Karlsruhe Institute of Technology

Quality assurance aspects for laser based eddy covariance measurements of atmospheric trace gases

Peter Werle

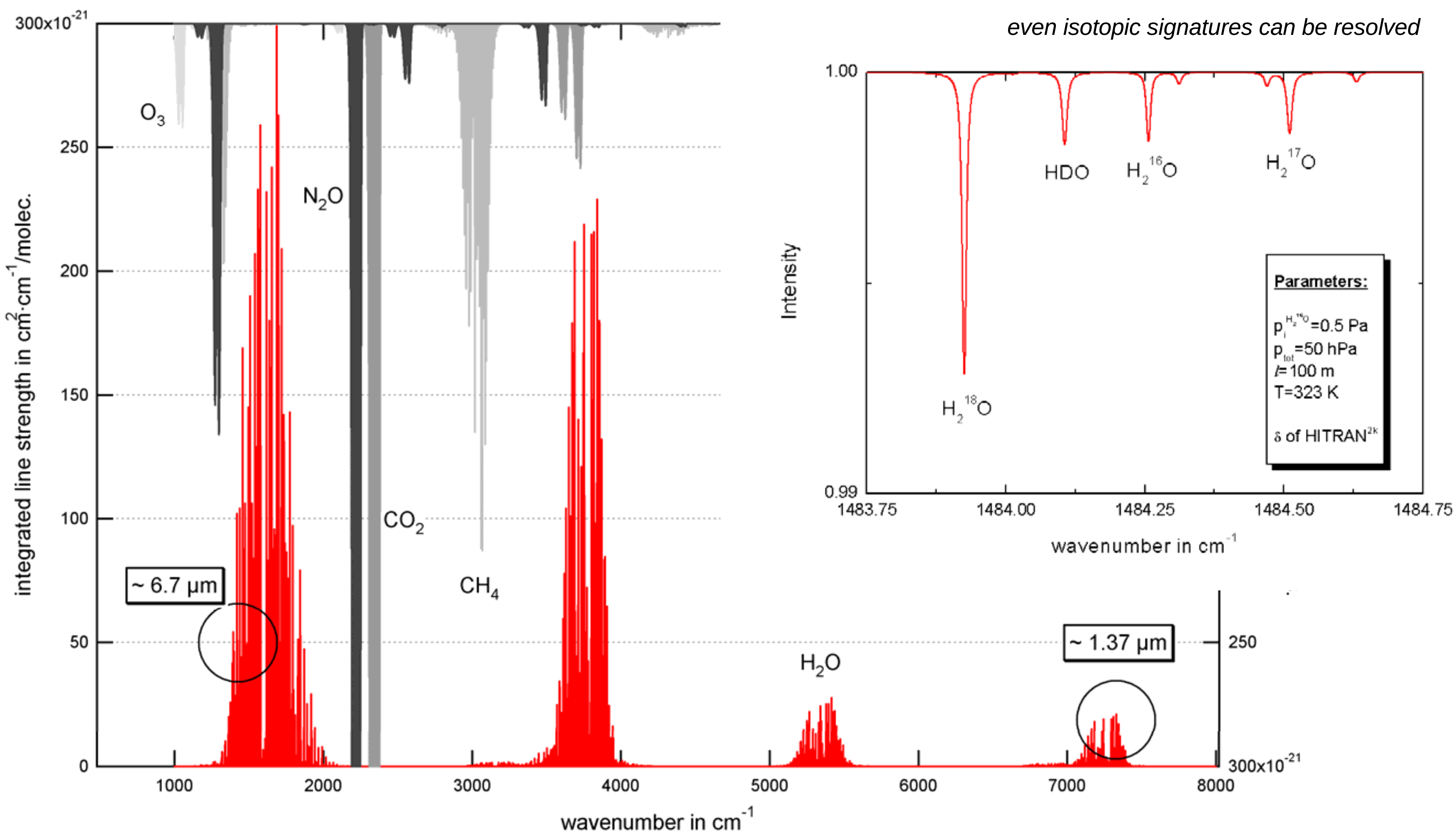
INSTITUTE OF METEOROLOGY AND CLIMATE RESEARCH, IMK-IFU, Kreuzeckbahnstrasse 19, 82467 Garmisch-Partenkirchen, Germany

Contact : Peter.Werle@kit.edu

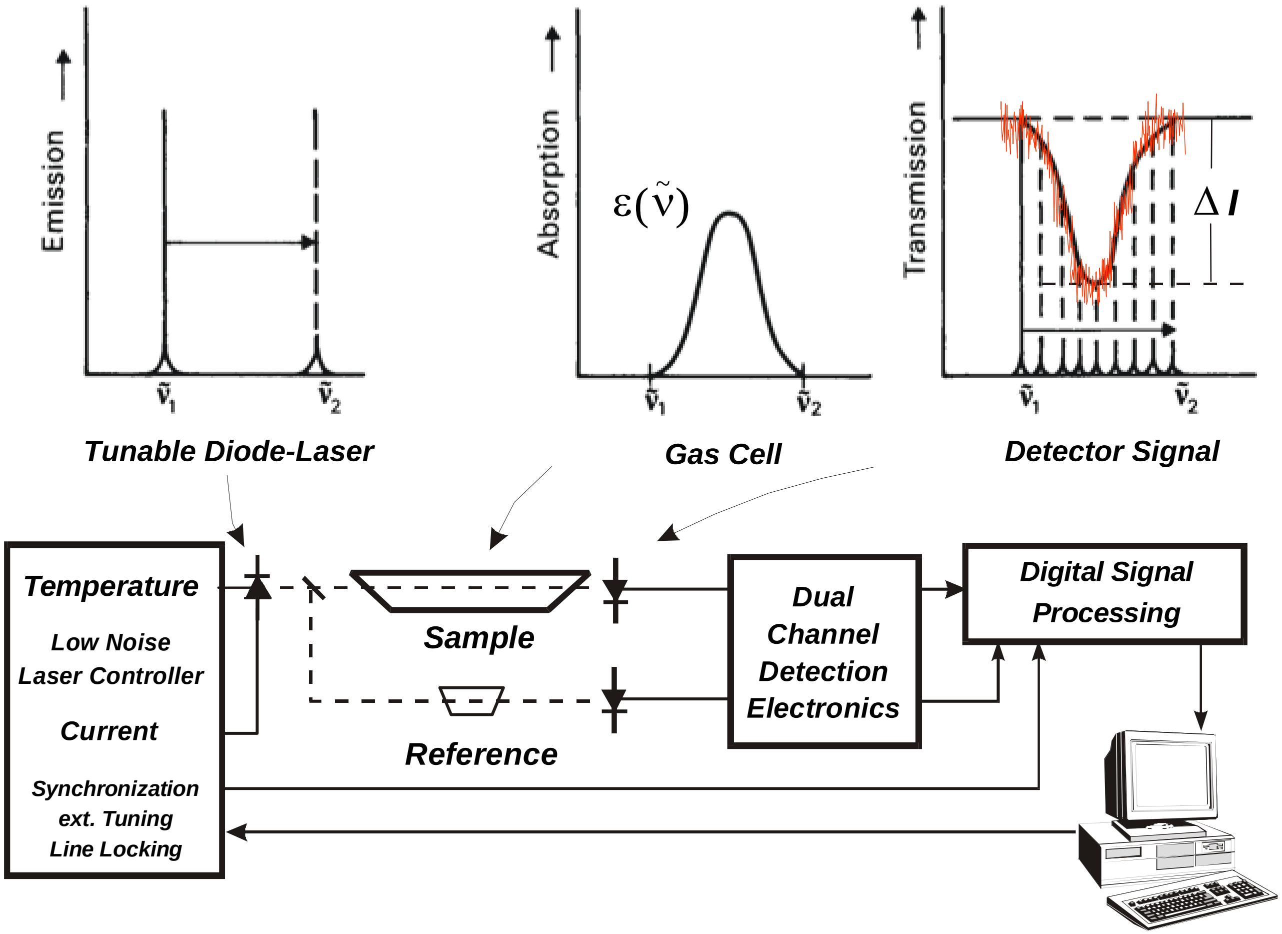
Outline

- A brief introduction to laser spectroscopy :
  principles & problems
- System stability is a key issue in all trace gas analyzers
- The concept of the two sample variance
- Frequency domain and time domain characterization
- Applications to gas sensing and flux measurements
- Literature samples

´Fingerprints´ for selective trace gas analysis



Laser based gas analyzers – „a trace gas radio“



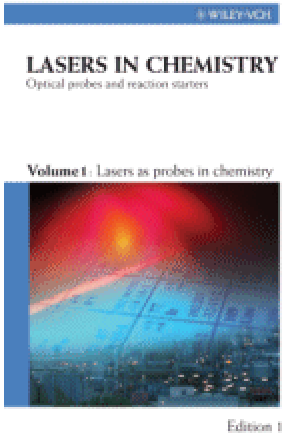
P. Werle, A review of recent advances in semiconductor laser based gas monitors, Spectrochimica Acta A54, 197-236, 1998 (183 references)

further reading : http://www.inoa.it/home/pwwerle/

P. Werle, F. D´Amato, S. Viciani
Tunable diode-laser spectroscopy: principles, performance, perspectives

Lackner (Ed.)
Lasers in Chemistry - Optical probes and reaction starters
Wiley-VCH, Weinheim (2008) pp. 255-275

... the new reference for lasers in chemistry …

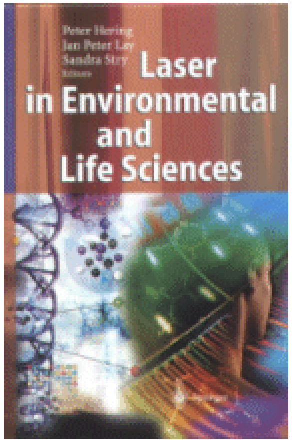


P. Werle
Diode-laser sensors for in-situ gas analysis:

Hering · Lay · Stry (Eds.)
Laser in Environmental and Life Sciences
Modern Analytical Methods

Springer Verlag, Heidelberg (2004) pp.223-243

… state of the art of laser-induced analytical methods in environmental and life sciences as an interdisciplinary approach …



state-of-the-art commercial fast ´*in situ*´ trace gas analyzers

KIT Karlsruhe Institute of Technology

AERODYNE RESEARCH Inc.

LI-COR® Biosciences

PSI PHYSICAL SCIENCES INC.

LGR

Garmisch-Partenkirchen FLAIR - 2009

PICARRO Reliable by Design

GAT

click for details

CAMPBELL SCIENTIFIC, INC.

norsk elektro optikk

NOVAWAVE

System Characterization

- Manufacturers need to specify and prove their system performance to the customer
- Researchers (users) need a tool that helps them to judge how „good“ their data are – *test the instrument´s health status*
- preferably a simple tool for „routine measurements“

Sample Variance

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

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

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

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

IEEE subcommittee on frequency stability …

… has recommended the two sample variance

J. von Neumann, R. H. Kent, H. R. Bellinson and B. I. Hart, "The mean square successive difference", Ann. Math. Stat. 12, 153-162 (1942).

to characterize atomic frequency standards and an experimental estimation of the square root of the so called "Allan variance" is

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

PROCEEDINGS OF THE IEEE VOL. 54, NO. 2 FEBRUARY, 1966

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 $N^{15}H_3$), the cesium beam frequency standard employed as the U. S. Frequency Standard, and rubidium gas 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 5 parts in 10^{13}.

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 are directly re-[illegible]ted to the inherent noise of a quantum device and its [illegible]ated electronics. For exa[illegible]ple, a [illegible] measur[illegible] 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.

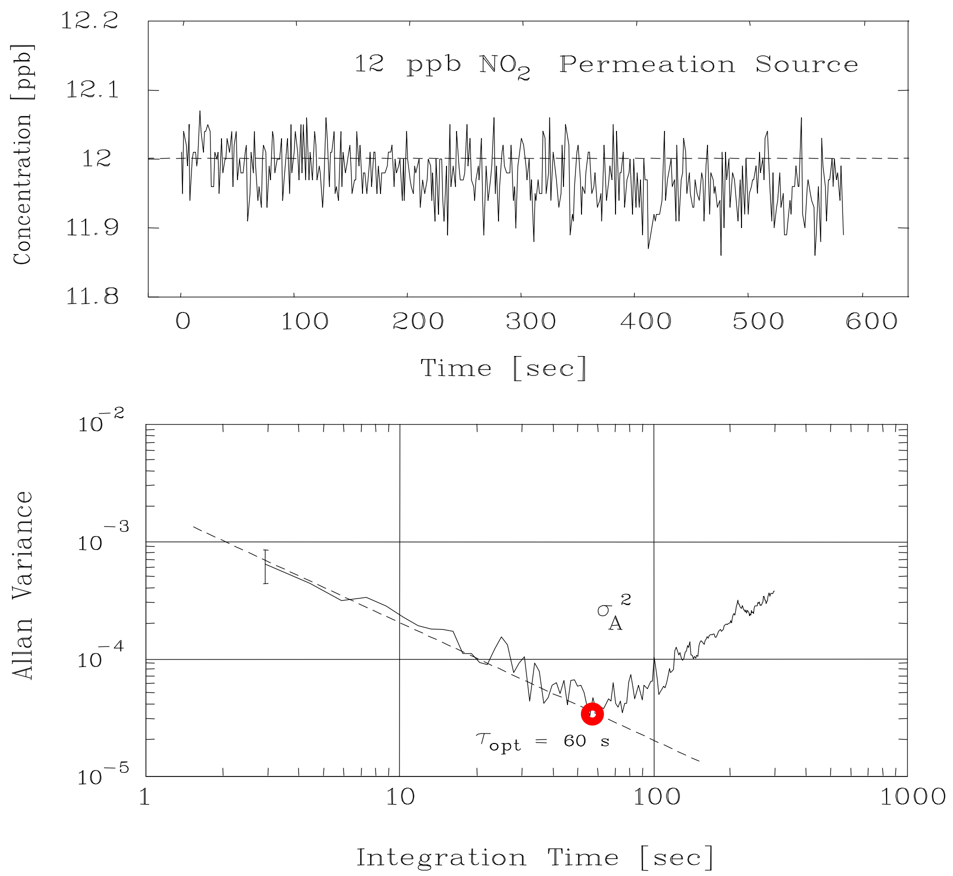
An analysis has already been made of the noise present in passive atomic frequency standards [1], such as cesium beams, but a classification of the types of noise exhibited by the maser type of quantum-mechanical oscillator has not been made in the long term area, i.e., for low frequency fluctuations. 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 becom[illegible] of special interest to [illegible] [illegible]sent on

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

Characterization of spectroscopic gas analyzers

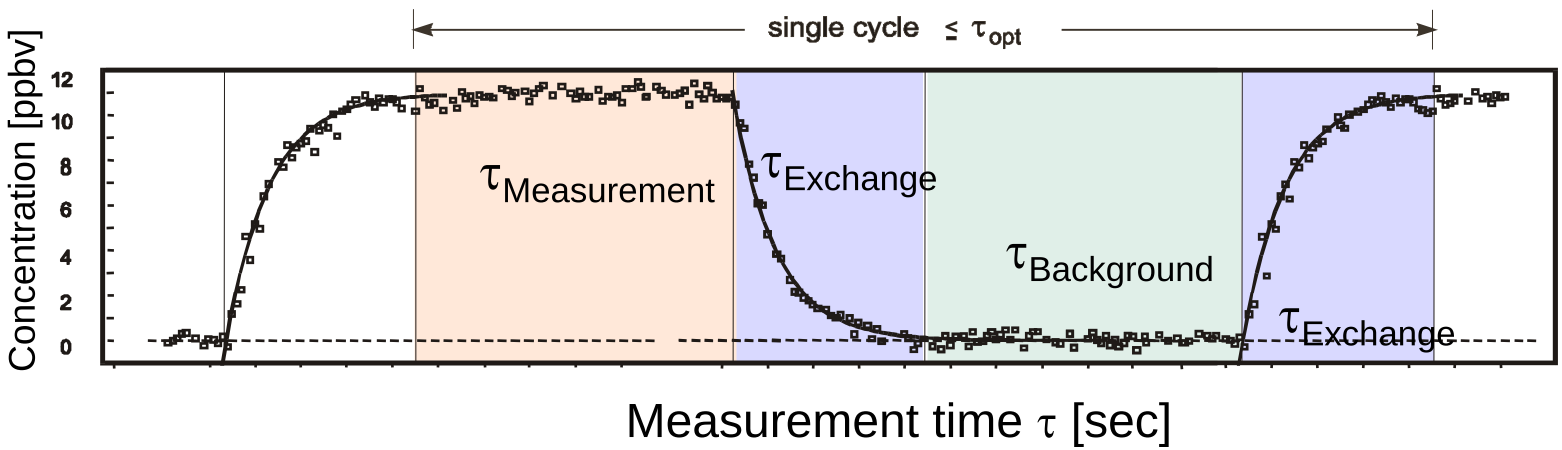
This concept has been first applied to characterize a laser trace gas analyzers in 1993 and since then this approach has become a well established tool for researchers and instrument developers to describe the performance of laseroptical trace gas sensors.

The time τ_{opt} is a characteristic feature of the stability of a given spectrocopic gas analyzer at a given site and given conditions.



P. Werle et al. „The limits of signal averaging in atmospheric trace gas monitoring“, Appl. Phys. B 57, 131-139 (1993).

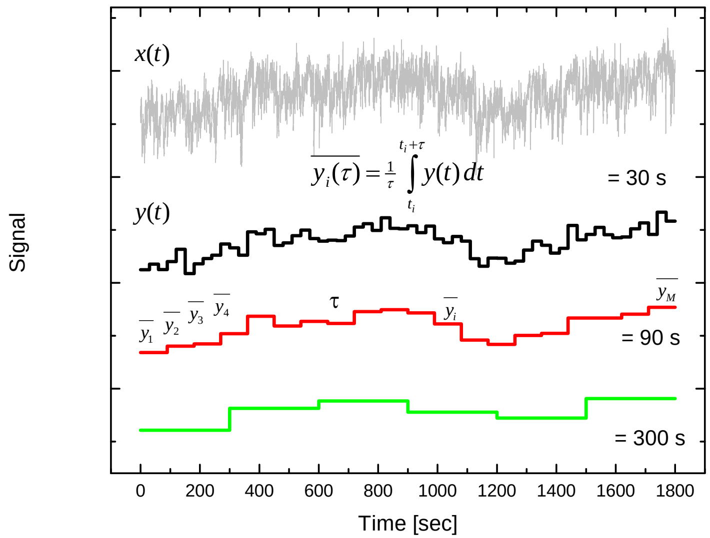
Consequences : The optimum measurement cycle

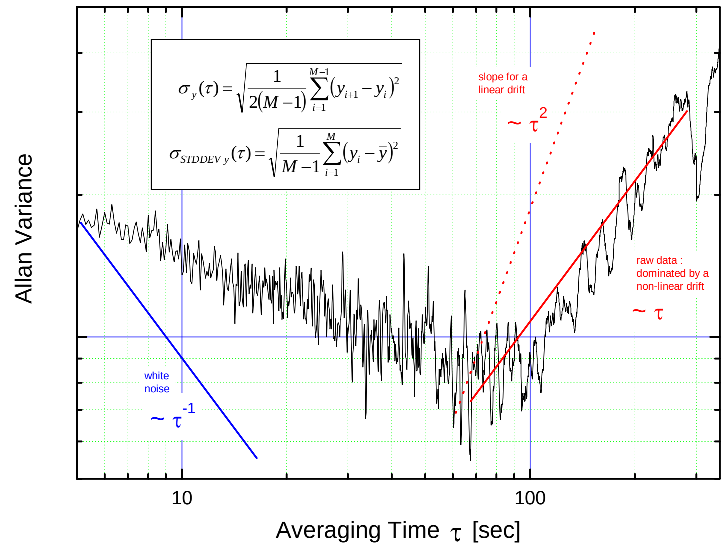


- to assure any relationship between ambient signals and background or calibration signals, the subtraction has to be done within τ_{opt}
- regular investigations of the appropriate measurement cycle at a given field site are a prerequisite for reliable measurements and long term instrument stability. (detailed instructions in the review paper listed below)

P. Werle et al. ,"Signal processing and calibration procedures for in-situ diode-laser absorption spectroscopy", Spectrochimica Acta A 60, 1685-1705 (2004)

An application : Detrending of time series data





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

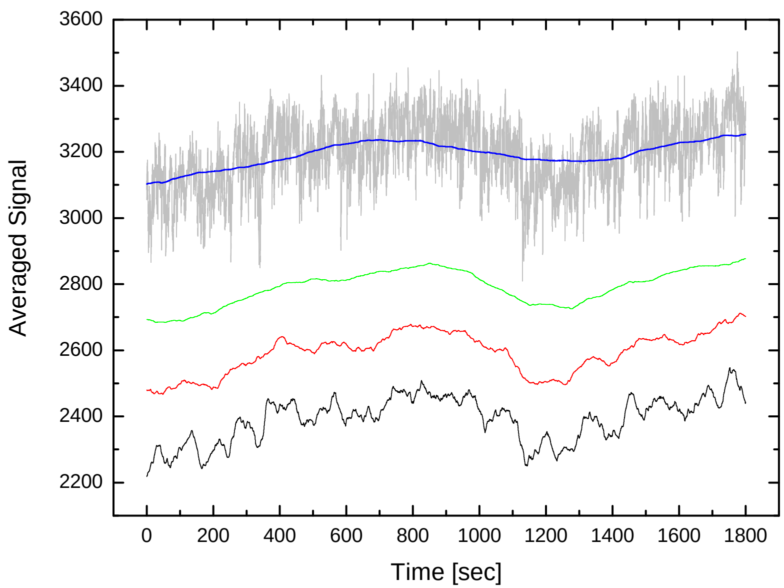
Plot of the two sample variance as a function of the sub-ensemble averaging time τ. The line following τ^{-1} indicates the expected behaviour for a "white noise" dominated system.

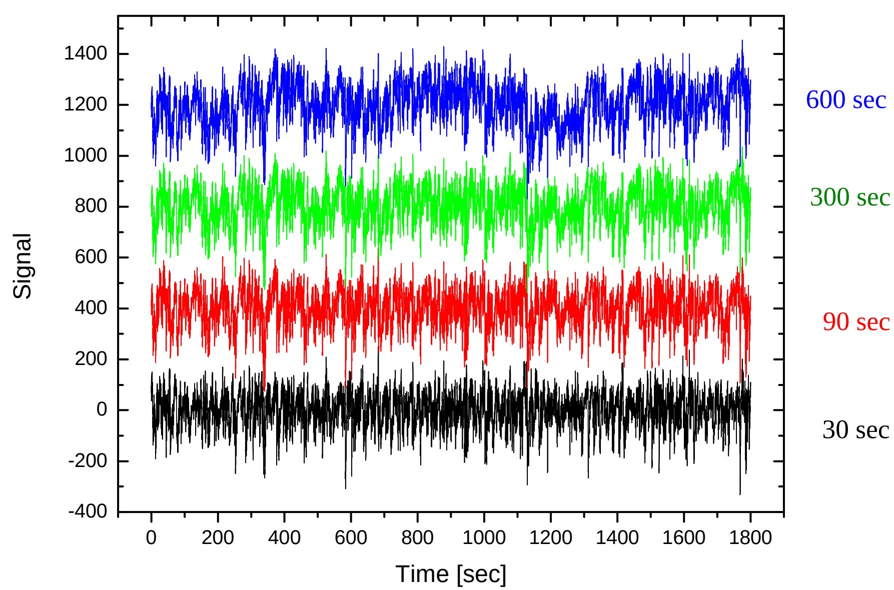
Detrending of time series data

Smoothing effect of the moving average filter with different time constants

Low pass filtered

High pass filtered

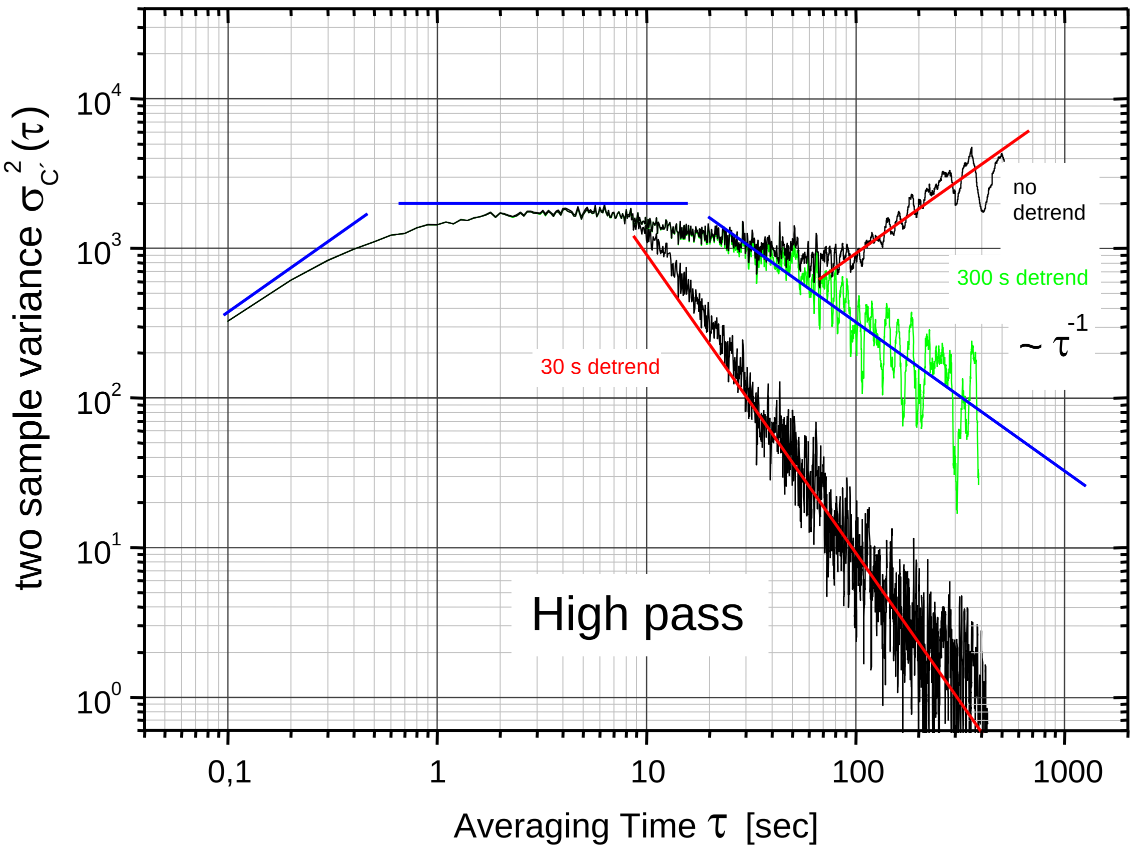




$$y[i] = \sum_{j=-(M-1)/2}^{(M-1)/2} \frac{1}{M} \cdot x[i-j]$$

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

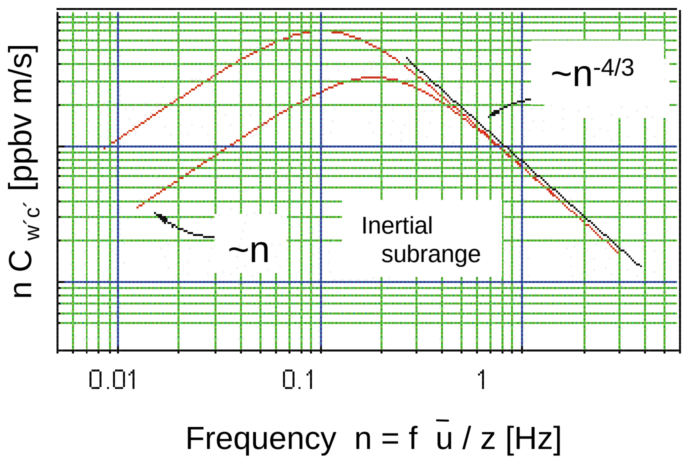
Stability Analysis and Filter Time Constant



Frequency domain and time domain

Frequency Domain

Cospectra and **Covariances**

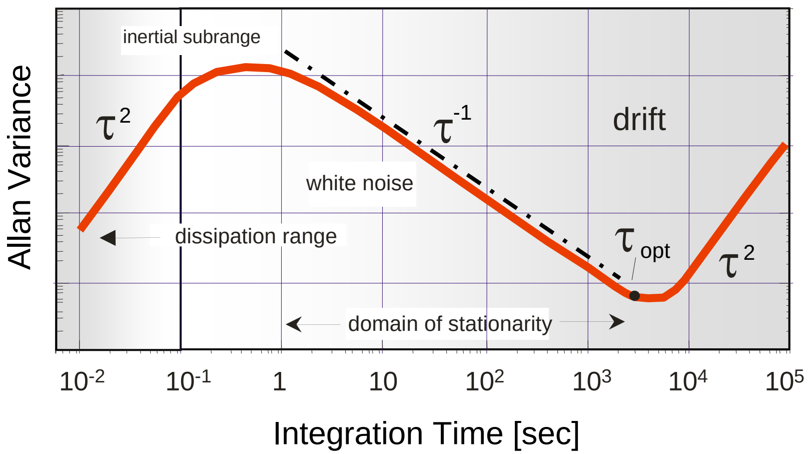


J.C. Kaimal et al., “Spectral characteristics of surface-layer turbulence“, Quart. J. R. Met. Soc. 98, 563-589 (1972)

„It is quite apparent that there is considerable similarity in the shapes of the logarithmic spectra and cospectra. On the high frequency side they fall off according to -2/3, **-4/3**, or *-3/2* depending on the parameter; on the low-frequency side the slope is very nearly +1 “

Time Domain

Two sample variance



P. Werle and R. Kormann, "Fast chemical sensor for eddy-correlation measurements of methane emissions from rice paddy fields “, Applied Optics 40, 846-858 (2001).

recent eddy covariance applications – an exercise

Karlsruhe Institute of Technology

Biogeosciences

Biogeosciences, 4, 715–728, 2007

Suitability of quantum cascade laser spectroscopy for CH_4 and N_2O eddy covariance flux measurements

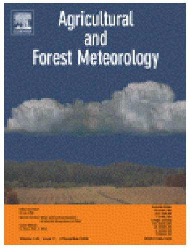
Atmospheric Chemistry and Physics

Atmos. Chem. Phys., 8, 431–443, 2008

A compact and stable eddy covariance setup for methane measurements using off-axis integrated cavity output spectroscopy

Journal of
Geophysical Research
113, D08304, 2008

Direct measurement of biosphere-atmosphere isotopic CO_2 exchange using the eddy covariance technique



Agricultural and
Forest Meteorology
Available online 9
September 2009

N_2O exchange over managed grassland: Application of a quantum cascade laser spectrometer for micrometeorological flux measurements