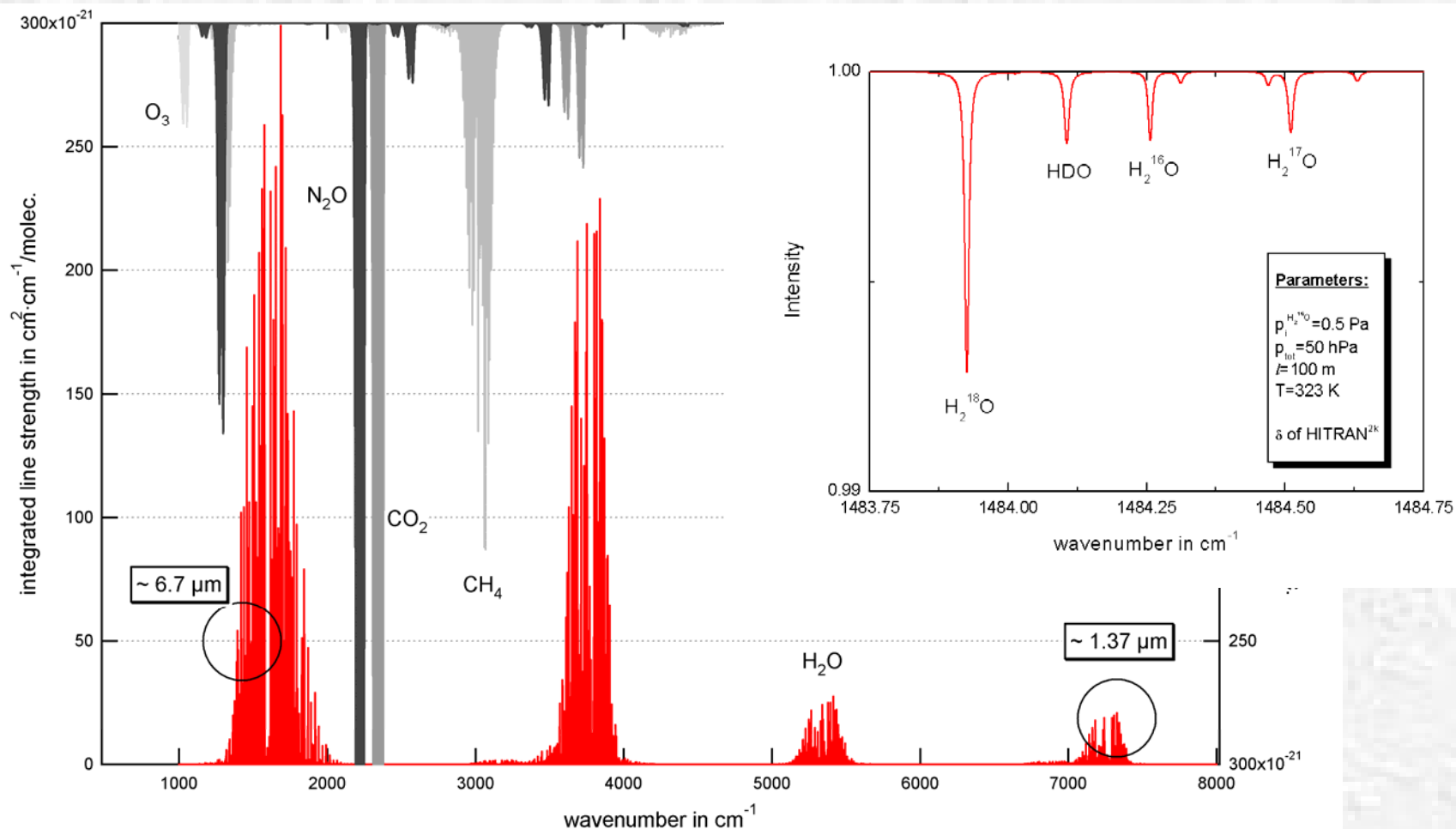
National Institute for Applied Optics, CNR-INOVA, Florence, Italy

Peter.Werle@kit.edu or Peter.Werle@inoa.it

H₂O - Fingerprints

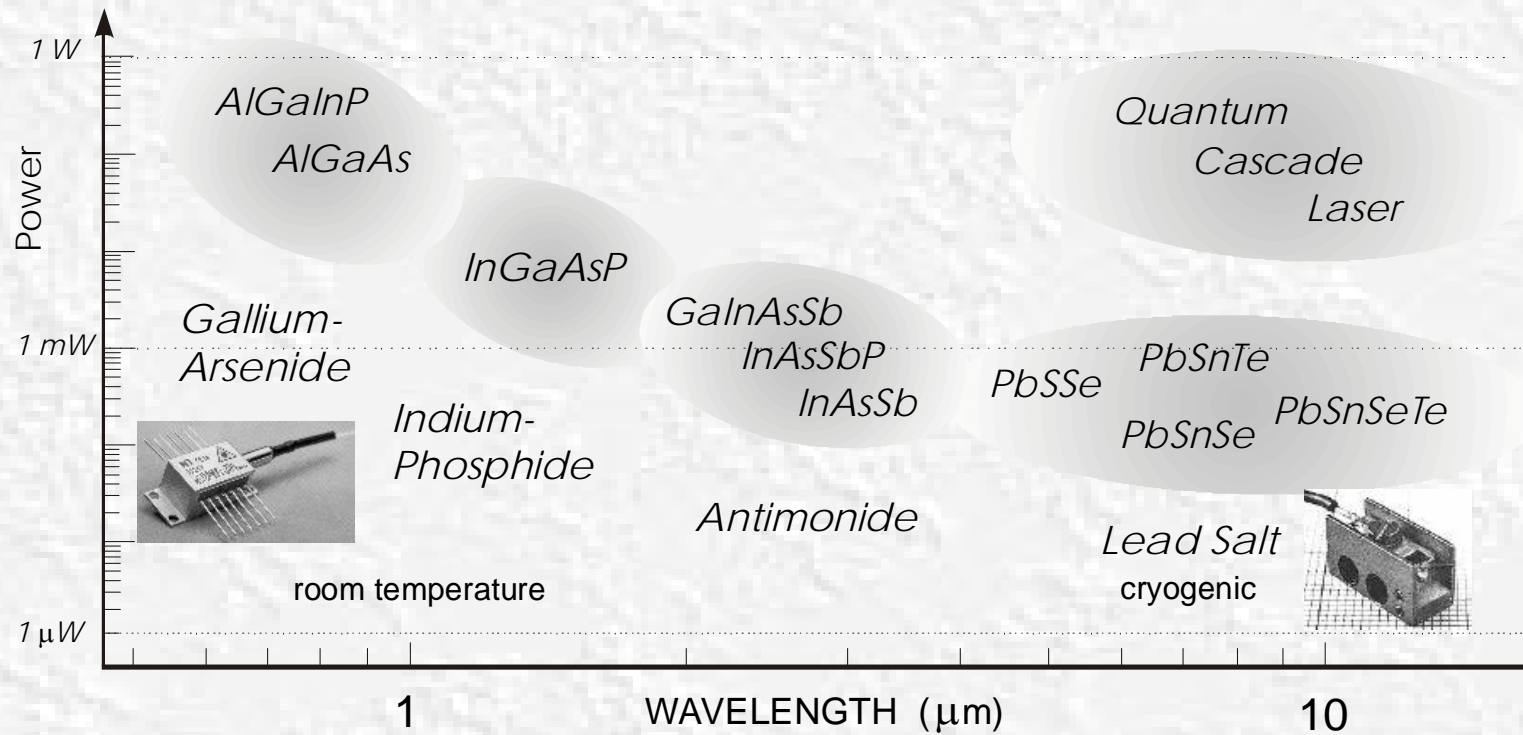


Spectral signatures in the near- and mid-infrared allow a unique quantitative identification of trace gases



Semiconductor Lasers

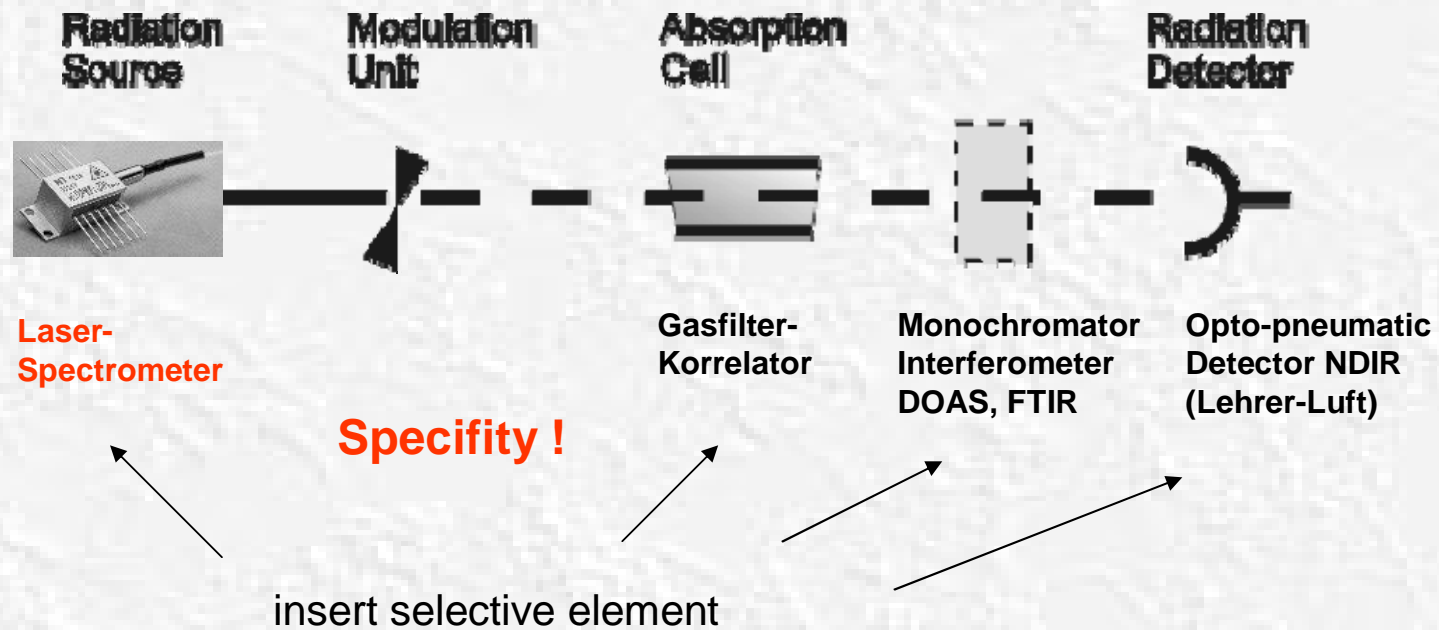
Relevant Characteristics for Gas Sensing



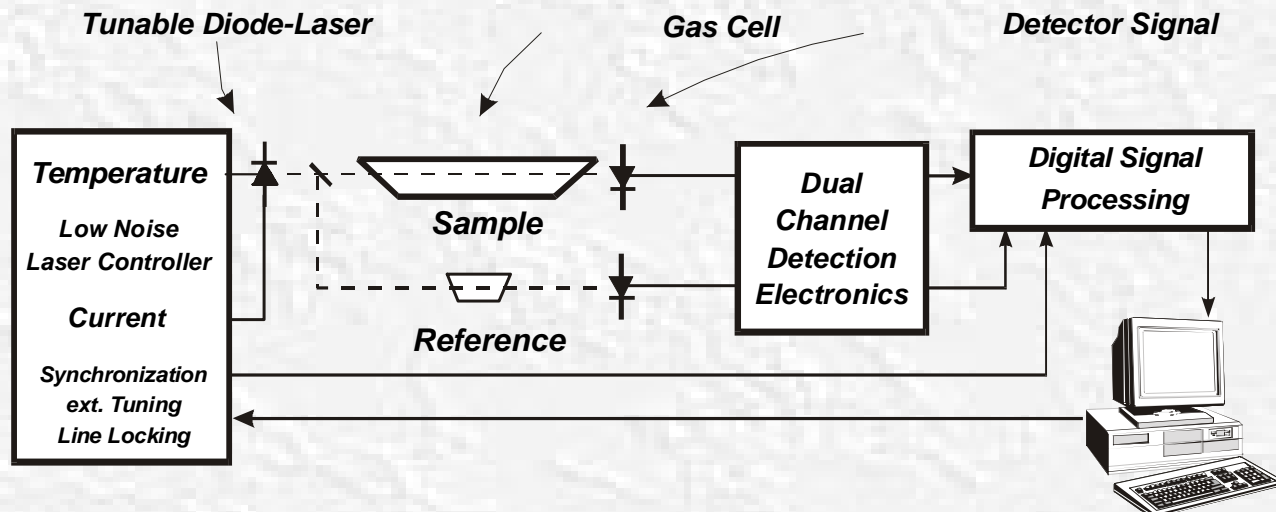
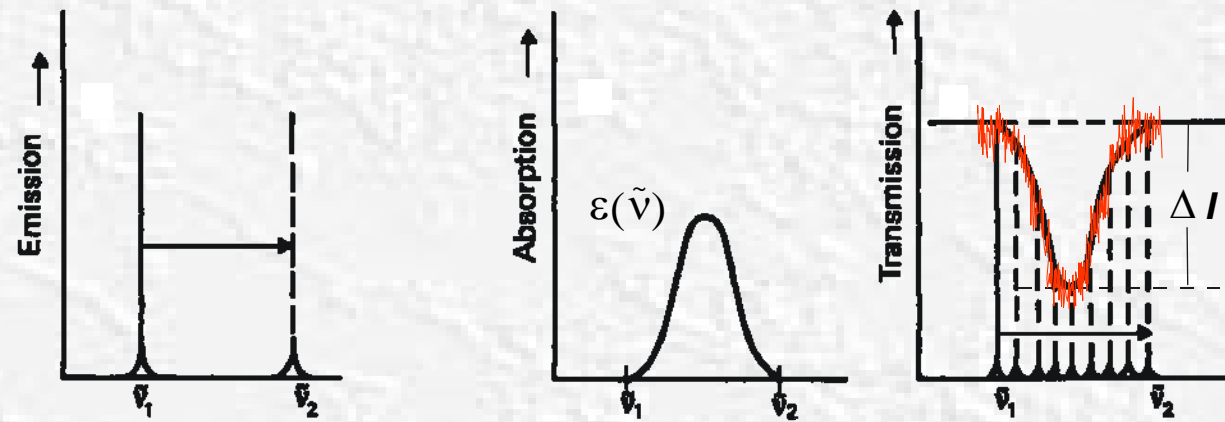
- Wavelength Range
- Output Power
- Noise Characteristics

- Far- Field / Beam Profile
- Impedance
- Temperature Range

Optical Gas Analysis



Laser Spectroscopy



Lambert-Beer's Law

$$I(\nu) = I_0(\nu) e^{-\varepsilon(\nu) c l}$$

in the limit of low extinction : $\varepsilon(\nu) c l \ll 1$

$$c = \frac{1}{\varepsilon(\tilde{\nu}) l} \left(\frac{\Delta I(\tilde{\nu})}{I_0(\tilde{\nu})} \right)$$

Apply sensitive measurement technique with sufficient detection limits (e.g. 10^{-5} with **modulation schemes**)

P. Werle, "A review of recent advances in semiconductor laser based gas monitors", Spectrochimica Acta A - Review 54, 197-236, (1998) (for paper click [here](#))

Select strong absorption line (e.g. from **HITRAN** Database) and check interferences !

Use long optical pathlength (White/Herriott **multi-pass cells**, e.g. 100m)

A Cryogenically Operated Laser Diode (COLD)



S. Viciani, F. D'Amato, P. Mazzinghi, F. Castagnoli, G. Toci, P. Werle, Appl. Phys. B90, 581-592 (2008) [View-PDF](#)

Laser sources:

single mode FP lead salt TDL

$\lambda = 5.8 \mu\text{m}$ for HNO_3 and H_2O

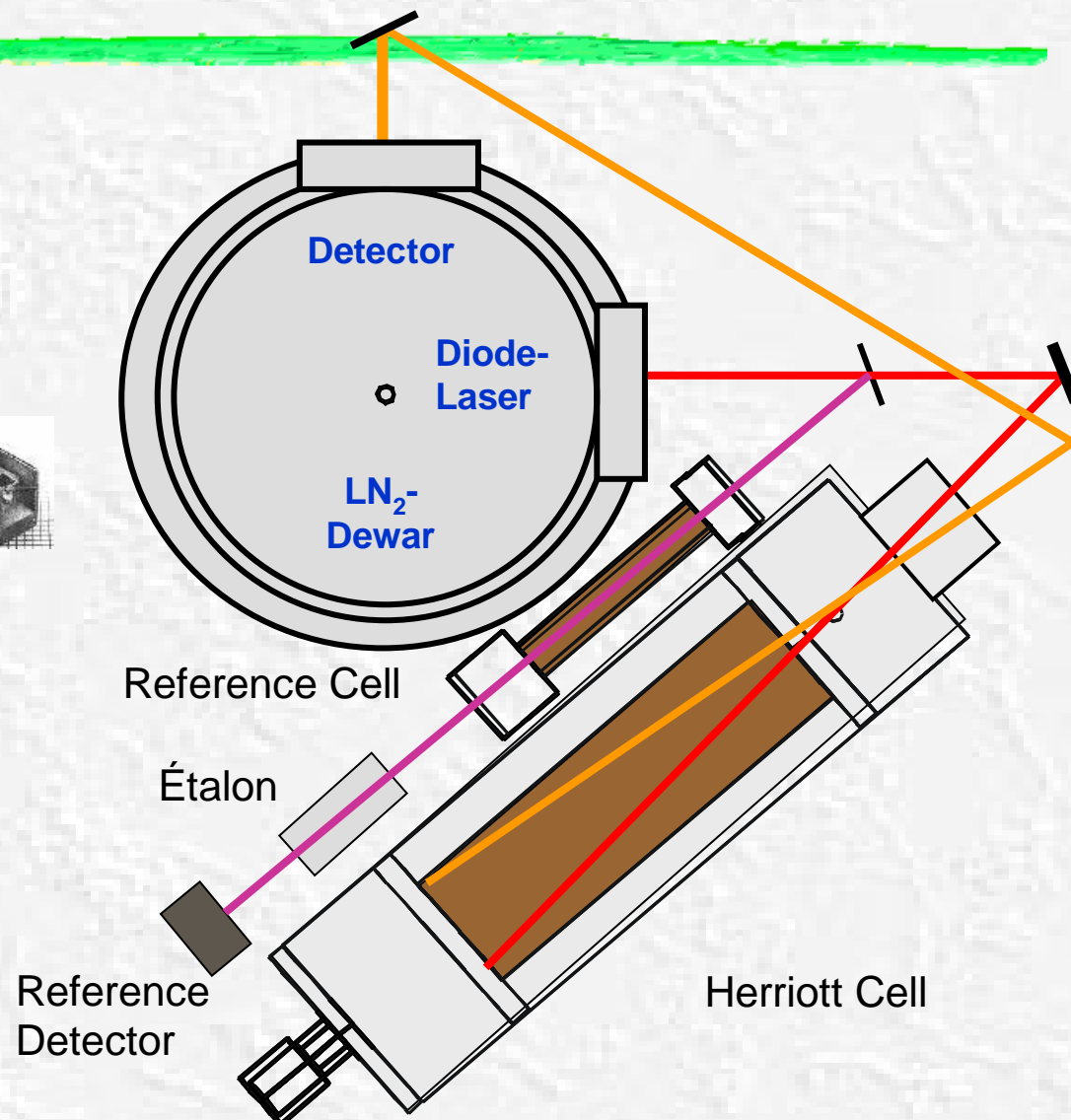
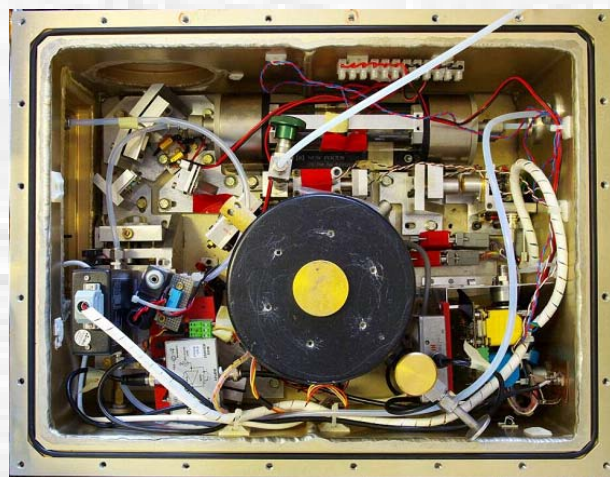
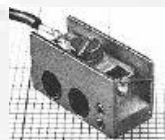
$\lambda = 4.6 \mu\text{m}$ for N_2O and CO

Multipass cell:

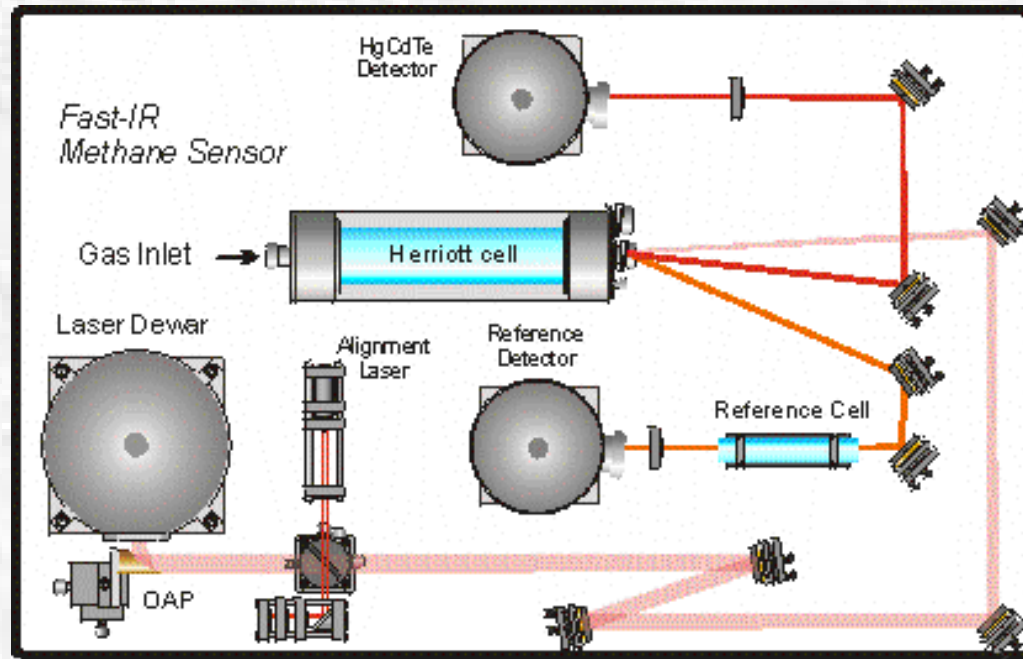
astigmatic Herriott cell

absorption path 36 m

low volume (0.3 l)



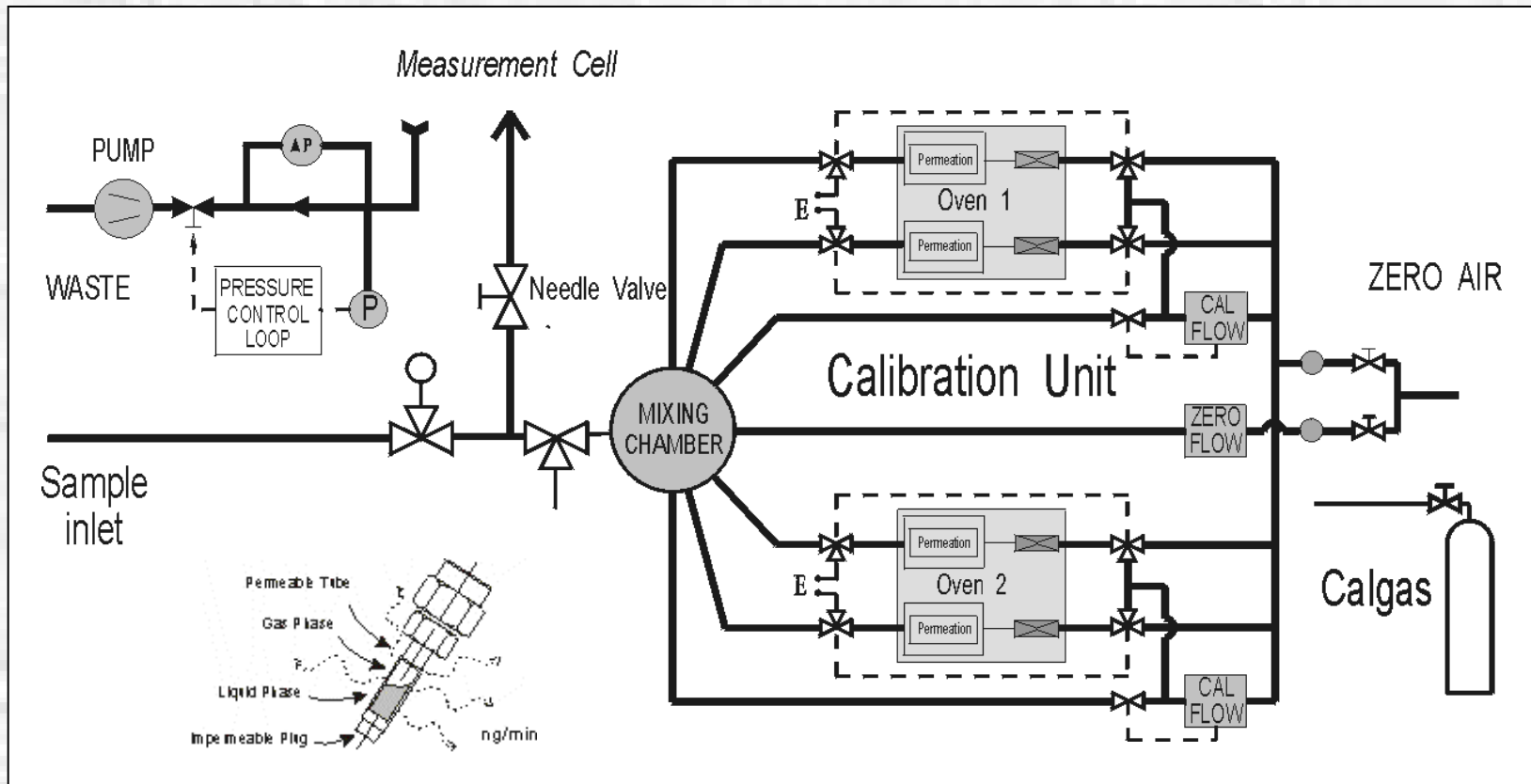
A „Field“ Diode Laser Spectrometer for Methane



P. Werle and R. Kormann, "A fast chemical sensor for eddy correlation measurements of Methane emissions from rice paddy fields", Appl. Opt. 40, 846-858 (2001). [View-PDF](#)



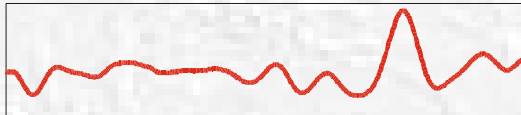
Dynamic Spectrometer Calibration is an issue



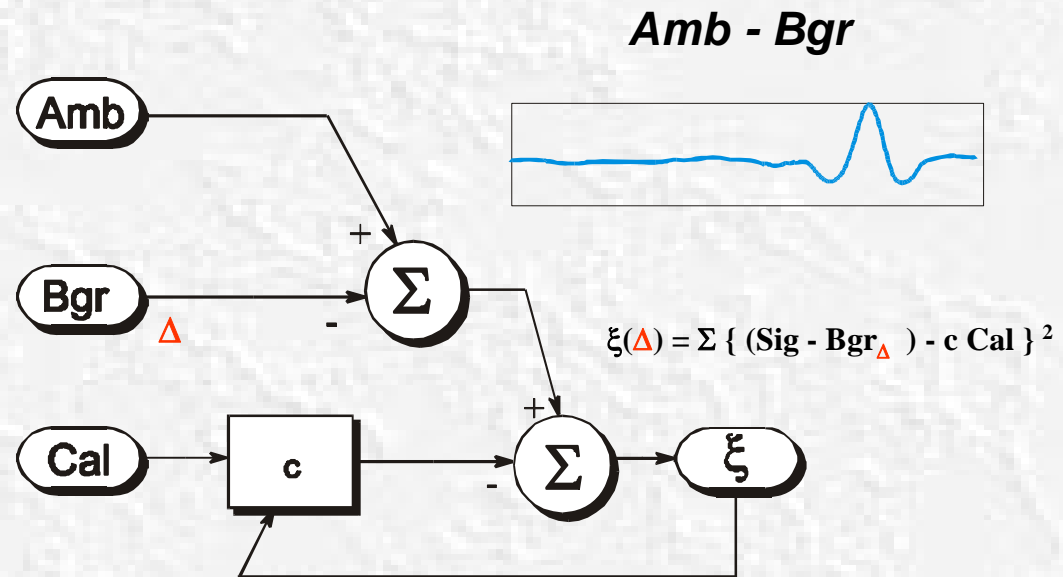
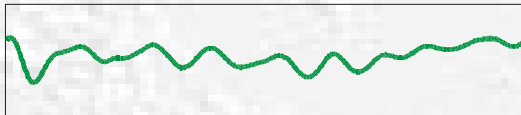
P. Werle, P. Mazzinghi, F. D'Amato, M. De Rosa, K. Maurer, F. Slemr, "Signal Processing and Calibration Procedures for in-situ Diode-Laser Absorption Spectroscopy", *Spectrochimica Acta A - Review* 60, 1685-1705 (2004) (for paper click [here](#))

Signal Processing is an issue

Measurement Signal (Amb)

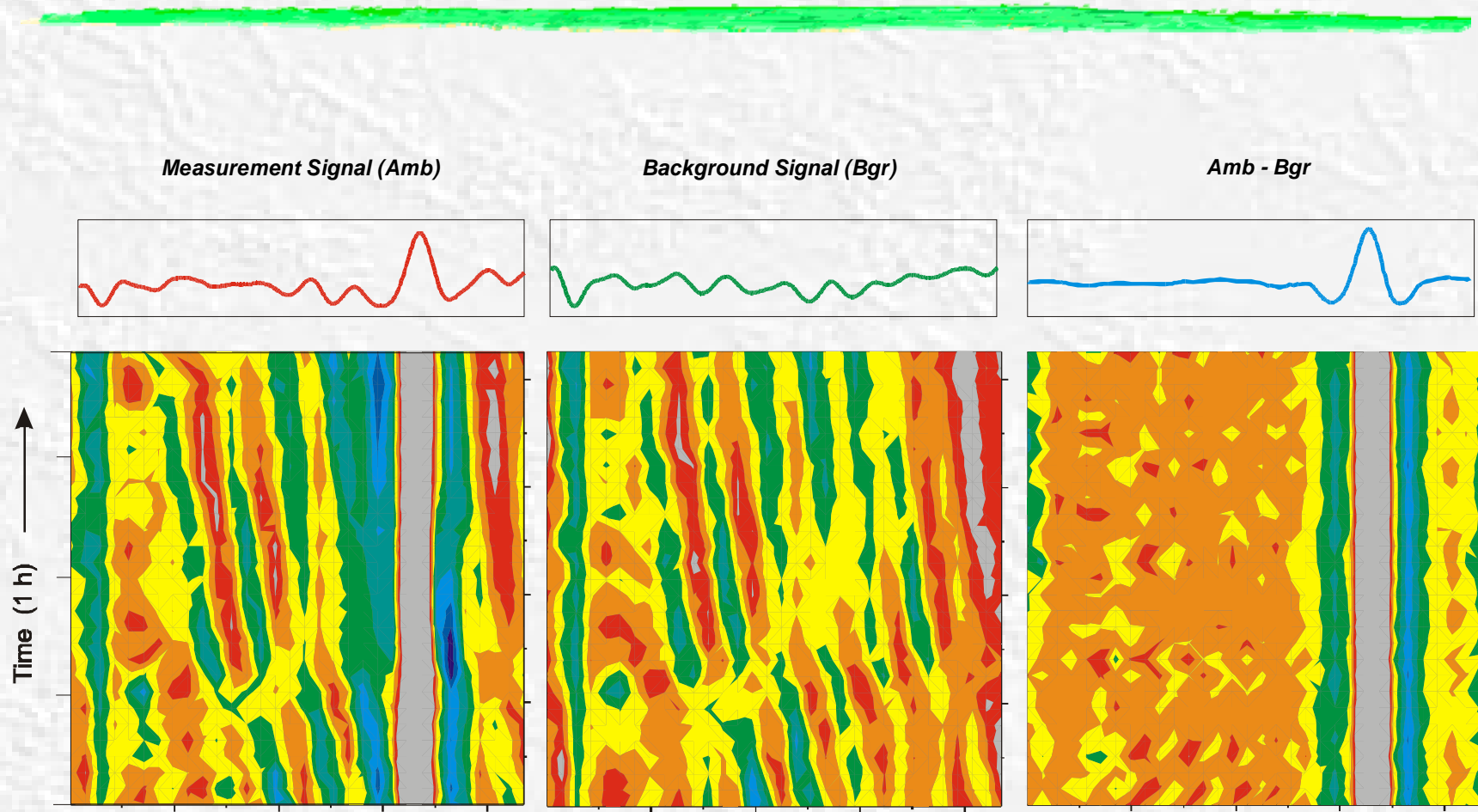


Background Signal (Bgr)



P. Werle, P. Mazzingh, F. D'Amato, M. De Rosa, K. Maurer, F. Slemr, "Signal Processing and Calibration Procedures for in-situ Diode-Laser Absorption Spectroscopy", *Spectrochimica Acta A - Review* 60, 1685-1705 (2004) (for paper click [here](#))

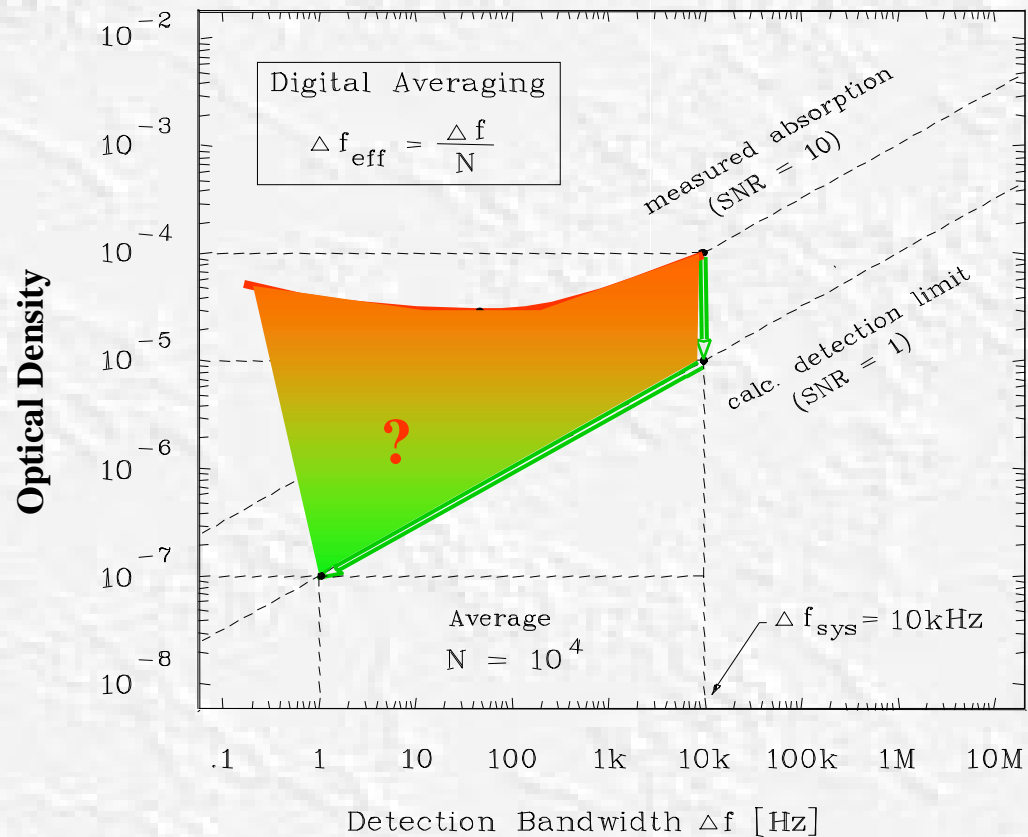
Background Drift



What are the Limits of Signal Averaging ?

What is the result of digital averaging of 10^4 spectra ?

Which curve does the detection limit follow ?



Sample Variance

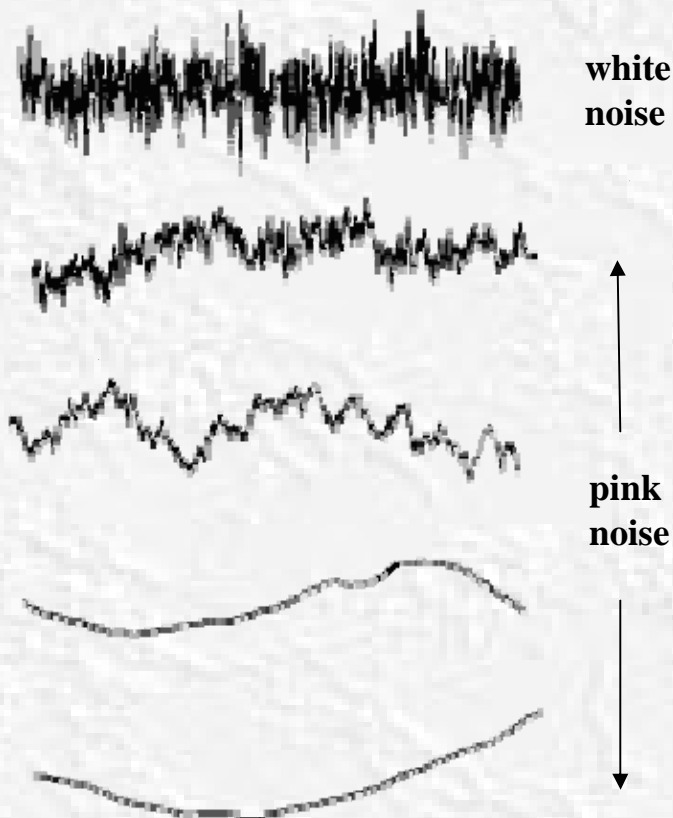
Typically, the sample variance is calculated from a data sample using the relation:

$$\sigma_{STD\ DEV\ y}(\tau) = \sqrt{\frac{1}{M-1} \sum_{i=1}^M (y_i - \bar{y})^2}$$

Where it is implicitly assumed that the y_i 's are random and uncorrelated (i.e., white) and where \bar{y} is the sample mean calculated from the same data set.

What happens to the standard deviation ...

... when a data set may be characterized by power law spectra which are more dispersive than classical white noise fluctuations ?



One can show that the standard deviation is a function of the number of data points in the set; it is also a function of the dead time and of the measurement system bandwidth. For example, using **flicker noise** as a model, as the number of data points increases, **the standard deviation monotonically increases without limit.**

Some statistical measures have been developed which do not depend upon the data length and which are readily usable for characterizing random fluctuations in precision oscillators.

IEEE subcommittee on frequency stability ...

... has recommended what has come to be known as the "Allan variance" taken from the set of useful variances developed, and an experimental estimation of the square root of the Allan variance is

$$\sigma_y(\tau) = \sqrt{\frac{1}{2(M-1)} \sum_{i=1}^{M-1} (y_{i+1} - y_i)^2}$$

This equation is very easy to implement experimentally as one simply need **add up the squares of the differences between adjacent values of y_i** , divide by the number of them and by two, and take the square root.

Statistics of Atomic Frequency Standards

DAVID W. ALLAN

Abstract—A theoretical development is presented which results in a relationship between the expectation value of the standard deviation of the frequency fluctuations for any finite number of data samples and the infinite time average value of the standard deviation, which provides an invariant measure of an important quality factor of a frequency standard. A practical and straightforward method of determining the power spectral density of the frequency fluctuations from the variance of the frequency fluctuations, the sampling time, the number of samples taken, and the dependence on system bandwidth is also developed. Additional insight is also given into some of the problems that arise from the presence of "flicker noise" (spectrum proportional to $|\omega|^{-1}$) modulation of the frequency of an oscillator.

The theory is applied in classifying the types of noise on the signals of frequency standards made available at NBS, Boulder Laboratories, such as: masers (both H and N²H₂), the cesium beam frequency standard employed as the U. S. Frequency Standard, and rubidium maser cells.

"Flicker noise" frequency modulation was not observed on the signals of masers for sampling times ranging from 0.1 second to 4 hours. In a comparison between the NBS hydrogen maser and the NBS III cesium beam, uncorrelated random noise was observed on the frequency fluctuations for sampling times extending to 4 hours; the fractional standard deviations of the frequency fluctuations were as low as 3 parts in 10¹¹.

I. INTRODUCTION

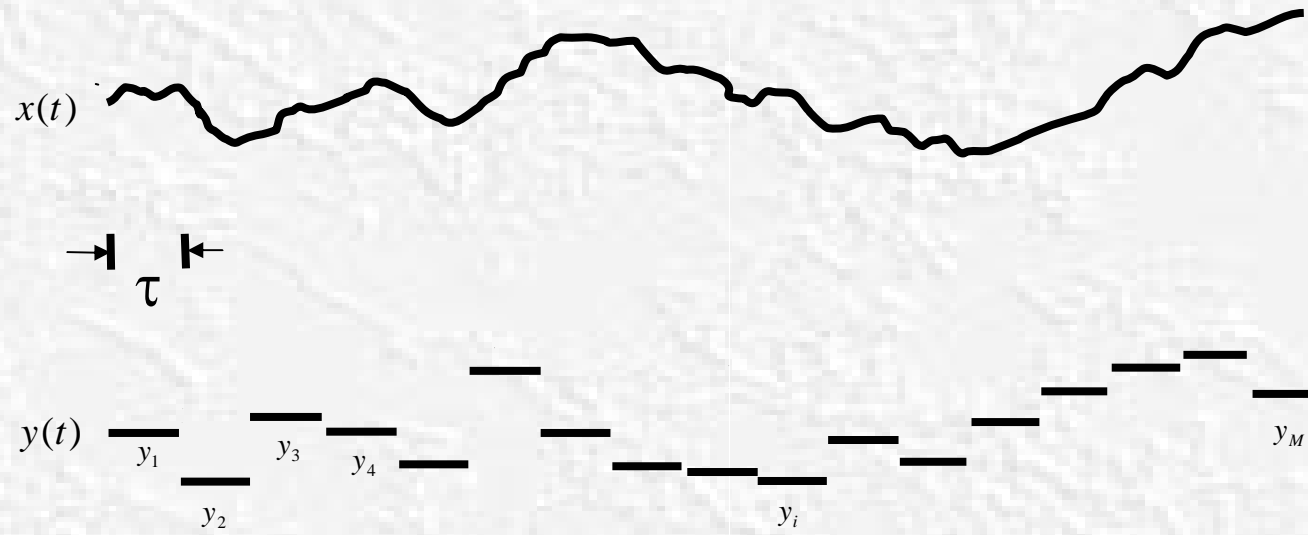
AS ATOMIC TIMEKEEPING has come of age, it has become increasingly important to identify quality in an atomic frequency standard. Some of the most important quality factors directly related to the inherent noise of a quantum device and its associated electronics. For example, a comparison of two

a frequency standard is to compare two such standards by measuring the period of the beat frequency between the two standards. It is again the intent of the author to show a practical and easy way of classifying the statistics, i.e., of determining the power spectral density of the frequency fluctuations using this type of measuring system.

An analysis has already been made of the noise present in passive atomic frequency standards [1], such as cesium beams, but a classification of the types of noise exhibited by the maser type of quantum-mechanical oscillator has not been made in the long term area, i.e., for low frequency fluctuations. Though this paper is far from exhaustive, the intent is to give additional information on the noise characteristics of masers. Because a maser's output frequency is more critically parameter dependent than a passive atomic device, it has been suggested [2] that the output frequency might appear to be "flicker noise" modulated, where "flicker noise" is defined as a type of power spectral density which is inversely proportional to the spectral frequency $\omega/2\pi$. It has been shown that if "flicker noise" frequency modulation is present on a signal from a standard, some significant problems arise, such as the logarithmic divergence of the standard deviation of the frequency fluctuations as the number of samples taken increases, and also the inability to define precisely the time average frequency. It thus becomes of special interest to determine the extent to which "flicker noise" is present on

D. W. Allan, "Statistics of atomic frequency standards,"
Proc. IEEE, vol. 54, pp. 221–230, Feb. 1966.

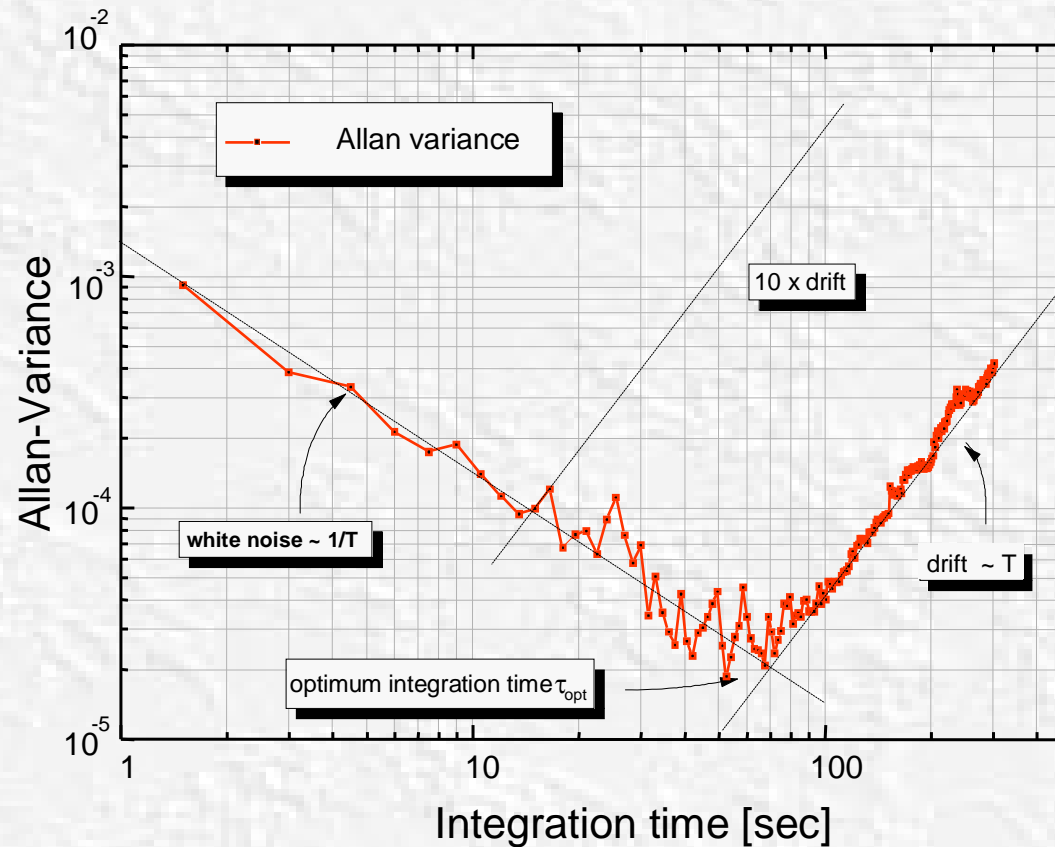
Sample Variance and Allan Variance



$$\sigma_{STD\ DEV\ y}(\tau) = \sqrt{\frac{1}{M-1} \sum_{i=1}^M (y_i - \bar{y})^2} \quad \sigma_y(\tau) = \sqrt{\frac{1}{2(M-1)} \sum_{i=1}^{M-1} (y_{i+1} - y_i)^2}$$

Time series $x(t)$ with indicated sample time τ over which each y is measured. Equations are for standard deviation and for estimate of $\sigma_y(t)$ for a finite data set of M measurements.

Allan Plot



"Allan-Plot" for two different drift components. The rightmost trace corresponds to the "white noise and drift" data shown before.

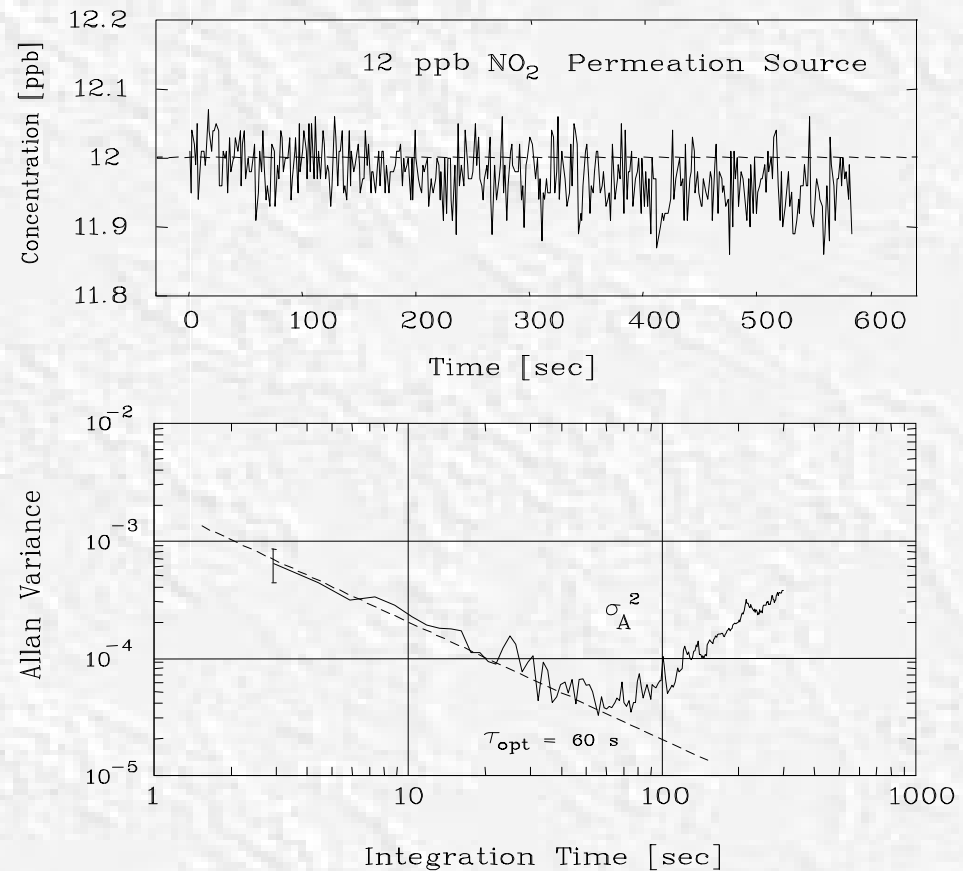
Minimum of Allan Plot defines maximum integration time (= detection limit !) for signal averaging

First application in trace gas analysis

The concept of the Allan Variance has been proposed and applied to characterize spectroscopic instrumentation

P. Werle, R. Muecke and F. Slemr, "The limits of signal averaging in atmospheric trace gas monitoring by tunable diode-laser absorption spectroscopy", Appl. Phys. B 57, 131-139 (1993). [View-PDF](#)

and has become a well established tool for researchers and instrument developers to describe the performance of laseroptical trace gas sensors.



Detection Limits

for atmospheric constituents for a sampling pressure of 30 mbar and T=296 K based upon a minimum detectable absorbance of 10^{-5} and 100 m optical path-length

Species	λ μm	ν cm^{-1}	S 10^{-19} cm/molec	γ_{ν} 10^{-3} cm^{-1}	γ_{ν} MHz	σ 10^{-17} cm^2/molec	DL pptv
N ₂ O	7.69	1301	1.56	2.77	83.1	1.92	70
CO	4.65	2151	1.89	3.85	115.5	1.85	73
CH ₄	7.56	1322	0.53	3.25	97.5	0.60	225
NO	5.33	1876	0.34	3.26	97.8	0.39	350
SO ₂	7.29	1372	0.49	3.86	115.8	0.41	330
NO ₂	6.25	1600	2.18	2.90	87.0	2.70	50
NH ₃	10.74	931	5.20	2.92	87.6	6.18	23
HNO ₃	5.81	1722	0.72	3.75	112.5	0.25	218
HF	1.24	7856	0.76	12.09	362.7	0.27	500
HCl	3.40	2945	5.03	4.30	129.0	4.51	30
HBr	3.78	2649	0.45	2.90	87.0	0.57	240
ClO	11.6	860	0.08	2.73	81.9	0.09	1500
OCS	4.87	2053	10.30	3.55	106.5	10.00	13
HCHO	3.56	2781	1.19	5.17	155.1	0.84	160
CH ₃ Cl	3.29	3040	0.02	4.12	123.6	0.02	7800
H ₂ O ₂	7.79	1284	0.45	3.52	105.6	0.43	320
H ₂ S	7.33	1365	0.01	4.89	146.7	0.007	20000
HCOOH	8.98	1113	0.44	3.32	99.6	0.44	310
HO ₂	7.08	1411	0.12	3.63	108.9	0.11	1200

Current Limitations

Problem:

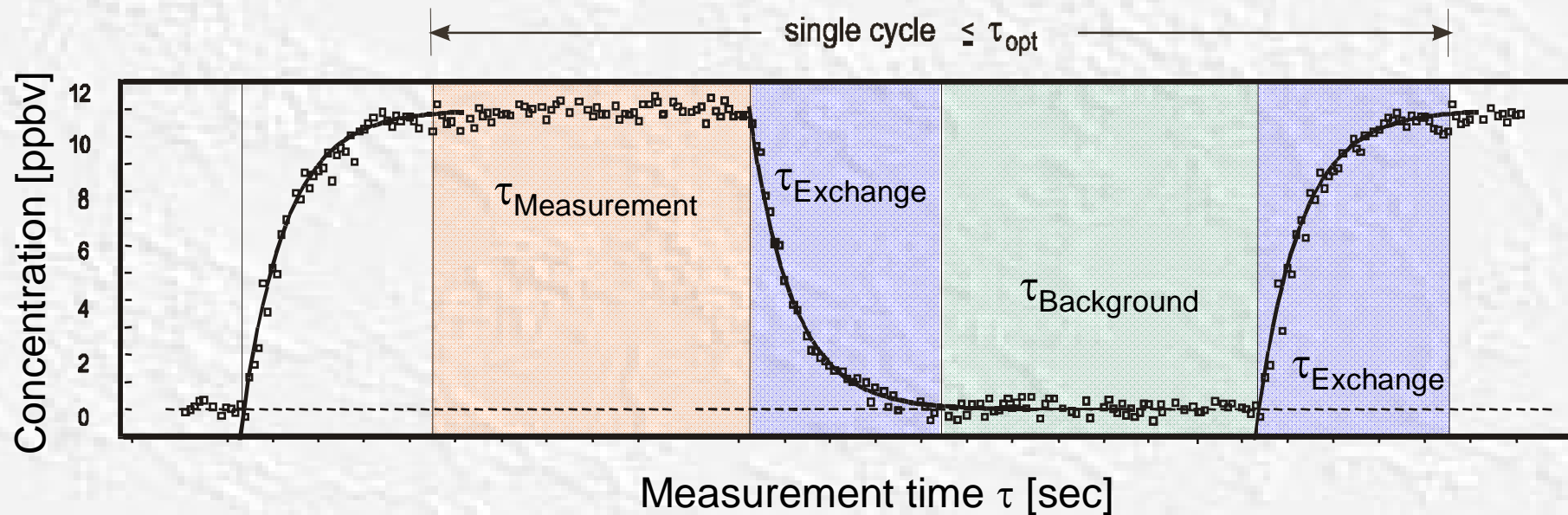
background is **time dependent**

Why:

moves due to small temperature/pressure drifts

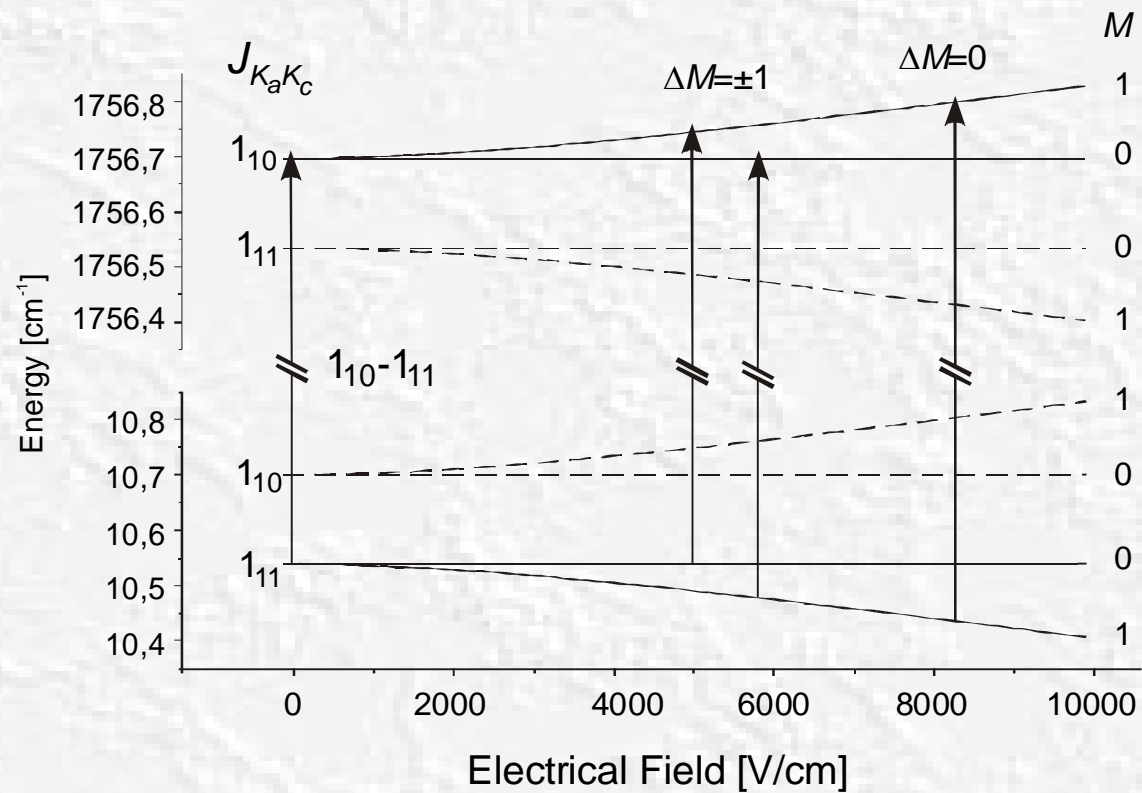


repeated background measurement necessary
duty cycle ~ 50% – 60%



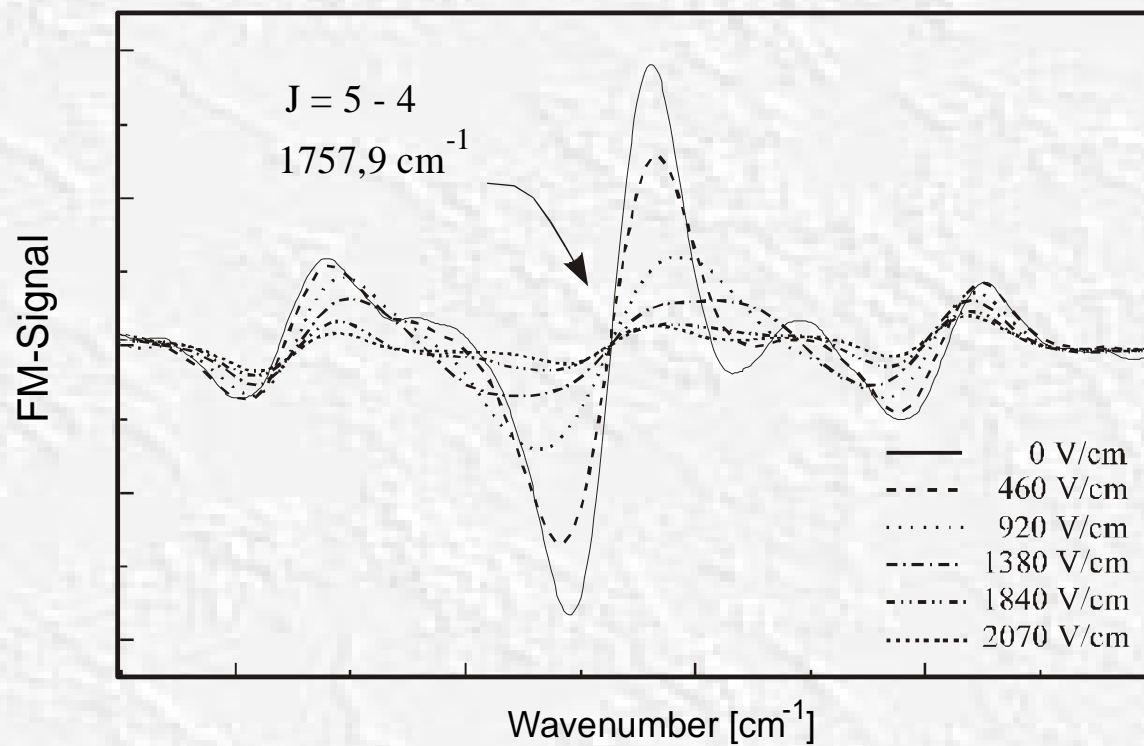
Concept : Sample Modulation - Stark Effekt

a periodic modulation of **sample** energy levels ...

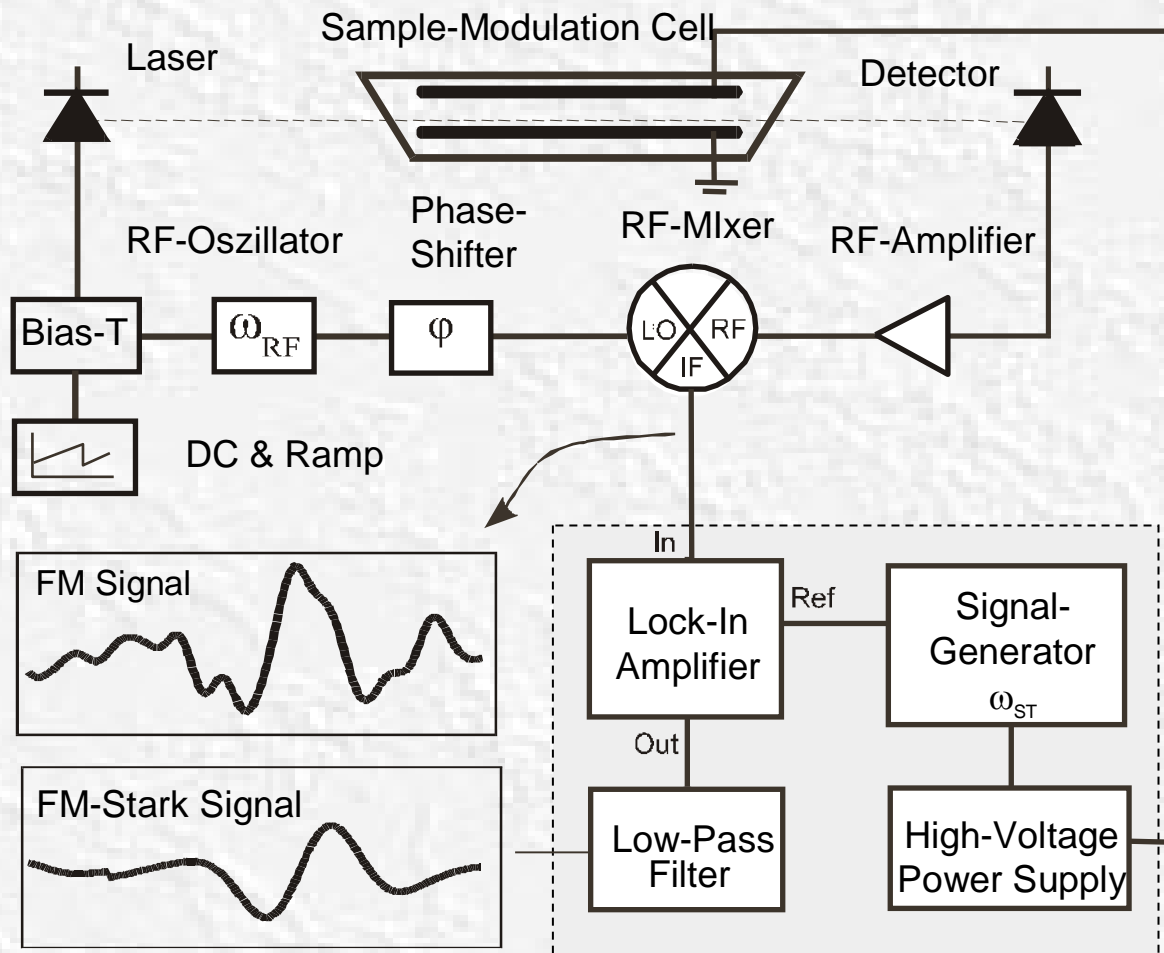


Background Suppression

... influences **signal from sample only** – background is not affected

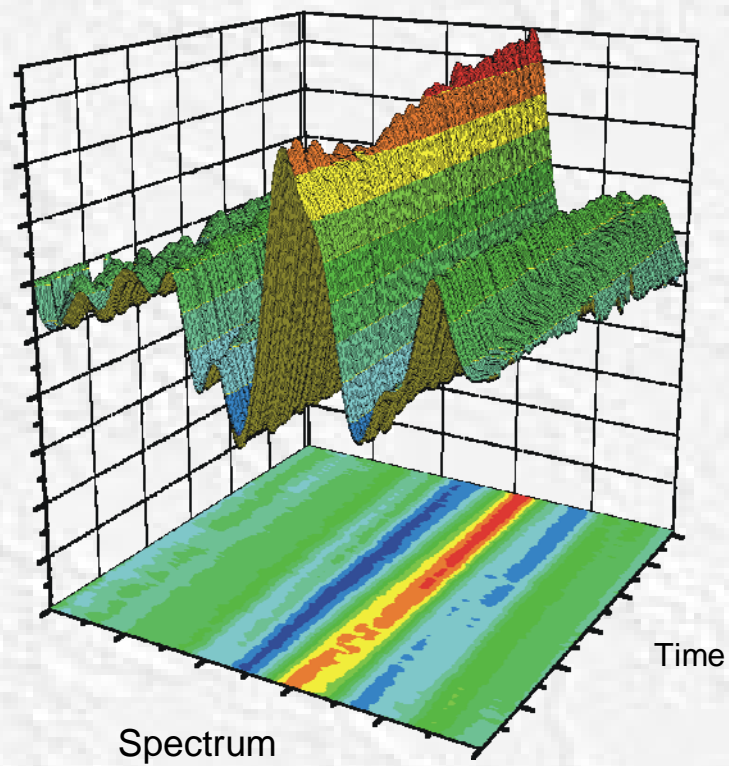


A Laser – Sample Double Modulation Setup

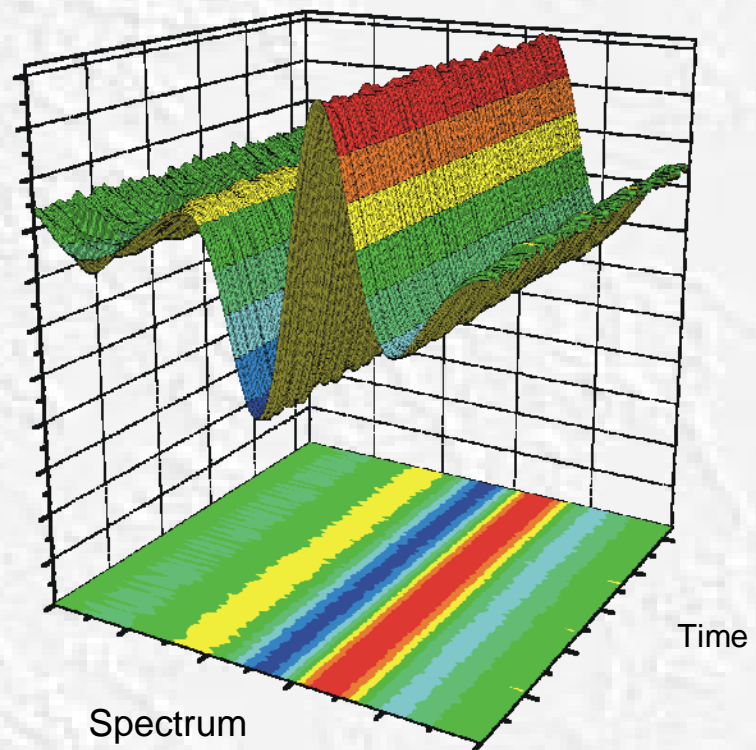


Signal comparison

no sample modulation

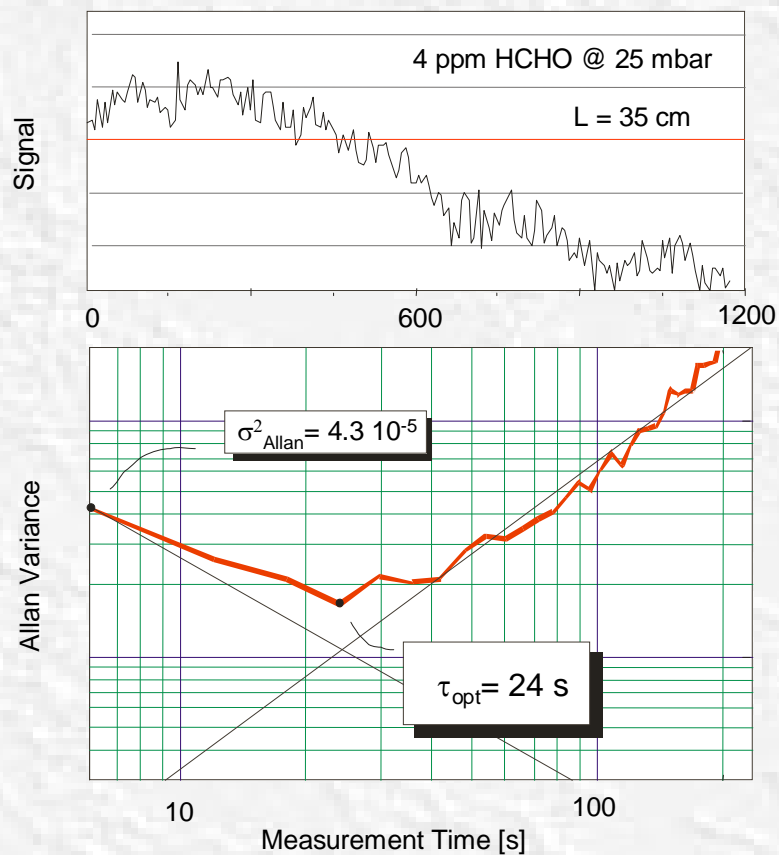


sample modulation

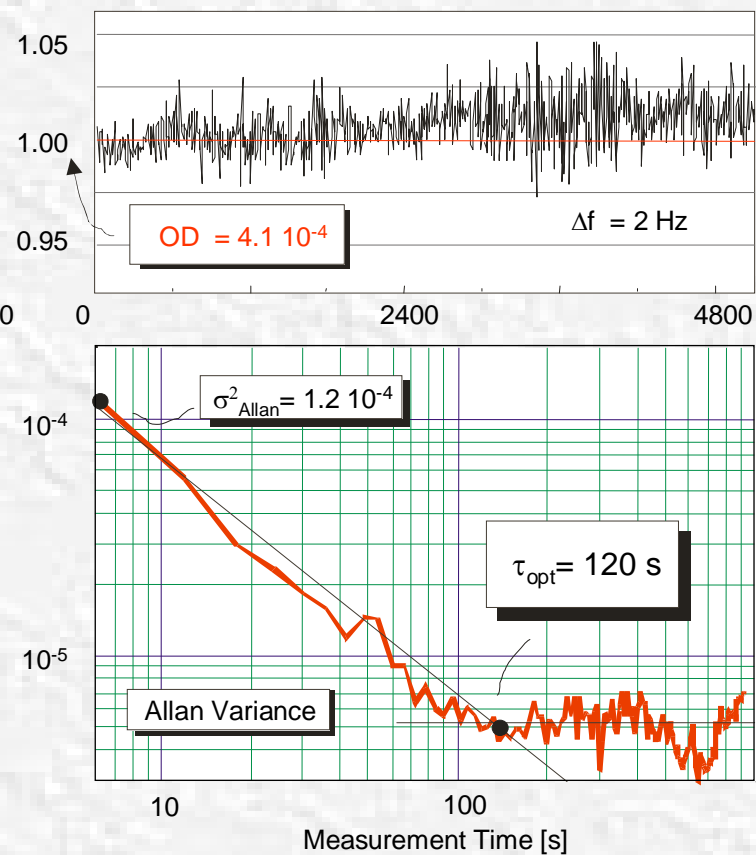


a promising approach ...

no sample modulation



sample modulation



... the next step

a **multi-pass cell** with **small volume** of 0.5 Liter for a fast gas exchange and a **laminar gas flow** to avoid turbulence



Stark Multipass Cell Design

ring mirror

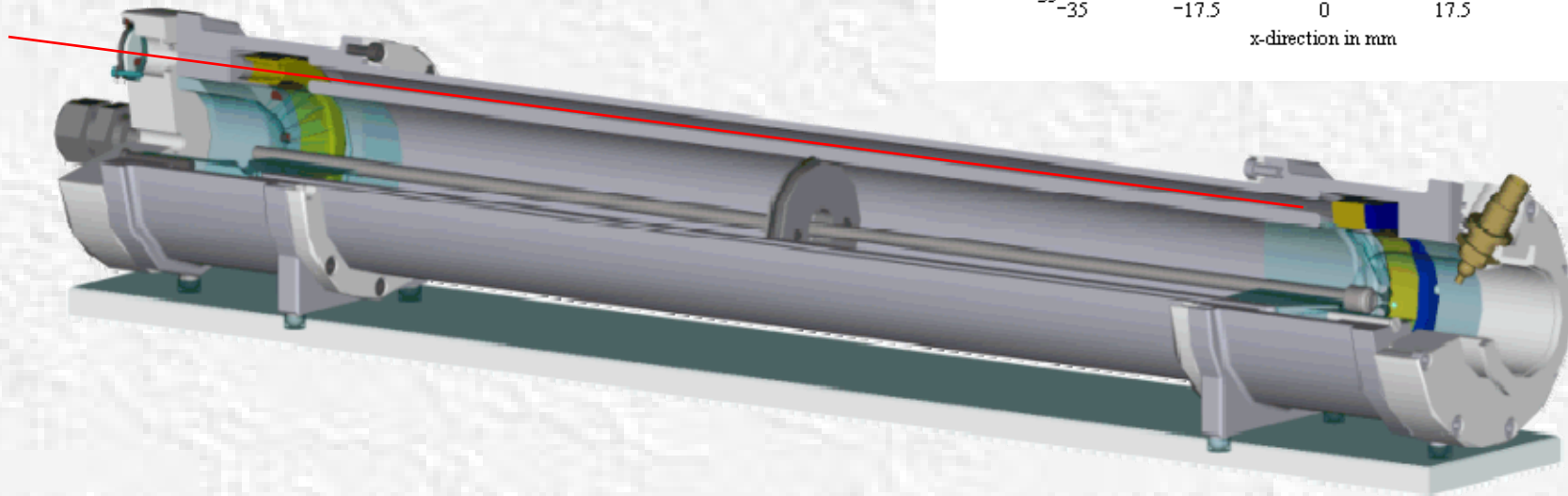
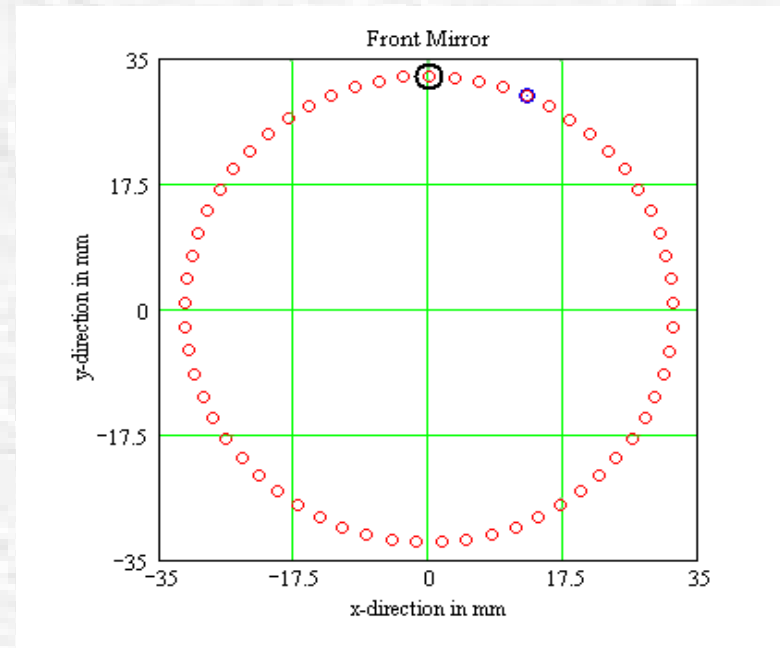
11 m radius

61 spots

122 passes

46 cm baselength

0,9 l Volume



Let's move from the laboratory to ...

Industrial Process Control & Emission Monitoring
High Purity Gases (Semiconductor Industry)
Plasma Diagnostics, Combustion Diagnostics,
Lifescience & Agriculture & Medicine

..

Environmental Research

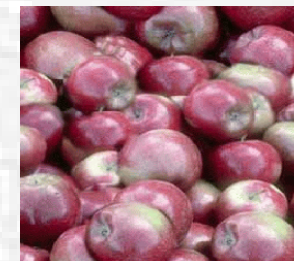
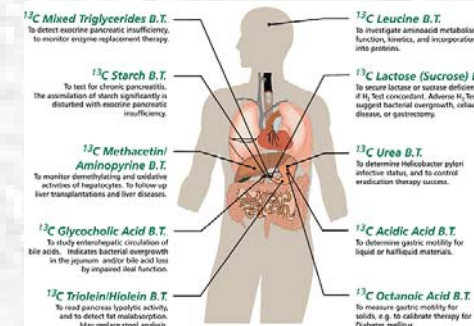
from the upper Troposphere



and lower Stratosphere

to Biosphere - Atmosphere

exchange over complex terrain



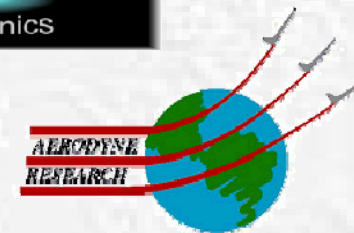
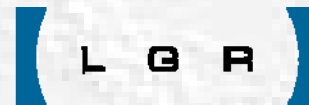
The state of the art

FLAIR - Industry Session

<http://www.inoa.it/flair/industry.htm>

... an assessment of the present status

Industrial Analytical Systems based on Tunable Diode-Lasers

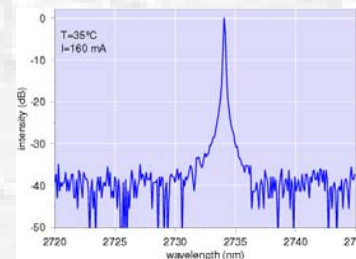
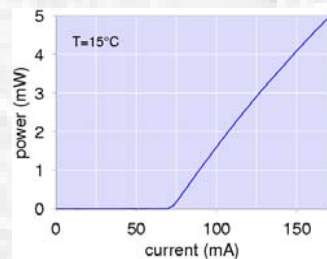
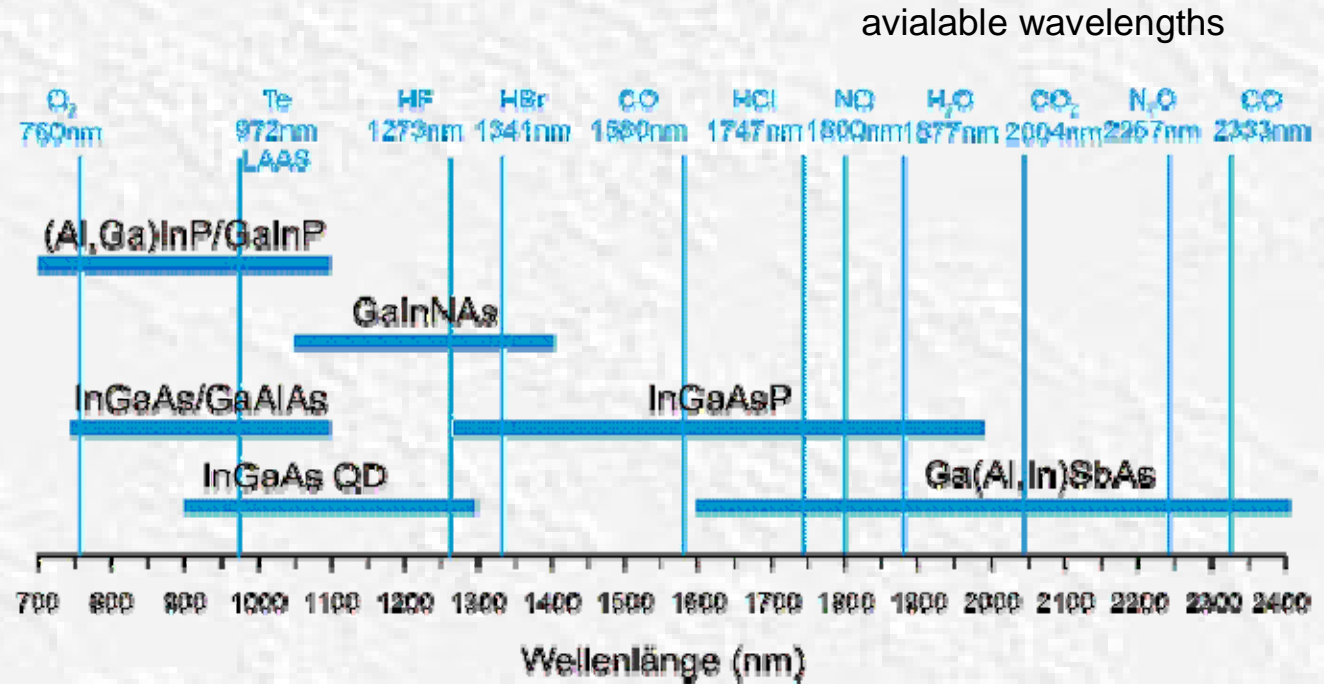
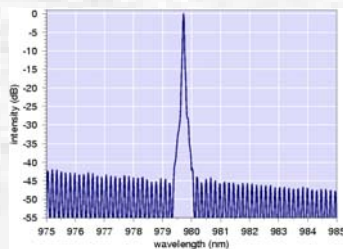
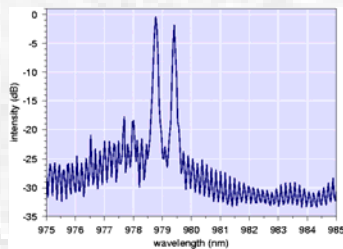
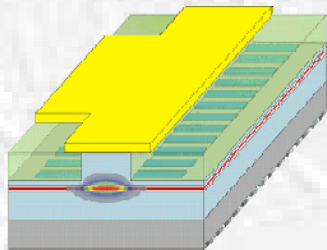


Norsk Elektro Optikk AS

SIEMENS

DFB Diode Lasers

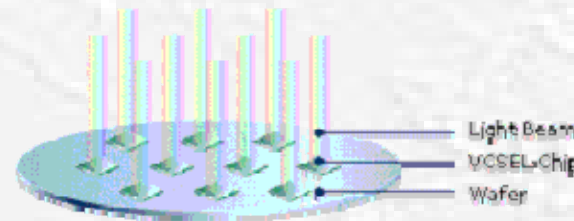
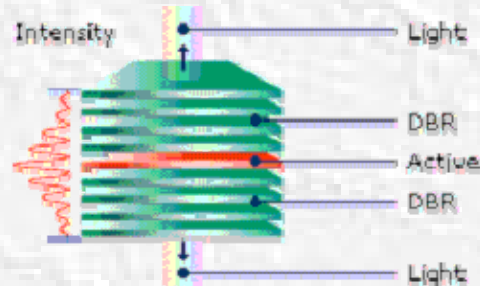
laterally coupled
DFB laser diode



2735 nm
 DFB laser diode
 for H₂O absorption

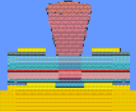
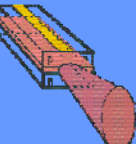
www.nanoplus.com

VCSEL

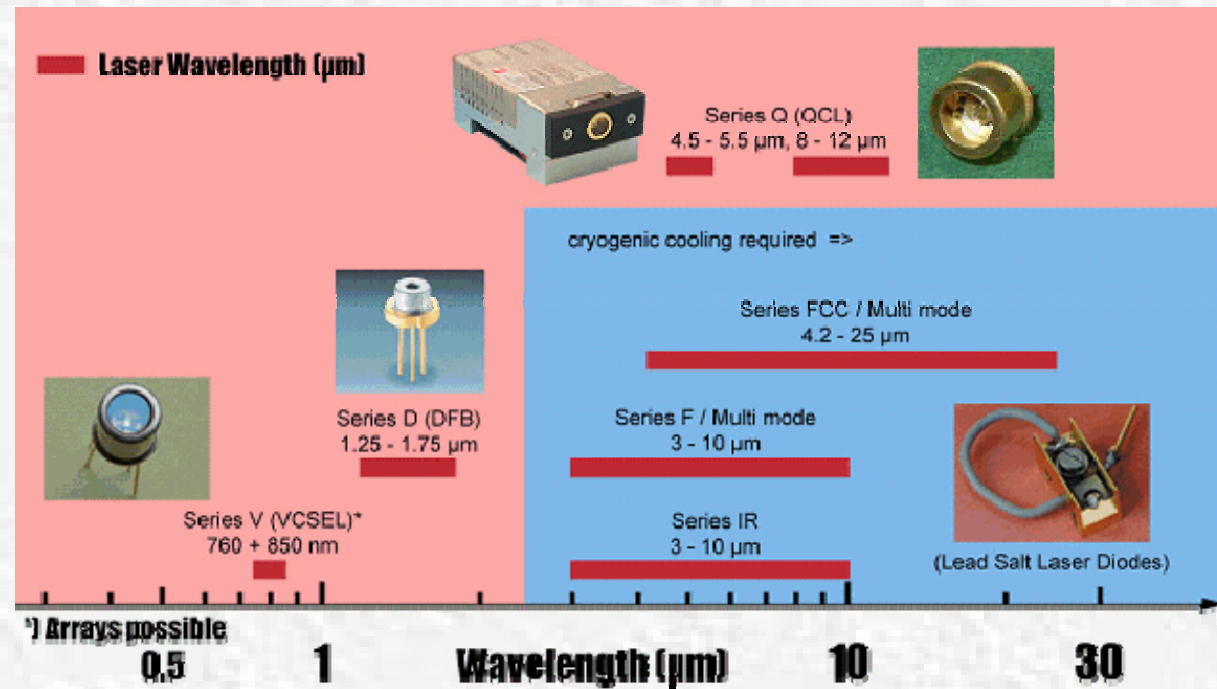
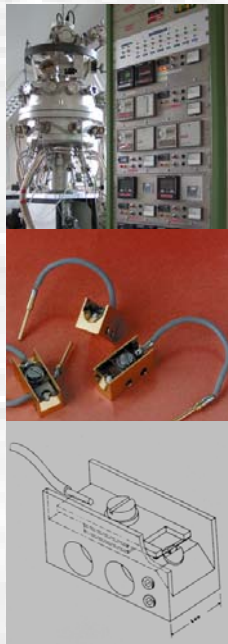


- Longitudinal single mode
- Circular and low divergence output beam
- High fiber coupling efficiency
- Small power consumption
- One and two dimensional arrays
- Simplified manufacturing, testing & packaging
- Low-cost potential

www.vertilas.com

Laser type	Threshold current	Output power	Current tuning rate	Current tuning range	Temperature tuning rate	Maximum modulation
VCSEL 	0.5–2 mA	0.4-3 mW	0.7 nm/mA	3-5 nm	~0.11 nm/°C	> 1 MHz
DFB 	20 mA	5 mW	<0.01 nm/mA	< 1 nm	~0.11 nm/°C	< 100 kHz

Lead Salt Diode Lasers



Lead-salt diode-laser

- Spectral Positions: 400 – 3250 cm^{-1}
- Spectral Resolution: 10^{-4} cm^{-1}
- min. power 0.1 mW up to typ. 1 mW
- CW and pulsed to MHz
- Current: 50 to 2,000 mA
- Temperature: 25 to 120 K
- Delivery time 6-8 weeks

www.lasercomponents.com



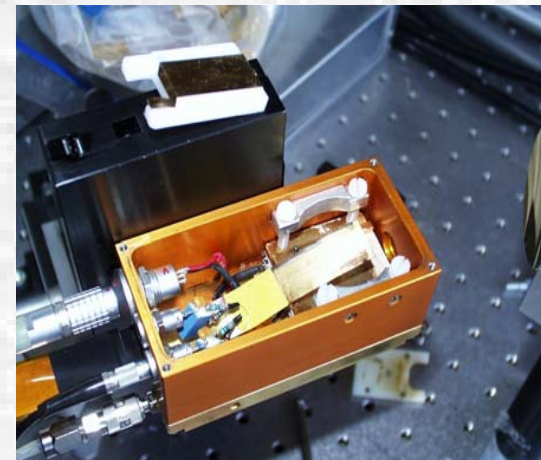
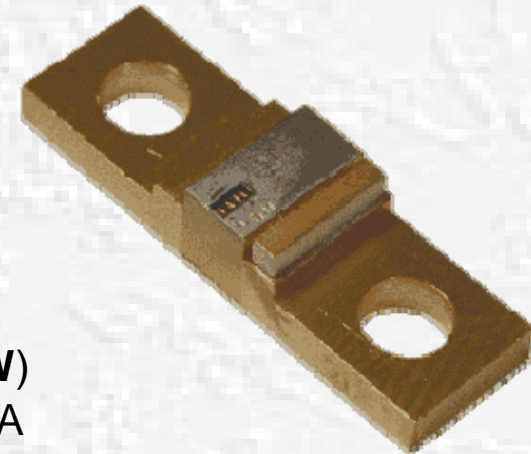
Quantum Cascade Laser

LN₂ and RT continuous-wave DFB

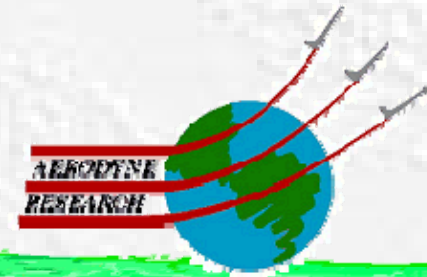
Available wavelengths off-the-shelf: 4.2 to 10.4 μm

Characteristics:

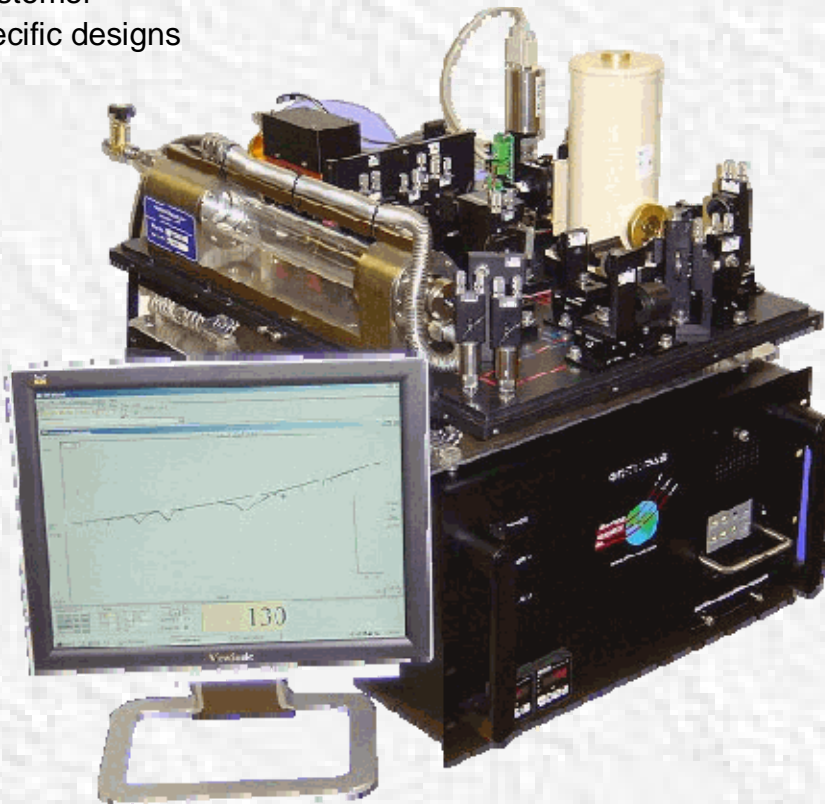
- Power typical 2 mW (max up to **100 mW**)
- Operating current: 0.3 - 2 A, typical 0.8 A
- Operating voltage: 8-10 V
- Tuning range: > **0.4%**
- Spectral linewidth ~ **3 MHz**



QCL Spectrometers

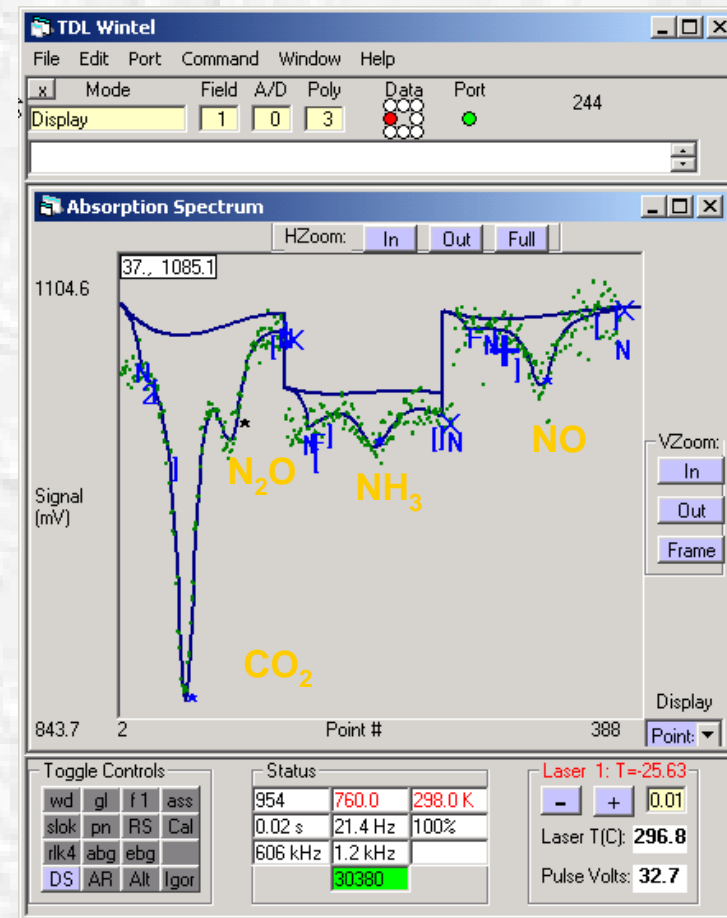


Customer
specific designs



Optical Module with QC lasers and
76 m astigmatic Herriott cell

www.aerodyne.com



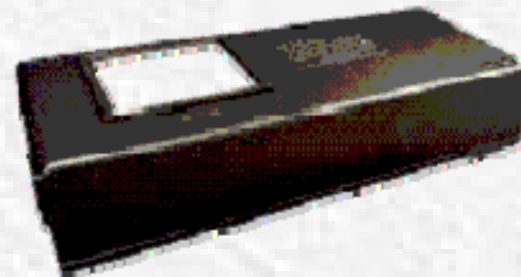
TDL Wintel Data Sample: 3 lasers, 4 gases, 20 ms

TDL & Cavity ring down instruments for Field Application



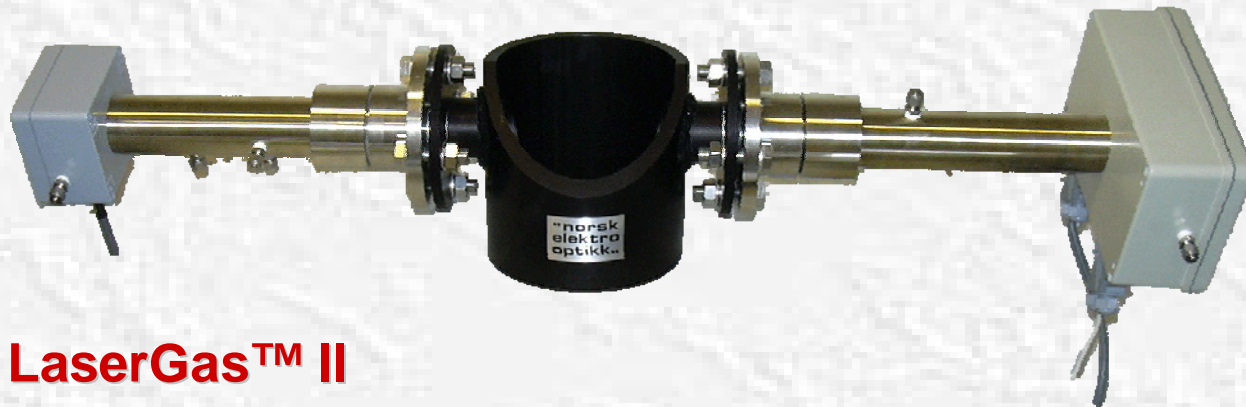
- Mirror-Reflectivity Measurements
- Thin-Film Absorption Measurements
- Substrate-Absorption Measurements
- Process Control and Validation
- Quality Control
- Testing of Optical Coatings
- Total Insertion-Loss Measurements
- Material Research
- Atmospheric Monitoring
- Industrial-Process Monitoring and Control
- Homeland Security
- Trace-Gas Sensing
- Optimization of Singlet-Oxygen Generators
- Chemical Oxygen-Iodine Laser Studies
- Fundamental Physical Sciences
- Plasma Decontamination
- Carbon Sequestration in Ocean Waters
- Eddy-Correlation Flux Measurements
- Chamber-Flux Measurements
- Combustion Diagnostics
- Trace-Gas Monitoring
- Leak Detection from Natural-Gas Pipelines
- Hydrological Applications
- Methane-Hydrate Studies
- Hydrothermal-Vent-Effluent Analysis
- Analytical Applications
- Biological-Science Applications
- Atmospheric Sciences
- Methanogenic-Bacteria Studies

www.lgrinc.com



LaserGas Monitor

Norsk Elektro Optikk AS



available as
Single Path Monitor
Dual Path Monitor
Multipass Monitor

LaserGas™ II

Compact design (transmitter and receiver only)

”Plug and play”

Ethernet connection

Modular design

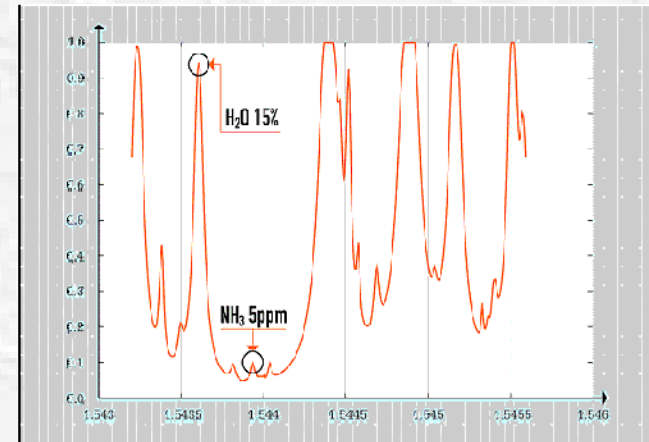
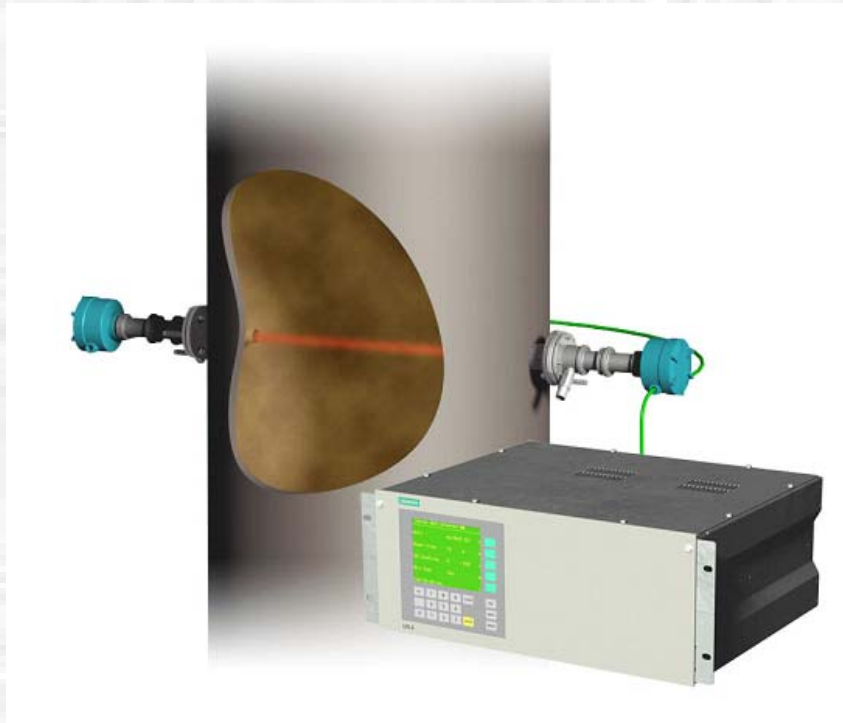
Optional Ex-p solution

www.neo.no



Process Analytics

SIEMENS



LDS 6

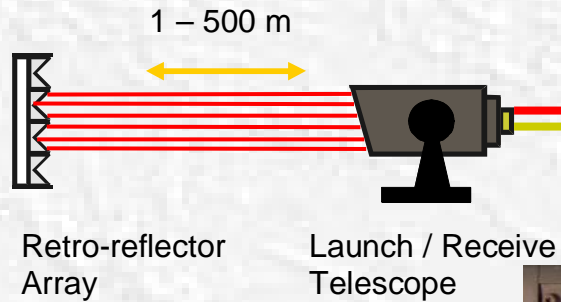
all **fibre coupling**, protection class IP 67
 $-30 < T_{\text{ambient}} < +70^{\circ}\text{C}$
sub-ppm resolution, 1 sec. response time
auto-calibration, no drifts
automatic compensation of changing
temperature, pressure, gas matrix, dust load
Sensors EEx ia, EEx n

www.siemens.com/processanalytics

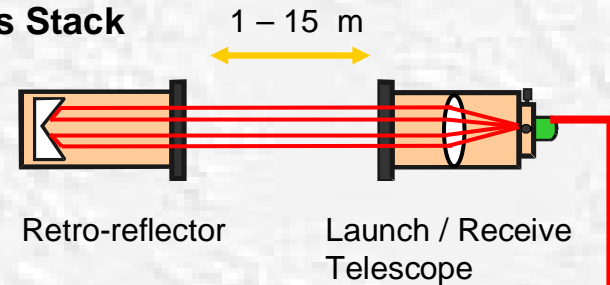
Versatile Instrumentation



LasIR-R : Remote Sensing



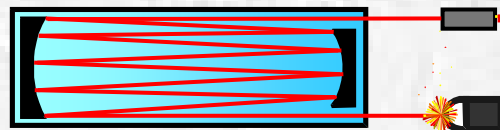
LasIR-S : Cross Stack



LasIR™



LasIR-P : Point Monitor



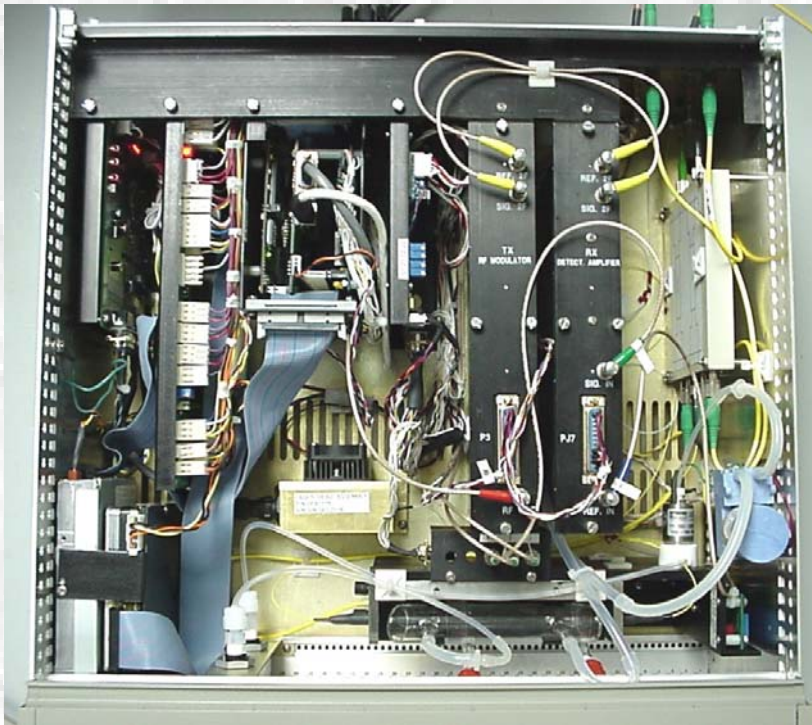
Multipass Absorption cell
(0.1 – 50 m analytical path)

LasIR-P : Point Monitor



Portable wand for leak detection
using single fiberoptic cable up
to 1 km long

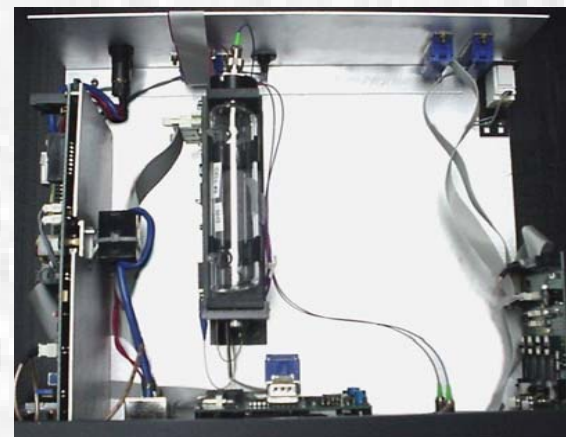
Progress ...



2-channel Analyzer (older model)

LasIR™

2-channel Analyzer (new model)





Field Laser Applications in Research

Airborne in-situ measurements ...

are a useful tool for calibration and validation of remote sensing instruments for atmospheric research

the **fast response** of TDLS allows detection of fine structures also when operating at the cruise speed of jet aircrafts

achieved scientific results indicates further area to be investigated by the next generation of airborne or satellite remote sensors

- **study of ultra-thin clouds** (UTTC, PSC)
- **small scale effects** leading to mixing phenomena very important in homogeneous and heterogeneous chemistry (tropical convection, polar vortex filaments)

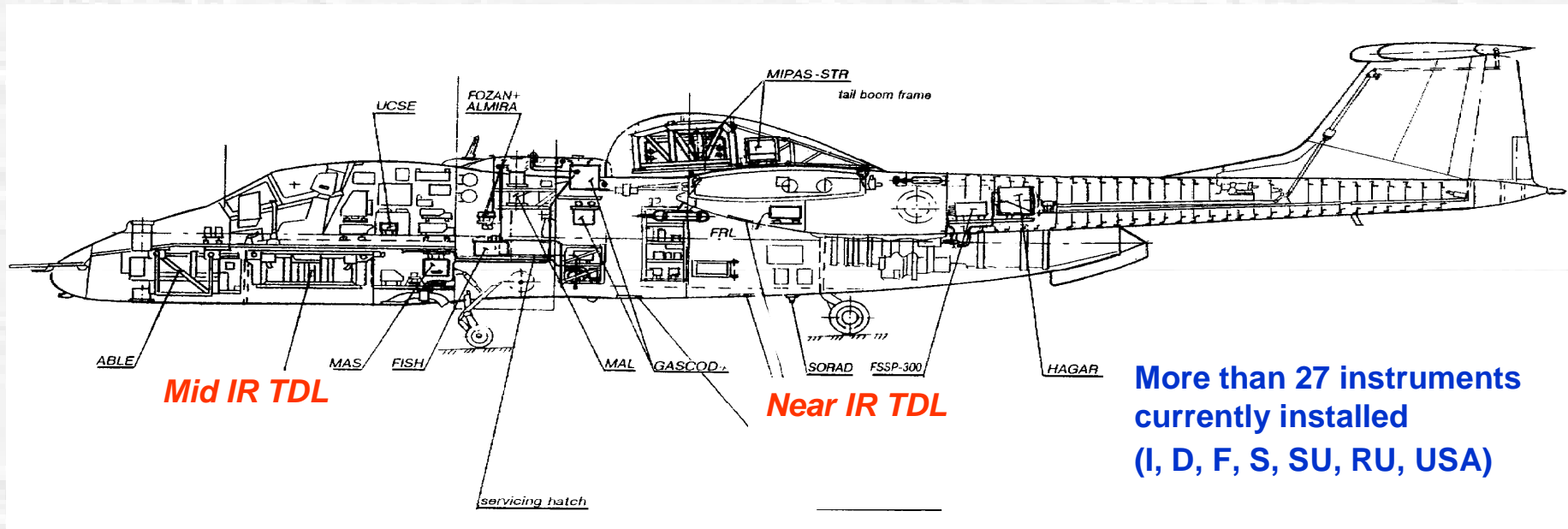


Stratospheric Research Aircraft



Aircraft	WB-57	ER-2	M-55	Proteus
Make	EEC	Lockheed	Myasishchev	Scaled Composites
Operated by	NASA	NASA	Geophysica EEIG	Angel Technol. Corp.
Birth	1944 (B57)	1955 (U2)	1988	1998
Flight parameters				
Altitude (m)	18000	21300	21830	18600 (22000 design)
Range (km)	4600	4100	4500	5500
Cruise Speed (m/s)	210	210	210	120
Payload (kg)	2700	1000	1500	3200
Duration (h)	6 h 30'	6 h 30'	5 h 40'	20

Instruments on M55 Geophysica



INOA instruments :

Mid-Infrared TDL for $\text{HNO}_3/\text{H}_2\text{O}$ or $\text{N}_2\text{O}/\text{CO}$

Near-Infrared TDL for CH_4 and CO_2

The TDLS on the Geophysica are part of a complete payload system including *in situ* and remote sensing instruments, particle analysis etc...

⇒ **This is necessary to achieve valuable scientific results**

Location of TDLs on M55 Geophysica



COLD
Mid-IR TDL

ALTO
Near-IR TDL

A Cryogenically Operated Laser Diode (COLD)

S. Viciani, F. D'Amato, P. Mazzinghi, F. Castagnoli, G. Toci, P. Werle, Appl. Phys. B90, 581-592 (2008) [View-PDF](#)



Laser sources:

single mode FP lead salt TDL

$\lambda = 5.8 \mu\text{m}$ for HNO_3 and H_2O

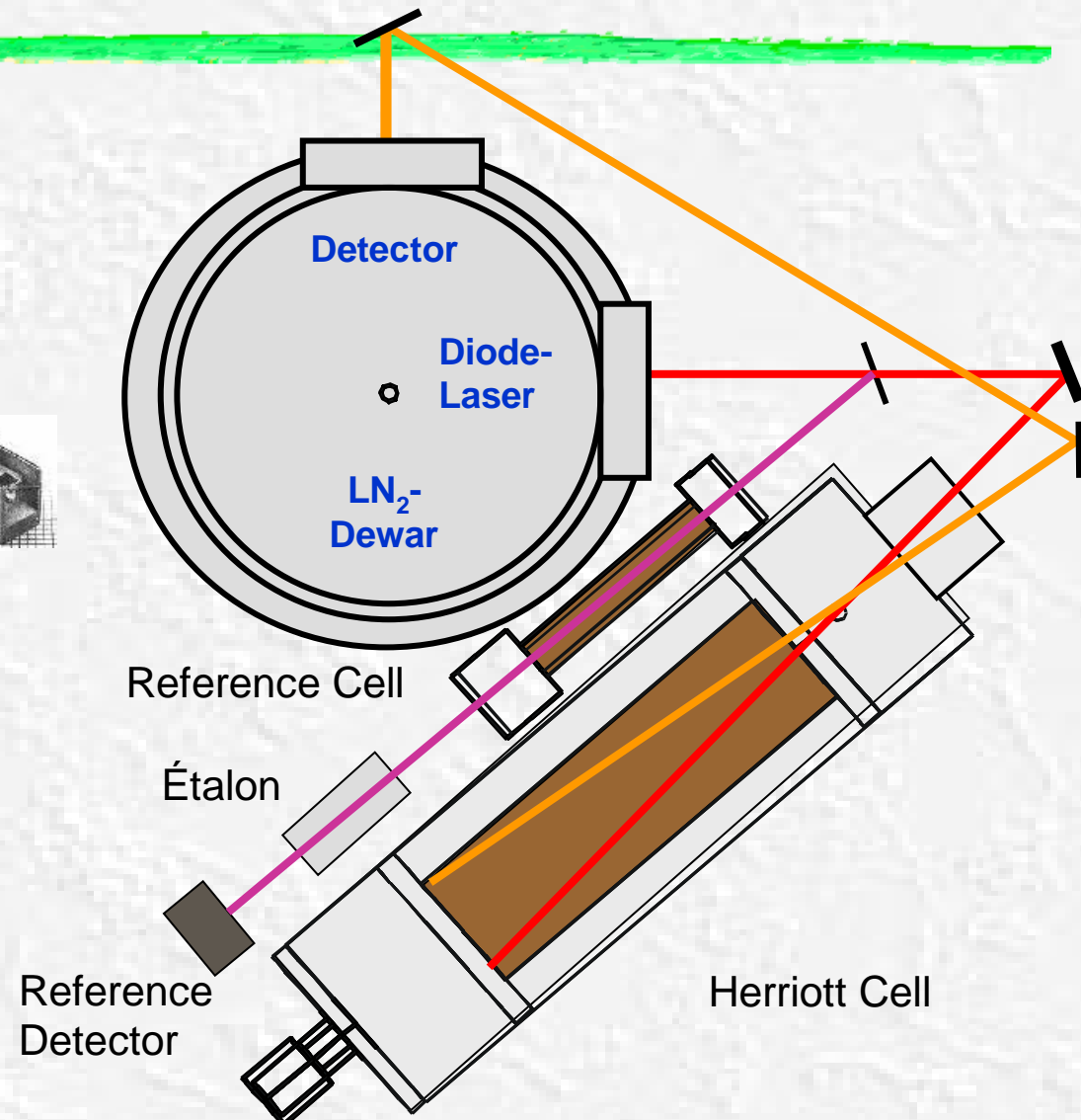
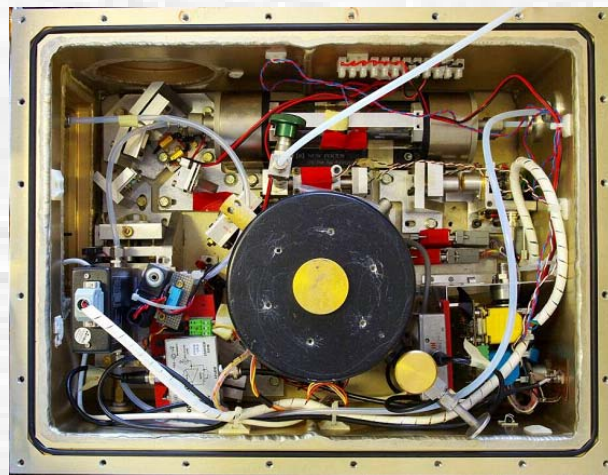
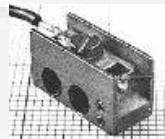
$\lambda = 4.6 \mu\text{m}$ for N_2O and CO

Multipass cell:

astigmatic Herriott cell

absorption path 36 m

low volume (0.3 l)





COLD – Data Processing

Acquisition

- direct absorption with fast sweep integration
- sample rate 5 MS/s @ 12 bit resolution
- 1000 points spectra acquired @ 2 kHz
- up to 64,000 averaged scans
- equivalent resolution up to 28 bit ($2.6 \cdot 10^8$)
- interleaved acquisition of reference spectra

Data processing

- FFT filtering and/or fringe subtraction
- lineshape fitting of the averaged spectra
- number density retrieved from HITRAN
- concentration calculated as $f(T, P)$

Achieved performance

Absorption sensitivity

< 10^{-5} in laboratory tests
 $\approx 10^{-4}$ during flights

Ultimate sensitivity is due to fringes, not to detection technique



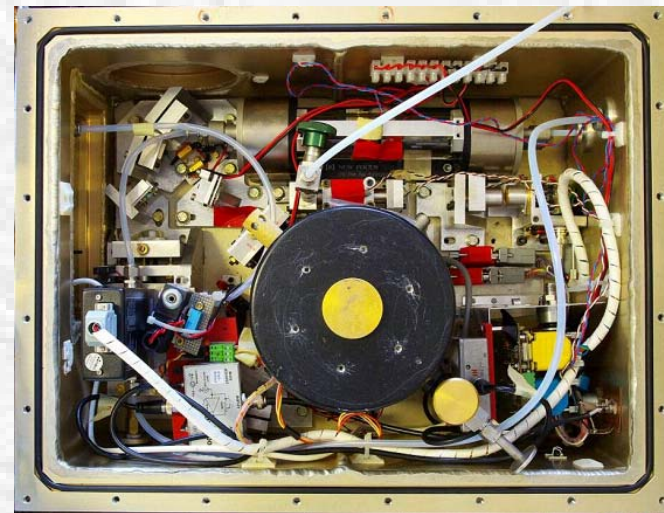
COLD after several campaigns

Learned from campaigns

Liquid nitrogen is not a problem
Actually sometimes it is an advantage

in case of power failure
⇒ the laser remains cool

in case of high humidity on ground
⇒ keeps the whole optics dry
⇒ used for flushing the cell



Reliability was found quite high

⇒ No laser failures during campaigns, just replacements for different targets
⇒ The same set of mirrors still in use after 6 years and 5 campaigns!
⇒ Alignment found very stable (no realignment required in campaigns).

Main problems were:

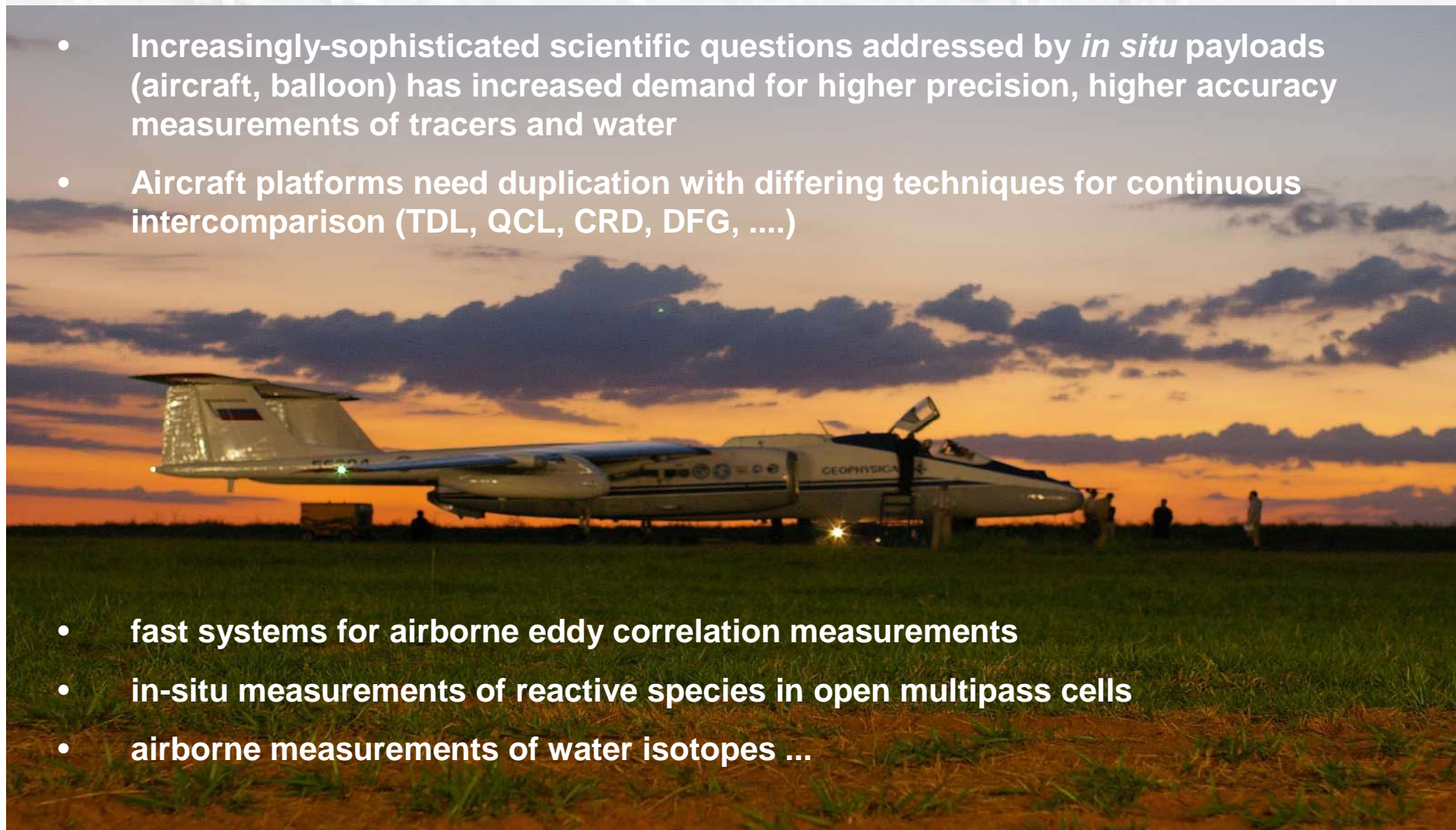
multimode emission from some lasers
communication failure with the laser controller

Future developments

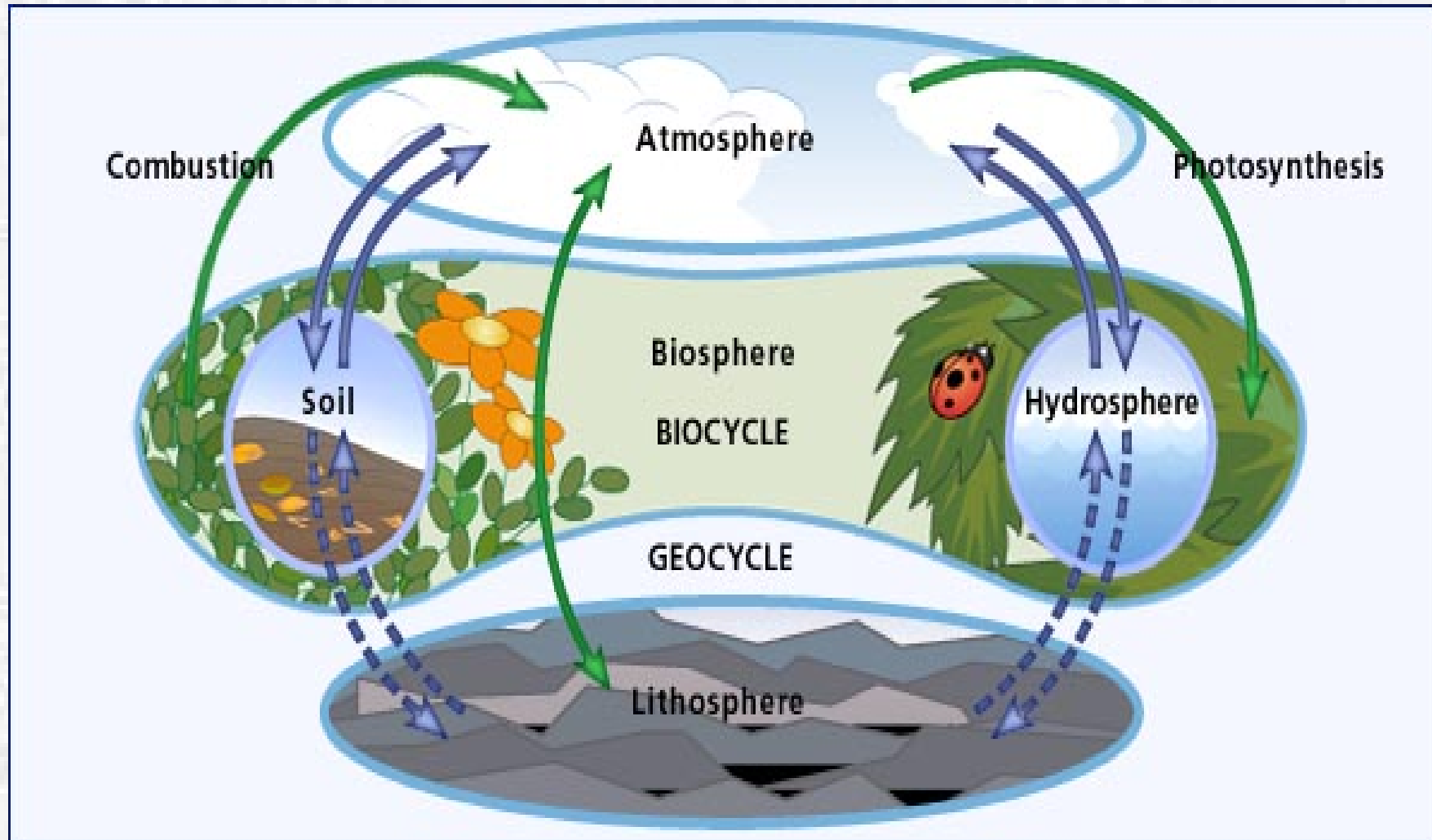


- Increasingly-sophisticated scientific questions addressed by *in situ* payloads (aircraft, balloon) has increased demand for higher precision, higher accuracy measurements of tracers and water
- Aircraft platforms need duplication with differing techniques for continuous intercomparison (TDL, QCL, CRD, DFG,)

- fast systems for airborne eddy correlation measurements
- in-situ measurements of reactive species in open multipass cells
- airborne measurements of water isotopes ...



Biogeochemical cycles - Turbulent Fluxes

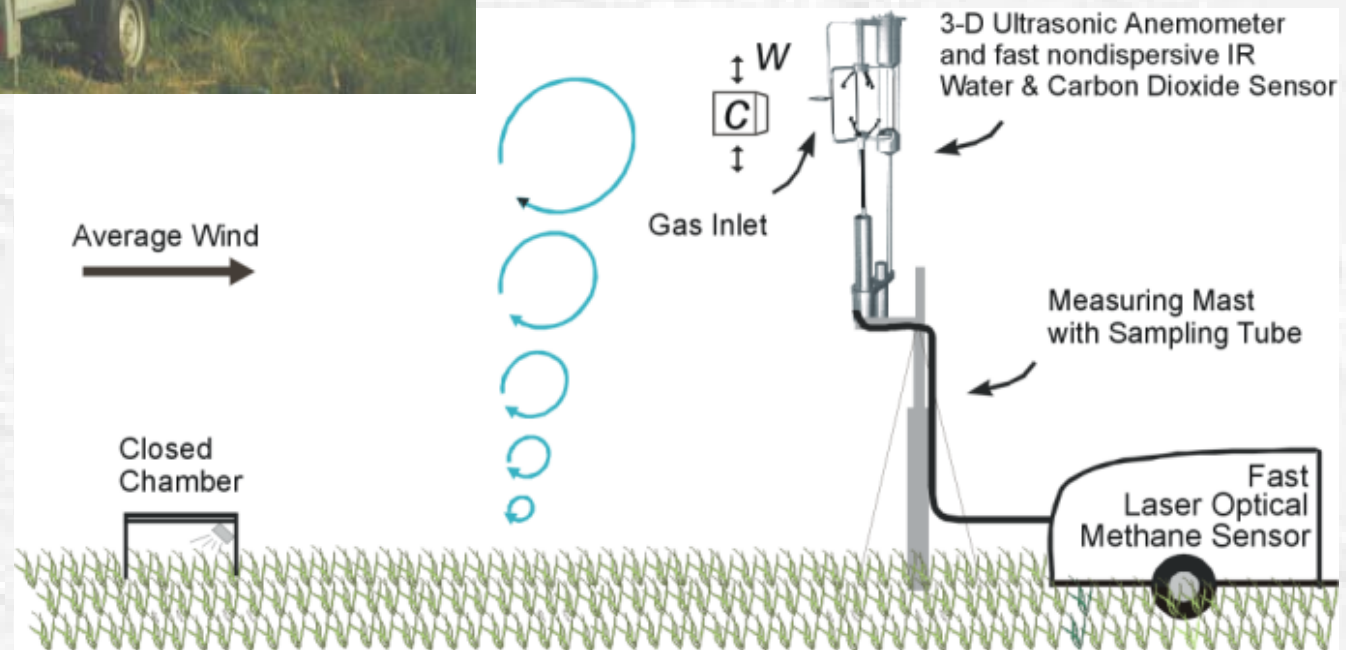


The fast diode-laser trace gas sensor



TO DO :

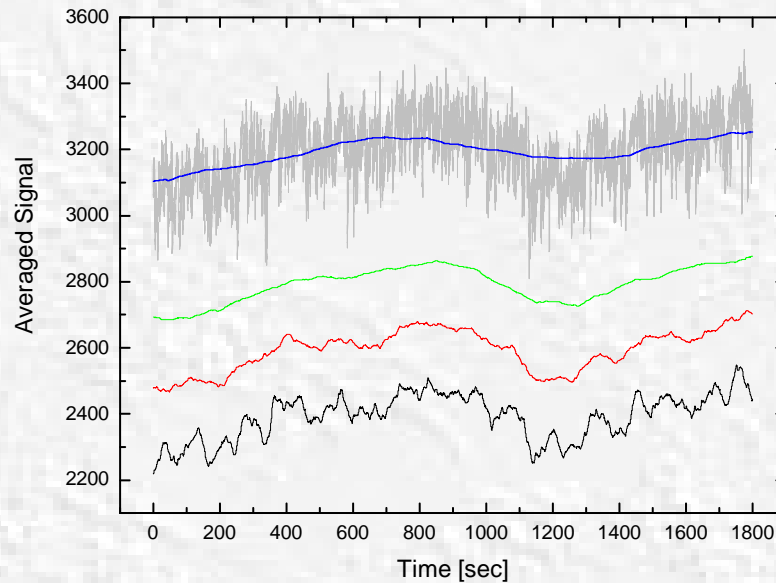
- detrending
- frequency spectra
- covariance and cospectrum
- time lag
-



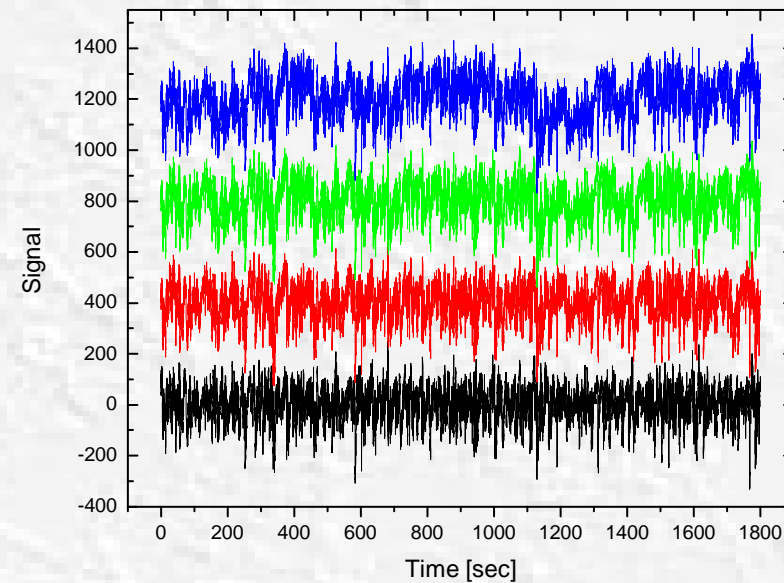
Detrending of time series data

Smoothing effect of the moving average filter with different time constants

Low pass filtered



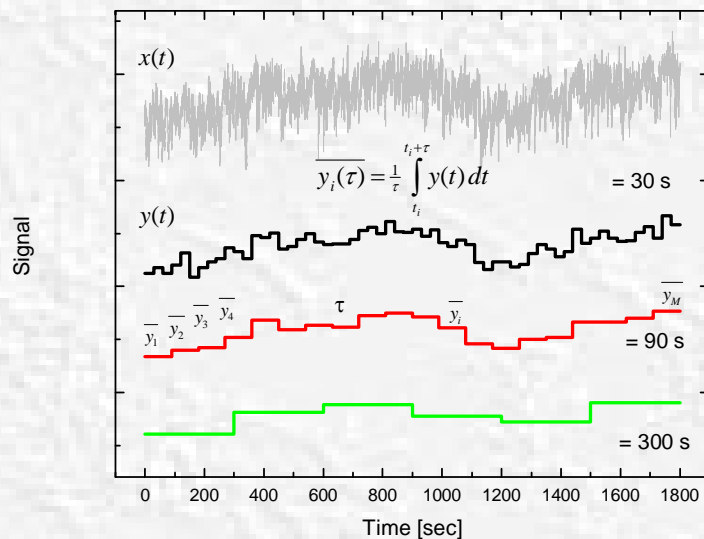
High pass filtered



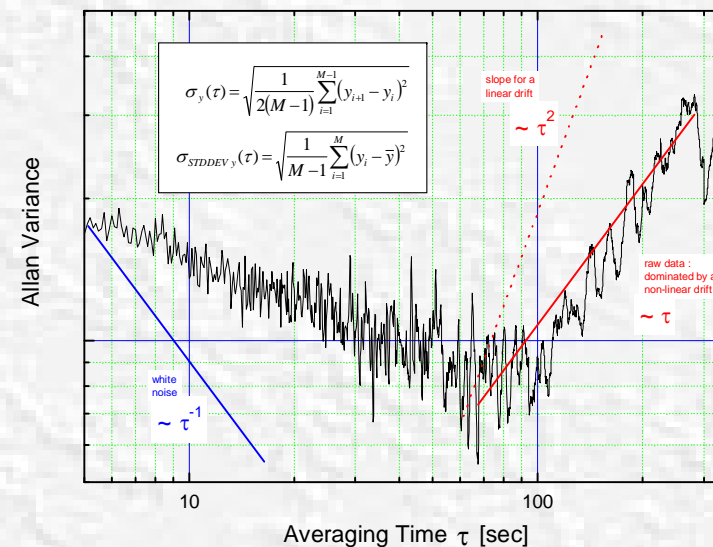
$$y[i] = \sum_{j=-(M-1)/2}^{(M-1)/2} \frac{1}{M} \cdot x[i-j]$$

$$y(t) = [\delta(t) - h(t)] * x(t)$$

Detrending : What is the optimum time constant ?

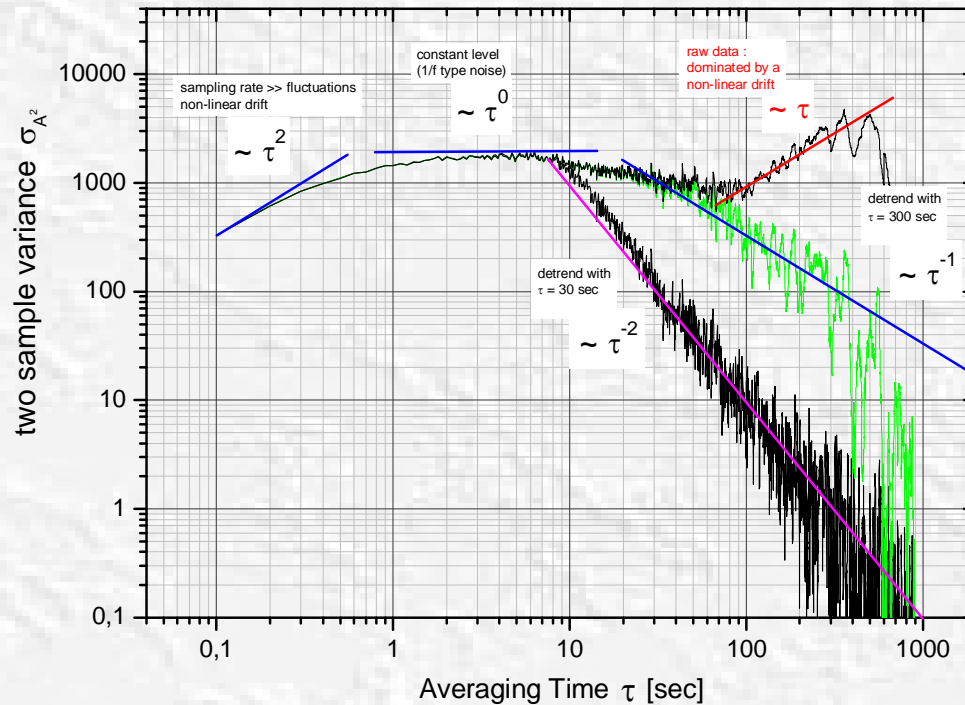


10 Hz time series data together with selected plots for subensemble averages with bin-sizes of 30s, 90s and 300s.



Plot of the two sample variance as a function of the subensemble averaging time t . The line following t^{-1} indicates the expected behaviour for a “white noise” dominated system.

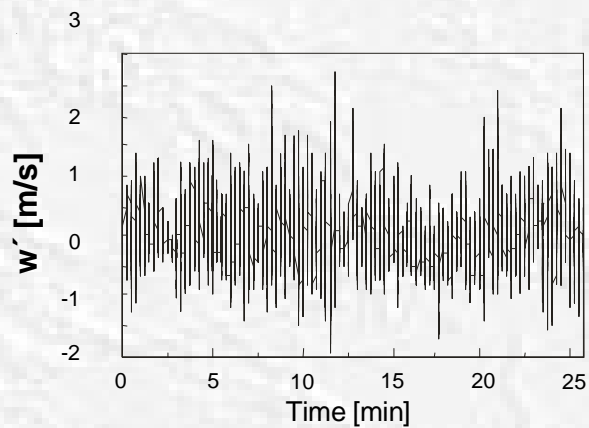
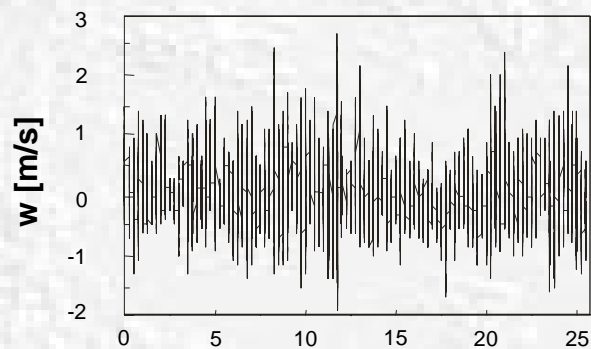
Stability Analysis vs Filter Time Constant



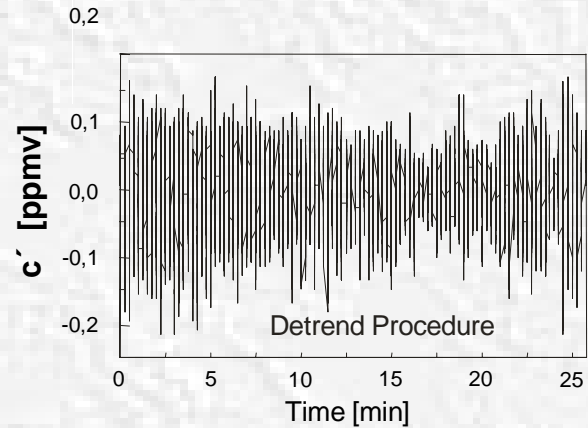
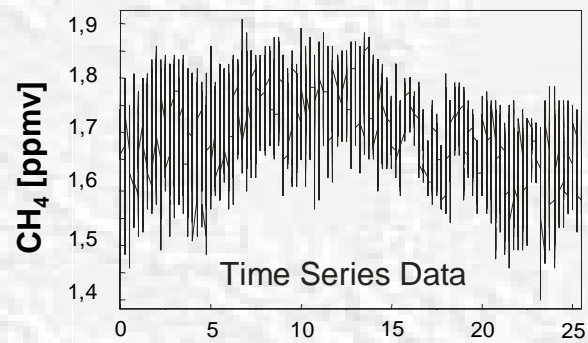
Two sample variance characterization of a trace gas concentration time series in the time domain. For averaging intervals below 1 s atmospheric turbulence is well resolved and appears as a 'non-linear drift', while in the range between 1s to 10s 'flicker noise' dominates. The upper right part is the drift dominated behaviour of the raw data. The middle trace can be considered as ideal and corresponds to the application of a 300 s moving average filter for detrending. The lower trace belongs to the 30 sec time constant.

Detrended time series data to get the fluctuations

Ultrasonic anemometer
vertical wind measurement

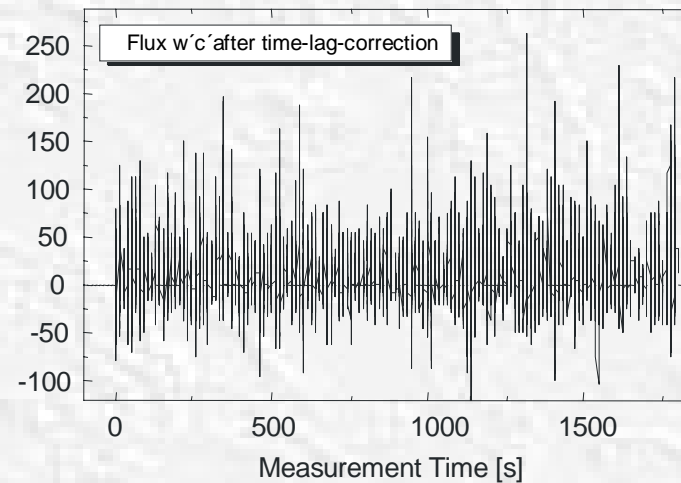
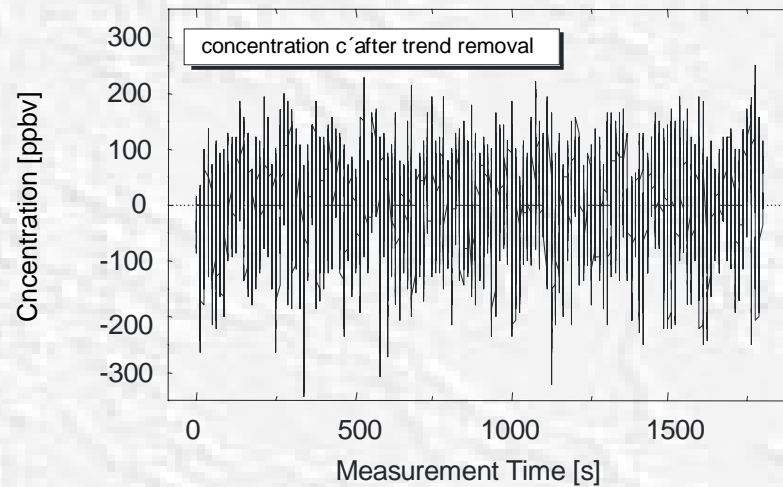
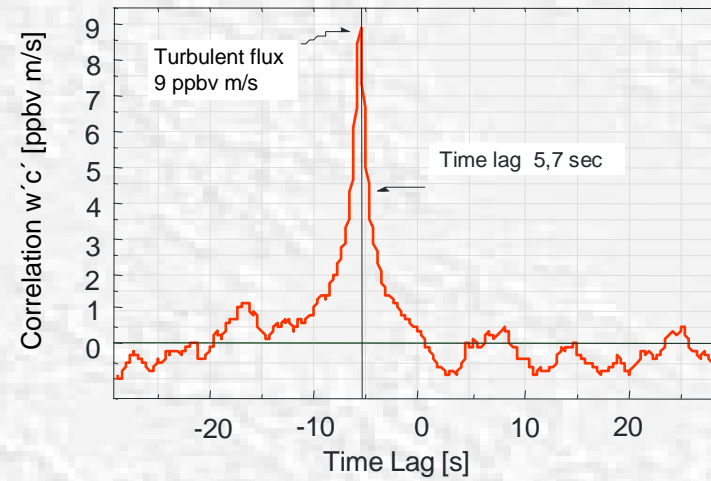
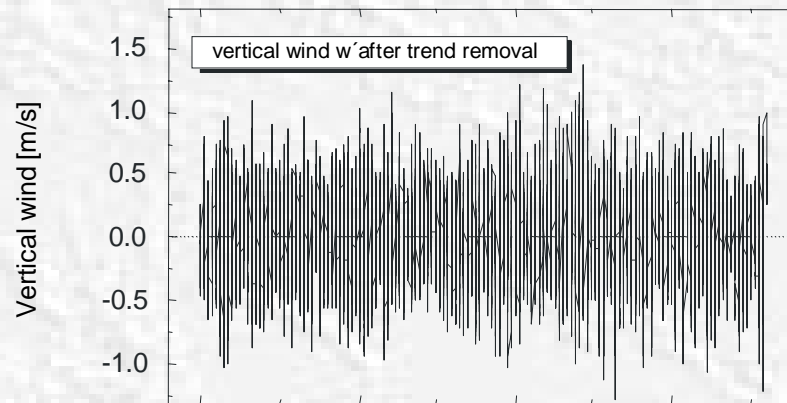


Concentration
measurement



„running means“ or „high-pass filtering“ : Allan Variance and be used to determine the high pass constant

Turbulent flux after time lag correction



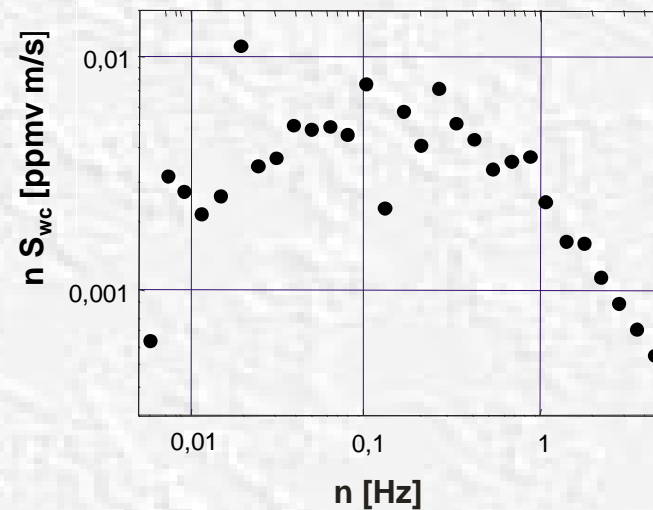
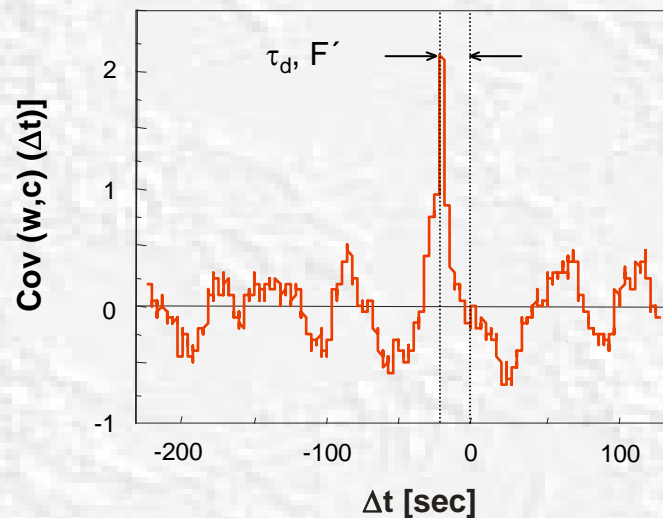
Covariance & Cospectrum

$$\text{Cov}[w,c](\Delta t) \propto \int w'(t+\Delta t) \cdot c'(t) \cdot dt$$

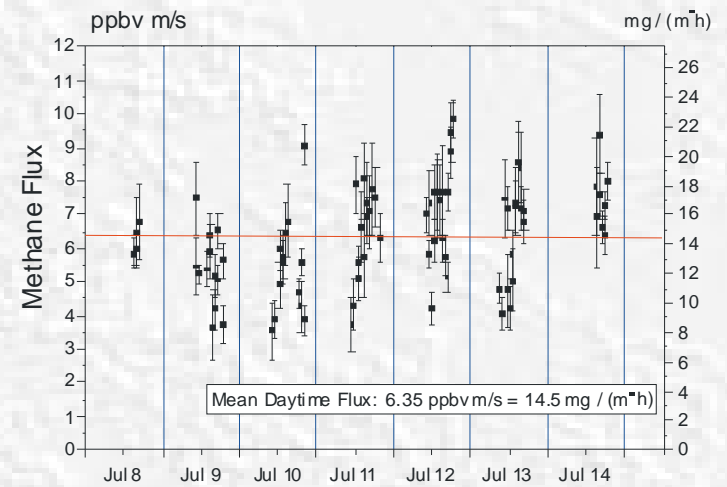
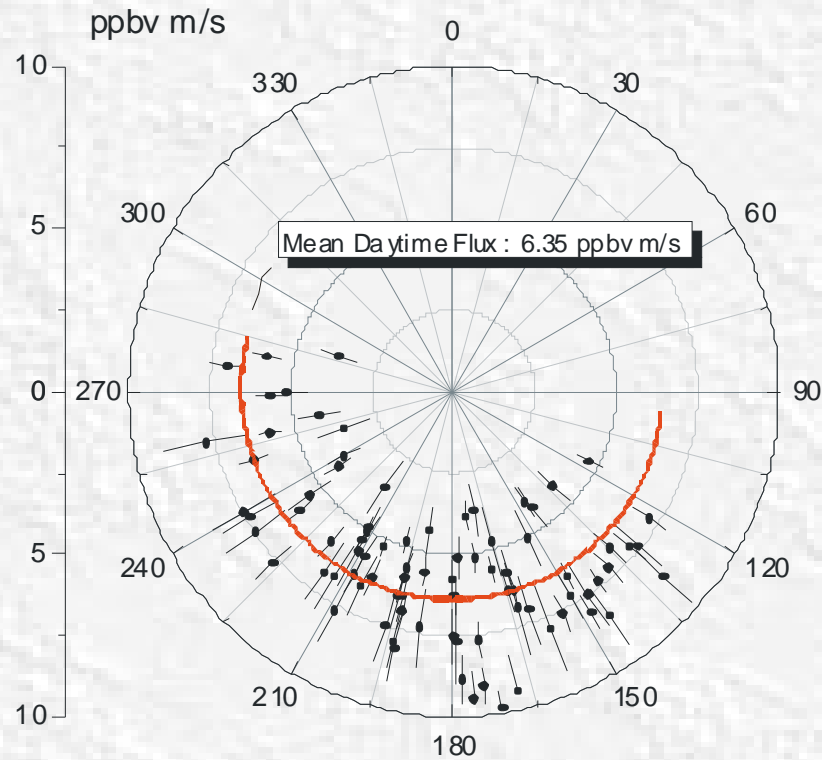
$$C_{w'c'}(n) \propto \text{Re} \left[W(n) \cdot C^*(n) \cdot e^{2\pi i n \tau_d} \right]$$

Turbulent Flux $F' = \text{Cov}[w,c](\tau_d)$

Time Lag $\tau_d \rightarrow$

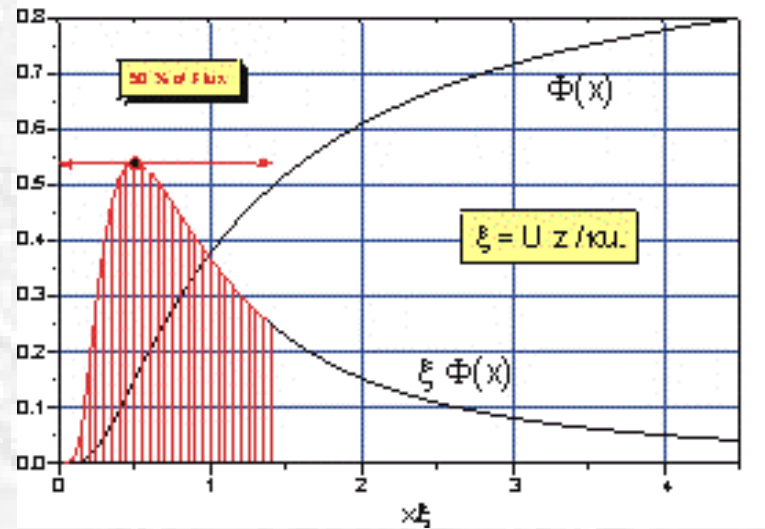
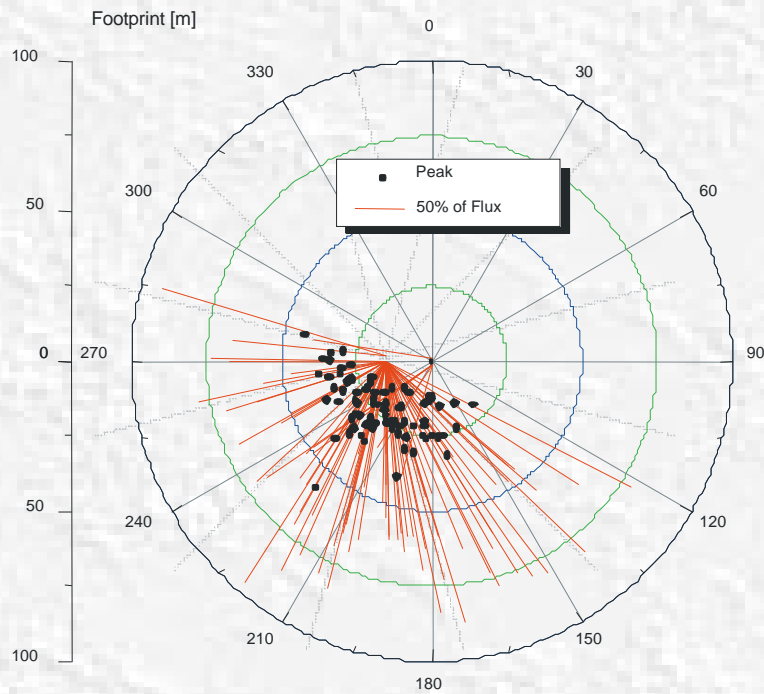


Mean daytime flux vs wind direction



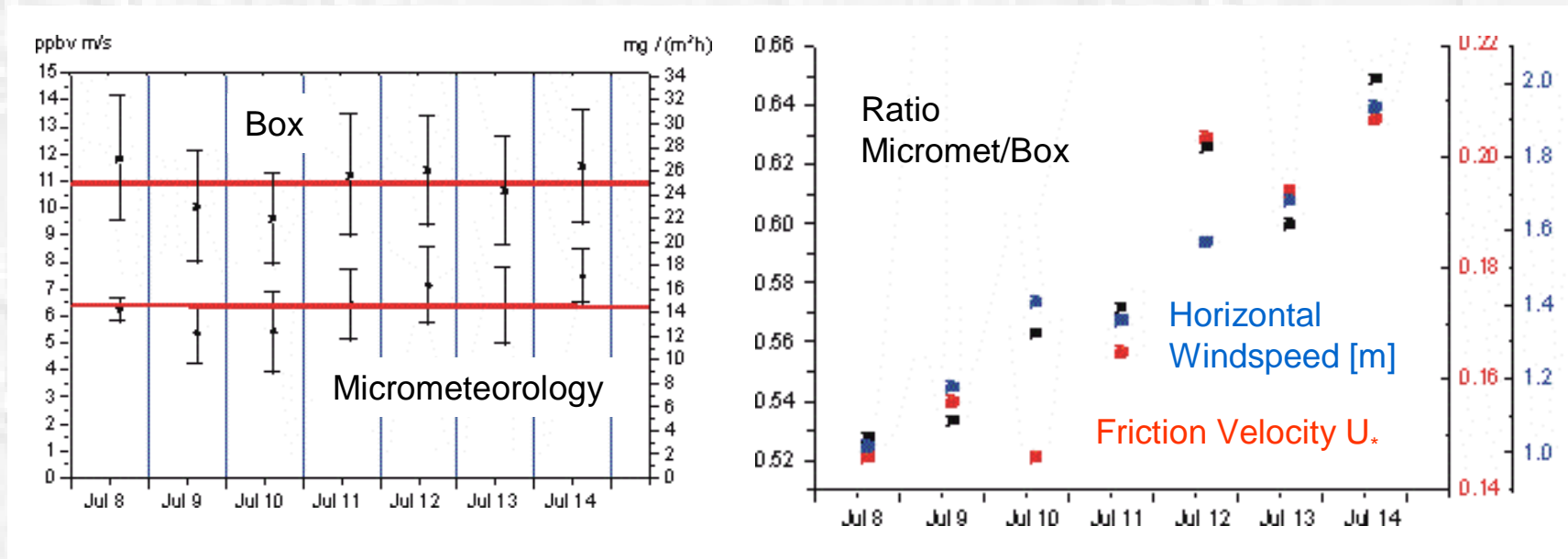
Mean daytime flux : 6,35 ppbv m/s

Footprint estimation



Schuepp et. al., Bound.-Lay. Met 50, 355 (1990)

Results



The closed chamber measurements reported to about **70%** higher CH₄ fluxes than the eddy correlation instruments (3 independent systems).

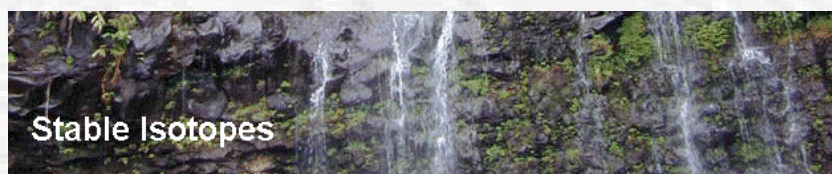
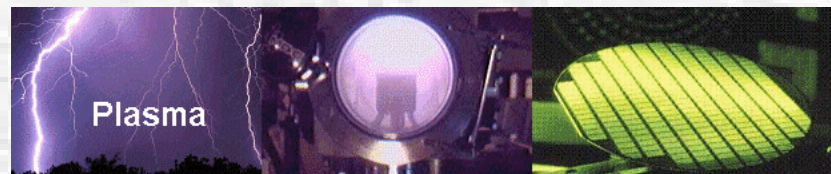
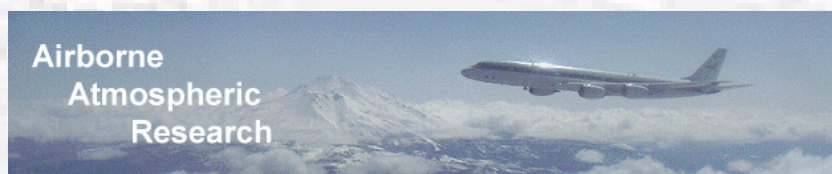
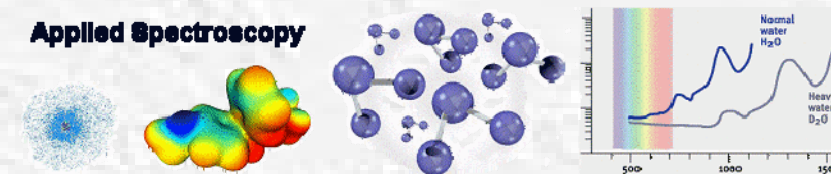
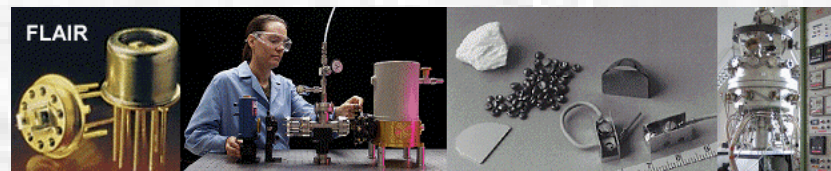


Closed chamber measurements may overestimate methane fluxes from rice paddy fields.

Werle, P., Kormann, R., 2001. A fast chemical sensor for eddy correlation measurements of Methane emissions from rice paddy fields. Appl. Opt. 40, 846-858.
Denmead, O.T., 2008. Approaches to measuring fluxes of methane and nitrous oxide between landscapes and the atmosphere. Plant Soil 309, 5-24.

For more **Field Laser Applications in Industry and Research**

FLAIR 2009 – Sept. 6-11, 2009 Garmisch-Partenkirchen, Germany



<http://imk-ifu.kit.edu/flair/>

Publications with references related to the presentation

- P. Werle, F. D'Amato, S. Viciani, "Tunable diode laser spectroscopy: principles, performance, perspectives", in: M. Lackner (ed) *Lasers in Chemistry – Probing Matter*, Wiley-VCH, Weinheim, 255-275 (2008).
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- S. Viciani, F. D'Amato, P. Mazzinghi, F. Castagnoli, G. Toci, P. Werle, "A cryogenic operated diode-laser spectrometer for airborne measurement of stratospheric trace gases", *Appl. Phys. B90*, 581-592 (2008) [View-PDF](#)
- C. Dyroff, P. Weibring, A. Fried, D. Richter, J.G. Walega, A. Zahn, W. Freude, P. Werle, "Stark-enhanced diode-laser spectroscopy of formaldehyde using a modified Herriott-type multipass cell", *Appl. Phys. B 88*, 117-123 (2007). [View-PDF](#)
- C. Dyroff, A. Zahn, W. Freude, B. Jänker, P. Werle, "Multipass cell design for Stark-modulation spectroscopy", *Appl. Opt. 46* (19), 4000-4007 (2007). [View-PDF](#)
- P. Werle, "Diode-laser sensors for in-situ gas analysis", in: P. Hering, P. Lay, S. Stry (eds) *Lasers in Environmental and Life Sciences – Modern Analytical Methods*, Springer Verlag, Heidelberg pp.223-243 (2004). [View-PDF](#)
- M. Pantani, F. Castagnoli, F. D'Amato, M. De Rosa, P. Mazzinghi, P. Werle, "Two infrared laser spectrometers for the in-situ measurement of stratospheric gas concentration", *Infrared Physics & Technology 46*, 109-113 (2004). [View-PDF](#)
- P. Werle, P. Mazzinghi, F. D'Amato, M. De Rosa, K. Maurer, F. Slemr, Review Paper "Signal processing and calibration procedures for in-situ diode-laser absorption spectroscopy", *Spectrochimica Acta A 60*, 1685-1705 (2004). [View-PDF](#)
- P. Werle and R. Kormann, "A fast chemical sensor for eddy correlation measurements of Methane emissions from rice paddy fields", *Appl. Opt. 40*, 846-858 (2001). [View-PDF](#)
- R. Kormann, H. Mueller and P. Werle, "Eddy flux measurements of Methane over the fen Murnauer Moos, 11°11'E, 47°39'N, using a Fast Tunable Diode-Laser Spectrometer", *Atmospheric Environment 35*, 2533-2544 (2001). [View-PDF](#)
- P. Werle and S. Lechner, "Stark-modulation-enhanced FM-spectroscopy", *Spectrochimica Acta A 55*, 1941-1955 (1999). [View-PDF](#)
- P. Werle and A. Popov, "Application of antimonide lasers to gas sensing in the 3-4 um range", *Appl. Opt. 38*, 1494-1501 (1999). [View-PDF](#)
- P. Werle, R. Muecke, F. D'Amato and T. Lancia, "Near-infrared trace gas sensors based on room-temperature diode-lasers", *Appl. Phys. B 67*, 307-315 (1998). [View-PDF](#)
- P. Werle, "Review of recent advances in laser based gas monitors", *Spectrochimica Acta A54*, 197-236 (1998). [View-PDF](#)
- P. Werle, "Spectroscopic trace gas analysis using semiconductor diode-lasers", *Spectrochimica Acta A 52* (8), 805-822 (1996). [View-PDF](#)
- P. Werle, B. Scheumann and J. Schandl, "Real time signal processing concepts for trace gas analysis by TDLAS", *Opt. Eng. 33*, 3093-3105 (1994). [View-PDF](#)
- P. Werle, R. Muecke and F. Slemr, "The limits of signal averaging in atmospheric trace gas monitoring by tunable diode-laser absorption spectroscopy", *Appl. Phys. B 57*, 131-139 (1993). [View-PDF](#)
- P. Werle and F. Slemr, "Signal-to-noise ratio analysis in laser absorption spectroscopy using optical multi-pass cells", *Appl. Opt. 30*, 430-434 (1991). [View-PDF](#)
- P. Werle, F. Slemr, M. Gehrtz and Chr. Braeuchle, "Wideband noise characteristics of a lead-salt diode-laser", *Appl. Opt. 28*, 1638-1642 (1989). [View-PDF](#)
- P. Werle, F. Slemr, M. Gehrtz and Chr. Braeuchle, "Quantum limited FM-spectroscopy with a lead-salt diode-laser: A comparison of theoretical and experimental data", *Appl. Phys. B 49*, 99-108 (1989). [View-PDF](#)

<http://www.inoa.it/home/pwwerle/papers.html>