Gas emission measurements with a FTIR gas analyzer - verification of the analysis method

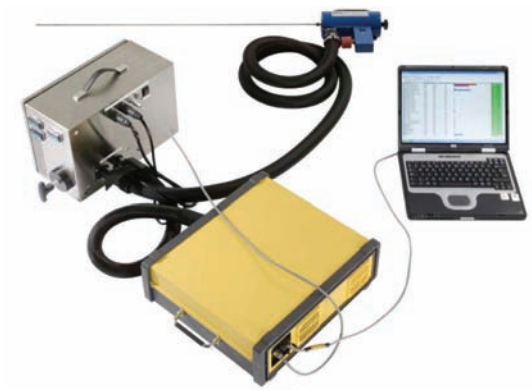
Kari Pieniniemi[1]* and Ulla Lassi[1],[2]
[1]University of Oulu, Department of Chemistry, FI-90014 University of Oulu, P.O.Box 3000
[2]Kokkola University Consortium Chydenius, P.O.Box 567, FI-67100 Kokkola

1 Introduction

A Gasmet DX 4000N FTIR gas analyzer (Gasmet Technologies 2006) has been used to measure and analyze gaseous emissions from the chemical industry and various combustion processes (Heikkinen 2007). Recently, there has been an increase in interest in the measurement and analysis of product gas composition from the wood gasification process and the emissions of wood gas fired gas engines and burners.
The aim of this paper is to develop the FTIR analysis method and to ascertain the accuracy and relevance of emission measurements within the chemical industry and various combustion processes.

2 Objectives of the investigation

A Gasmet FTIR gas analyzer (Figure 1a) is a powerful tool for analyzing complicated gas mixtures to enable qualitative and quantitative analysis of approximately 50 gaseous compounds simultaneously. It can be used as a laboratory instrument or as a continuous emission monitoring system. In addition, it has some significant benefits over a conventional gas analyzer; drying of the gas mixture is not required (as water is a measureable compound), interferences can be easily removed, and only the gas phase FTIR spectrum is added to the analysis. Furthermore, analysis can be repeated at any time after measurement has been taken. Calibration gas mixtures are not necessary, since only the single component calibration is required.



C:\Calcmet\Library\071122\Methane CH4_01200 ppm diluted.ref			
001 Water vapor H2O	0.0000	vol-%	0.0004
023 Toluene C7H8	628.2262	ppm	0.2139
035 2-Methylnaphtalene C11H10	293.2688	ppm	0.2887
024 Styrene C8H8	258.3832	ppm	0.3203
033 Naphtalene C10H8	204.6166	ppm	0.3588
016 Hexane C6H14	160.7295	ppm	0.2158
037 Acetone C3H6O	138.3569	ppm	0.3832
013 Ethane C2H6	98.4614	ppm	0.2088
026 m-Xylene C8H10	69.0013	ppm	0.2906
014 Ethylene C2H4	30.7307	ppm	0.2825
020 Acetylene C2H2	18.9268	ppm	0.2316
038 Methanol CH4O	15.9483	ppm	0.3817
008 Sulfur dioxide SO2	15.5433	ppm	0.1854
009 Ammonia NH3	10.1705	ppm	0.0329
006 Nitrogen monoxide NO	0.4270	ppm	0.0001
002 Carbon dioxide CO2	0.0164	vol-%	0.0021
004 Carbon monoxide CO (High)	0.0133	vol-%	0.0104
059 Methane CH4_High	1200.000	ppm	0.0000
		ppm	1.1177
			0.7967
			0.5270

C:\Calcmet\Library\071122\Methane CH4_01200 ppm diluted.ref			
001 Water vapor H2O	0.0000	vol-%	0.0000
023 Toluene C7H8	0.0000	ppm	0.0000
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016 Hexane C6H14	0.0000	ppm	0.0000
037 Acetone C3H6O	0.0000	ppm	0.0000
013 Ethane C2H6	0.0000	ppm	0.0000
026 m-Xylene C8H10	0.0000	ppm	0.0000
014 Ethylene C2H4	0.0000	ppm	0.0000
020 Acetylene C2H2	0.0000	ppm	0.0000
038 Methanol CH4O	0.0000	ppm	0.0000
008 Sulfur dioxide SO2	0.0000	ppm	0.0000
009 Ammonia NH3	0.0000	ppm	0.0000
006 Nitrogen monoxide NO	0.0000	ppm	0.0000
002 Carbon dioxide CO2	0.0000	vol-%	0.0000
004 Carbon monoxide CO (High)	0.0000	vol-%	0.0000
059 Methane CH4_High	1200.000	ppm	0.0000
			0.0000
			0.0000
			0.0000

Figure 1 *a) Gasmet DX4000N, portable sampling unit, and portable probe with heated lines; b) An example of analysis of pure 1200 ppm CH_4 reference spectrum (left) and the same analysis after interferences have been removed (right).*

One of the most significant disadvantages of using a Gasmet FTIR analyzer is that the development of the analysis method can occasionally be time consuming, especially if the spectral interferences are to be removed. If the analyzer is used without any spectral correction, the analysis results can be rather misleading (as shown in Figure 1b).

*Correspoding author, E-mail: kari.pieniniemi@oulu.fi

3 Results and discussion

3.1 Verification of the Analysis Method

Gas analysis of a FTIR gas analyzer can be verified by using real gas mixtures (containing all gas compounds with known compositions and concentrations). This is not always possible, and therefore, FTIR spectra of pure gas compounds with known concentrations can be used to verify and estimate the accuracy of the analysis method.

According to Lambert Beer's law, FTIR spectrum of a gas mixture is a linear combination of its independent components (Figure 2).

$$A(\nu) = \sum_{i=1}^{n} a_i(\nu) \cdot c_i \cdot L \qquad (1)$$

where
i = i^{th} gas component (CO, CO_2, H_2O, etc)
n = total number of gas components
c_i = concentration of the ith component (ppm)
L = absorption path length (5m in Gasmet FTIR)
$\nu = 1/\lambda$ = wave number (1/cm)
$a_i(\nu)$ = absorption coefficient of the ith gas component (CO, CO_2, H_2O, etc)
A (ν) = absorbance spectrum of the gas mixture containing n gas components (i = 1, 2,…, n)

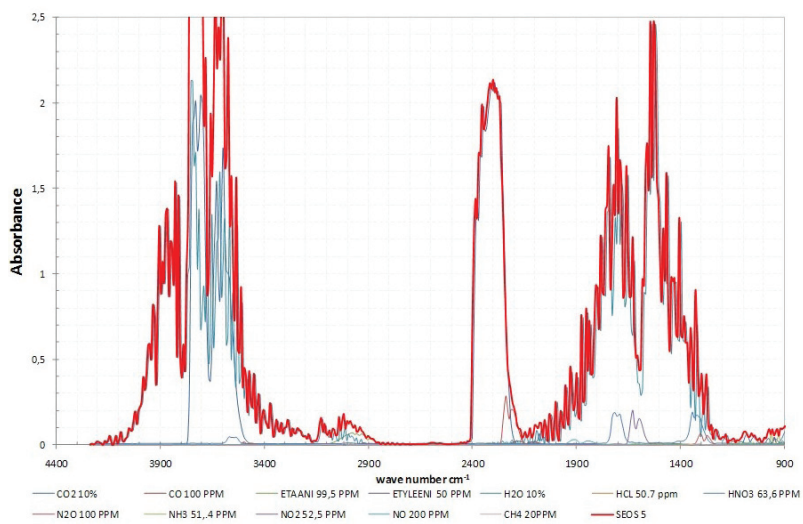

Figure 2 *Linear combination (red) of the independent gas components of known concentration.*

Absorption coefficient of an individual gas component ai(**v**) is specific for a identified compound and can be used to calculate a new FTIR spectrum with different concentration using equation (3).

$$a_i(\nu) = \frac{A_i(\nu)}{c_i \cdot L} \tag{2}$$

where
$A_i(\mathbf{v})$ = known FTIR spectrum of compound I (reference spectra)
c_i = concentration associated with the known spectrum $A_i(\mathbf{v})$ (ppm)

$$A_k(\nu) = a_i(\nu) \cdot c_k \cdot L = A_i(\nu)\left(\frac{c_k}{c_i}\right) \tag{3}$$

where
$A_k(\mathbf{v})$ = FTIR spectrum of a gas component i associated with the new concentration c_k
$a_i(\mathbf{v})$ = absorption coefficient of the ith gas component (CO, CO_2, H_2O, etc)
c_k = new concentration of the ith gas component (CO, CO_2, H_2O, etc)
FTIR spectrum of the gas mixture with known concentrations is a linear combination of the FTIR spectrum of the individual gas components

$$B(\nu) = \sum_{k=1}^{n} A_k(\nu) \tag{4}$$

where
B (**v**) = absorbance spectrum of the gas mixture containing n gas components (i = 1, 2,…, n) with known concentrations (Figure 2)

The analysis method for emissions of product gas combustion was evaluated by making a synthetic gas mixture by linear combination of known reference spectra (Figure 2). The resulting synthetic gas mixture was then analyzed using a CASMET analysis program. Results indicated that in most cases the calculated concentrations were within 3 % of the actual concentrations of the synthetic gas mixture (see Table 1).

Table 1 *Analysis results of known combustion gas mixtures.*

Gas component	Unit	Calculated conc.	Actual conc.	Difference conc.	Difference %
Water vapour H_2O	vol-%	10.8	10	0.777	8 %
Carbon dioxide CO_2	vol-%	10.0	10	0.020	0 %
Carbon monoxide CO	ppm	98.2	100	-1.828	2 %
Nitrous oxide N_2O	ppm	97.4	100	-2.647	3 %
Nitrogen monoxide NO	ppm	199.9	200	-0.113	0 %
Ammonia NH_3	ppm	50.6	51.4	-0.785	2 %
Hydrogen chloride HCl	ppm	52.0	50.7	1.334	3 %
Methane CH_4	ppm	20.7	20	0.671	3 %
Ethane C_2H_6	ppm	97.6	99.5	-1.898	2 %
Ethylene C_2H_4	ppm	49.3	50	-0.702	1 %

3.2 Correction of the Measured Concentration and Calibration of the Wave number and Absorbance Scale of the FTIR Analyzer

Changes in the conditions during the measurements of reference and sample spectra can be taken into account by using a constant concentration calibration transfer spectra (CTS) measured at the sampling site and during the measurement of the reference spectra.

$$R_{LPS} = \left(\frac{L_R}{L_S}\right) \cdot \left(\frac{T_S}{T_R}\right) \cdot \left(\frac{P_R}{P_S}\right) = \frac{c_S}{c_R} \tag{5}$$

R_{LPS} = scaling factor to correct path length and pressure variation between the measurement of the reference and sample spectra
C_S = measured concentration of the CTS during sampling
C_R = measured concentration of the CTS during the measurement of the reference spectra
L_R = reference spectra path length
L_S = sample spectra path length
T_S = absolute temperature of the sample gas (K)
T_R = absolute temperature of the reference gas (K)
P_S = sample cell pressure
P_R = reference spectrum sample pressure

This comparison allows the detection of any instrument malfunctions and quantitatively account for spectral differences which are related to optical retardation, path length and temperature variations (Lay 1993). A measured concentration can be corrected by multiplying itself with a scaling factor (EPA Test Method 320).

$$c_{corr} = R_{LPS} \cdot c_{calc} \tag{6}$$

where
c_{corr} = concentration corrected for path length
c_{calc} = measured concentration (output of the analytical program)
Calibration Transfer Spectra (CTS) can be produced for any suitable gaseous compound with an accurate

concentration, but in most cases 100 ppm ethylene is commonly used (Lay 1993). The concentration between the reference and measured CTS must be within ±5 % of the mean value (EPA Test Method 320).

4 Relevance of the investigation

A Gasmet FTIR gas analyzer is a powerful tool for quantitative analysis of complicated gas mixtures. Despite its many advantages, the development of an analysis method can be time consuming and the results can sometimes be misleading. To overcome these drawbacks, the instrument has to be calibrated and the analysis method has to be verified using known gas mixtures or pure gas components with known concentrations. Unfortunately making real gas mixtures of known compositions is not always possible and instead synthetic gas mixtures can be used. This increases the accuracy and relevance of the method used in the emission measurements.

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SkyPro conference: http://nortech.oulu.fi/SkyPro/index.html

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