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FTIR-S for measuring agricultural emissions

Comparison of gas cell and open path measurements

Fourier transformed infra-red spectroscopy (FTIR-S) is suited for the analysis of gas concentrations in agriculture in that the method can cover widely-diffused sources (measurement path of up to 500 m) in open path mode and in the gas cell mode identify single sources with high accuracy. Comparison of both measuring methods show that the difference in detected concentrations of about 2% is associated with the fact that the evaluation was taken from a gas cell spectrum. Since this procedure can be avoided in the field, the error does not appear; the transferability of the calibration is guaranteed.

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Emission, FTIR, measurement technique

Literature information can be received from the publishers under LT99605 or via Internet http://www.landwirtschaftsverlag.com/landtech/local/fliteratur.htm

The use of the Fourier transformed infrared spectroscopy (FTIR-S) in the measuring of climate and ecologically-damaging gases stemming from emissions in agriculture, and the application of equipment from the Landtechnik Weihenstephan (LTW), has been comprehensively covered in this publication and in other places [1 – 4]. At the same time, the procedures for quality assurance and control, the calibration and the quality parameters achieved, have also been addressed.

A reservation, however, has always been expressed concerning the declaration of measurement security, limits of proof and further parameters: the not yet tested transferability of the calibration on open path measurements carried out with a gas cell. A gas cell consists of a cylinder which is rinsed with a measuring gas. The cylinder has two mirrors between which the IR-beam is reflected many times. The open path measurements take place without a cell directly between emitter and spectrometer.

The measurements presented here serve in the investigation of this transferability.

Introduction

Basically, the FTIR spectroscopy works like all IR processes: between an emitter and a detector the gas which is to be investigated absorbs radiation particles with characteristic wave numbers and particular strength. Through this, the type and concentration of gas can be determined. This association is described in the Beersche Law:

$$(I_{\nu} = I_{0,\nu} \exp - (\alpha_{\nu,G} \cdot l \cdot c_G) \qquad (1)$$

From this follows:

$$A = \ln(I_{\nu}/I_{0,\nu}) = - c \cdot \alpha_{\nu,G} \cdot l \qquad (2)$$

If the length of the measurement path l, the absorption coefficient α (characteristic for the gas G and the wave number ν) and the relationship of the radiation *I* which hits the detector (in the case of a particular wave number ν) to the emitted radiation I_0 are known, then the concentration *c* is able to be determined. The absorbency, that is the logarithm out of the relationship of the intensities, is denoted with *A*.

Between gas cells and open path measurements exist – where the path length is the same- the following important principle differences:

- Number of windows: in the case of an open path measurement, the IR light beam is coupled through a window, in the case of gas cell measurements additionally through the two windows of the gas cell.
- Number of mirrors: with a gas cell measurement, the multiple reflections via mirrors in the cell have added to them the beam route changes within the spectrometer. Mirrors are also used to link, in the spectrometer, the IR beams both inside and outside the cell.
- Different emitters: the graph lines (total intensity over electrical performance) of each emitter are different. Additionally, the emitters must be operated at different temperatures and therefore different Planck curves (intensity over wave number) in that strong loss of intensity through the multiple reflection and the windows take place in the gas cell.

Spectral analysis

An univariate method for spectral analysis is presented in [1 to 4]. A multivariate method, which attracts a greater area of a spectrum for analysis, is said to give measurement values with less scatter [5]. The cls method

Table 1: Relative differences between gas cell and open path measuring in the concentration of H_2O and CH_4 in %

time	H_2O	CH_4
14:10	- 1,19	0,56
14:14	- 1,47	- 1,10
14:23	- 1,68	0,79
14:27	- 1,61	- 0,95
14:48	- 2,08	0,64
14:53	- 1,61	1,18
15:05	- 2,10	1,01
15:10	- 2,47	1,55
15:19	- 2,71	0,52
15:24	- 2,70	2,12
15:32	- 2,42	2,55
15:37	- 2,26	1,23

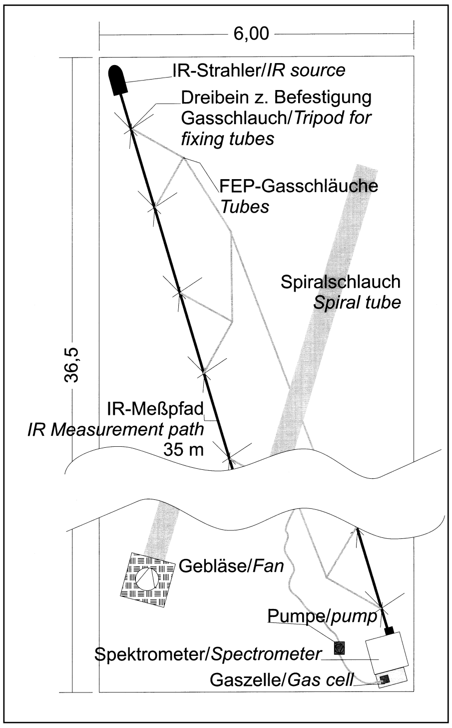

Fig. 1: Diagram of experiment design (not to scale)

(classical least squares, [6]) used as I_0 spectrum, one which does not include the identification marks (signatures) of the gases of interest, as the I-spectrum of the real measurement spectrum (2). Both these spectra are divided between one another and logarithmed which then gives an absorbency spectrum. The absorbency spectrum is compared segmentwise with calibration spectra of known concentrations and path lengths, where the calibrations spectrum is scaled to such an extent that it gives the best possible match (smallest rectangular error).

Current knowledge

As already pointed out, calibration spectra for FTIR open path measurements with gas cells were produced. While the authors of relevant regulations for open path measurements [7 to 9] with VDI-DIN and US-EPA (United States Environmental Protection Agency) know this dilemma. No solutions have, however, been put forward. Up until now, there has been no report in the literature over a direct comparison of open path and gas cell measurements under otherwise identical conditions.

Measuring technique

With the instrument used by the LTW the IR light beams – according to the positioning of the swivel mirror – were linked via the telescope (open path measurement) as well as over a second optical entrance out of the gas cell.

The gas cell comprises a quartz glass profile tube with elliptical base area. This is positioned between two stainless steel flanges. The path length was a maximum of 42 m. Via a transfer optic which also contains the emitter, the gas cell is joined with the spectrometer via six gold-coated mirrors.

Trial design

The trial was carried out in an old storage cellar of the Weihenstephan Brewery (*fig. 1*). Above the measurement path, eight suction points for the gas cell were distributed. Via a „tree“ made of FPE-measurement gas tubes (inner diameter 4 mm) it was guaranteed that the probe from each measurement point had the same length of tube to overcome. A pump at the end of the tree sucked the air in; the gas cell was attached on the pressure side and the cell was rinsed with a throughput of 360 l/hour. A good through-mixing of the space was guaranteed by a fan with a volume capacity of 1000 m^3/h.

Results and discussion

The creation of an absorbency spectrum from open path and gas cell spectra offers a way, according to equation 2, of determining the concentration difference between the two measuring modes. The measurable absorbency peaks show, however, the form of an „oscillation“.

The phenomenon can be explained through a varied movement of the basis line, by otherwise almost the same forms of spectral lines. These „artificial“ absorbencies lead to a false interpretation in the determination of concentrations by the software. Thus a more direct comparison cannot be carried out.

Because of this, the absorbency spectra are formed in each case with a spectrum of the gas cell during nitrogen rinsing. In that the background spectrum now applied does not follow the progress of the measurement spectrum, the „oscillation“ mentioned above does not take place. It was, unfortunately, not possible to produce a background spectrum of the open path measurement. For that, the whole cellar area would have to be filled with nitrogen.

In that a time lag of 10 minutes exists between the gas cell and open path measurements, the concentration of the gas cells were compared with the linear interpolation of the open path spectra before and after the measurement of the gas cells. The differences thus achieved are given in *table 1* as a reproduction of a typical measurement series. Water and methane were shown as representative for all investigated gases, representing two wave number regions within the spectrum.

It is noticeable that, with water, all are divided from their middle values. In the case of methane, all with the exception of the value of 15:05. A coincidental division (which is also not a normal division) value cannot, therefore, be assumed. With the time, the results of the differences rise further. With gas cell measurements the concentrations for water lie lower, for methane the concentrations are lower with open path measurement.

The recognised phenomena can be explained with a movement of the basis line, which is strengthened over the length of the trial period, between the open path measurement spectrum and the background spectrum (gas cell).

The differences between the progress of the background spectrum (gas cell) and the measurement spectrum (gas cell) become increasingly larger the later the measurement spectrum is taken up. Such effects can be caused through an alteration in time of the mirror alignments in the spectrometer, because of temperature differences, for example. The basis line correction through a cubic function was in this case not sufficient.

Conclusions

The differences between the gas cells and the open path measurement found in the evaluation can be traced back to an unavoidable error: the open path measurement has to be compared with a background spectrum achieved from the gas cell, in order that a concentration can be given. Despite the same length of path, there occurs with this differences in the spectrum caused, for example, by the window of the gas cell. The differences in the concentrations lie, in general, at 2% (relative).

In the case of a typical open path measurement the background spectrum would only hold all the gases in the background concentrations. These would be arrived at by measurements taken in the wind before the source. The measuring path would then be laid in the downwind from the source. In this way, a background spectrum from an open path measurement can be employed for determining increases in concentrations. Thus can one avoid the error noted above.