Tunable diode laser absorption spectroscopy of atomic potassium in a KOH-seeded flat flame

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To my love, Anders ...
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Abstract

Potassium (K) is the main ash-forming element released from biomass during thermochemical conversion. A better understanding of K chemistry and monitoring of K species is needed to optimize combustion systems. Since K species are highly reactive and prevailing concentrations depend on the conversion conditions, accurate quantification requires in situ measurement techniques. Tunable diode laser absorption spectroscopy with a single-mode distributed feedback laser is used to probe the D1 transition of atomic potassium, K(g), at 769.9 nm. The large current tuning range of the diode laser (5 cm$^{-1}$) enables monitoring the wings of the absorption profile. Fitting to the acquired line shape wings is used as a strategy to enhance the dynamic range of the sensor and measure K(g) concentrations even under optically thick condition. A potassium-rich combustion environment is simulated by converting KOH salt in a premixed methane/air flat flame. Quantitative measurements of K(g) are made at 75 positions in the flame. This yields radial K(g) profiles at three different heights in the plume above the KOH salt and an axial profile at the burner center. The acquired average K(g) concentrations are corrected for effective plume size, i.e. the absorption path length determined from the radial profiles. Knowledge of the K(g) distribution in flames can lead to a better understanding of K release and primary reaction kinetics.
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Nomenclature

Symbols

\( a(\nu) \) \hspace{1em} \text{Absorption coefficient}

\( B_p \) \hspace{1em} \text{Pressure broadening coefficient}

\( C \) \hspace{1em} \text{Concentration of the target species}

\( c \) \hspace{1em} \text{Speed of light in vacuum}

\( \chi(\nu,C,P,T) \) \hspace{1em} \text{Lineshape function}

\( d \) \hspace{1em} \text{Etalon thickness}

\( \delta \nu_D \) \hspace{1em} \text{FWHM of Gaussian lineshape function}

\( \delta \nu_L \) \hspace{1em} \text{FWHM of Lorentzian lineshape function}

\( \delta \nu_V \) \hspace{1em} \text{FWHM of Voigt lineshape function}

\( \gamma \) \hspace{1em} \text{Damping coefficient}

\( h \) \hspace{1em} \text{Planck constant}

\( I_0 \) \hspace{1em} \text{Intensity of the incident light}

\( I_A \) \hspace{1em} \text{Intensity of the transmitted light through the sample}

\( K \) \hspace{1em} \text{Boltzmann constant}

\( l \) \hspace{1em} \text{The length of the gas sample}

\( M \) \hspace{1em} \text{Molecular mass}

\( \nu \) \hspace{1em} \text{Frequency of the laser light}
Nomenclature

\( \nu_0 \) Center frequency of the transition

\( \nu_{\text{exp}} \) Experienced frequency of the laser light by atoms and molecules

\( P \) Gas pressure

\( Q(T) \) Total partition function at arbitrary temperature

\( Q(T_0) \) Total partition function at reference temperature

\( S(\nu, T) \) Transition line strength at arbitrary temperature

\( S(\nu, T_0) \) Transition line strength at reference temperature

\( T \) Gas temperature

\( T_0 \) Reference gas temperature

\( v \) Velocity of the atoms and molecules

Acronyms / Abbreviations

\( BG \) Background signal

\( DBR \) Distributed Bragg reflector lasers

\( DFB \) Distributed feedback lasers

\( FP \) Fabry-Perot etalon

\( FWHM \) Full width at half maximum

\( HAP \) Height above the plate

\( TDLAS \) Tunable diode laser absorption spectroscopy
Chapter 1

Introduction

Laser-based absorption spectroscopy is a non-invasive technique for fast and selective detection of atoms and molecules via their unique absorption features in specific spectral regions. Quantification is based on Beer-Lambert’s law. The method is widely used for detection of gases in industrial, environmental and combustion applications [1, 2].

Biomass is an organic material, such as wood, agricultural crops and wastes that can be used for heat and power production by combustion. Since biomass is a renewable and CO$_2$-neutral energy source, extensive studies are performed to improve the efficiency of the process and increase the share of biomass in the energy system. The overall efficiency in industrial reactors is often limited by operational problems, for example due to material corrosion. These problems are partly caused by the high concentration of alkali metals in biomass, and the subsequent release of K species, mainly potassium chloride (KCl) and the intermediate species potassium hydroxide (KOH) and atomic potassium, K(g), to the gas phase. Another important issue is the emission of soot particles and other aerosols (for which KCl can be a precursor) to the environment [3].

Given the importance of potassium, there is a high interest in detection of K species in combustion environments with laser-based techniques [4–8]. While detection of KCl and KOH requires rather complex instrumentation, the strong electronic transitions of atomic potassium from the ground state to the first excited state around 770 nm can conveniently be probed with relatively inexpensive diode lasers. It is investigated whether K(g) detection can be used as a measure for initial K release during biomass combustion and gasification. Depending on the conversion conditions and type of biomass, K(g) can be present in a wide range of concentrations. Recently, TDLAS was used for wide dynamic range K(g) detection, also under optically thick and partially opaque conditions [3]. This sensor has shown to
be suitable to quantify K(g) in close vicinity of biomass particles during thermochemical conversion [3], and in larger laboratory and pilot-scale reactors during biomass combustion and gasification [9, 10].

The aim of this work was to use an existing TDLAS setup to measure the distribution of atomic potassium K(g) in the plume of burning KOH salt converted in a premixed methane/air flat flame. The concentration of K(g) was recorded as a function of height above the burner and radial position of the flame. The acquired average concentration at plateau of each measurement point was plotted to determine the distribution of K(g) in the plume. This can assist in the development kinetic mechanism of K compounds.

This thesis consists of four main parts: Theory (chapter 2), experimental setup and procedure (chapter 3), result and discussion (chapter 4) and summary and conclusion (chapter 5). In theory part, first laser absorption spectroscopy is introduced and then the shape of the absorption line under different kind of broadening was explained. After that, tunable diode laser spectroscopy technique and its advantages was presented following by a short summery of the function of diode lasers. This section is ended with a short introductory of the biomass combustion and its alkali metal release as a limit in the usage of this clean energy source. In experimental setup and procedure part, the instrument being used in the setup as well as experimental work are explained. In result and discussion part, the results being obtained by experimental work are presented. In summary and conclusion part, the content of the whole report is summarized. There are also two additional sections at the end of this thesis which contain photos of the setup (Appendix A) and two tables of average concentrations values at all measurement points (Appendix B).
Chapter 2

Theory

2.1 Laser absorption spectroscopy

Spectroscopy is a technique that relies on the interaction of electromagnetic radiation with matter. When the amount of radiation absorbed by certain atoms and molecules in a sample is studied, then this analysis is classified as absorption spectroscopy.

When a laser beam is used as radiation source in absorption spectroscopy, the method is called laser absorption spectroscopy. The simplest technique within this scheme is direct absorption spectroscopy. It is based on sending the laser beam through a sample of length of \( l \) and then measuring the intensity of transmitted light in relation to the incident light intensity (Fig. 1).

![Fig. 1 Schematic of direct absorption spectroscopy. The intensity of the laser light, \( I_0 \), will be decreased to \( I_A \) after passing a sample with absorption coefficient, \( a(\nu) \) and length, \( l \).](image)

This technique, which is mostly used for absorption measurement of the gaseous samples, has a number of advantages. The most important one is that it is non-invasive, meaning that it does not have a destructive effect on the sample. The second advantage is selectivity. Individual molecular species have a unique set of allowed transitions and spectrum, thus, employing a laser with appropriate wavelength, transitions can be probed and the presence of a given species can be detected. Finally, it is quantitative without calibration, since if
the intensities of incident light, $I_0$ and transmitted light, $I_A$ are measured, knowing the path length $l$, the absorption coefficient, $a(\nu)$ ($\nu$ is the frequency of the light) can be calculated using the Lambert-Beer law [11]:

$$I_A = I_0 \exp[-a(\nu)l], \quad (2.1)$$

Knowing $a(\nu)$, the concentration of the atoms or molecules, $C$, can be extracted from:

$$a(\nu) = S(\nu, T) \chi(\nu, C, P, T) CP, \quad (2.2)$$

if the transition line strength, $S(\nu, T)$, the lineshape function, $\chi(\nu, C, P, T)$ and the total gas pressure, $P$, is known [3]. The factor, $a(\nu)l$, in the equation 2.1 are known as absorbance.

### 2.1.1 Transition line strength

Each molecule has several transitions with different line strengths. Therefore, if a stronger transition is chosen, more light would be absorbed from the same molecule [12]. Transition line strengths for different species at a certain reference temperature can be obtained from databases, such as HITRAN [13] and NIST [14].

It is important to know that the line strength is temperature dependent through population of lower-state states energy, $E''$. If a database gives a line strength, $S(T_0)$, at reference temperature, $T_0$, the line strength at an arbitrary gas temperature, $T$, can be obtained from:

$$\frac{S(T)}{S(T_0)} = \frac{Q(T)}{Q(T_0)} \exp\left(-\frac{hcE''}{k} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \cdot \frac{1 - \exp\left(-\frac{h\nu_0}{kT}\right)}{1 - \exp\left(-\frac{h\nu_0}{kT_0}\right)}, \quad (2.3)$$

where $S(T)$ is the strength at arbitrary temperature, $Q(T_0)$ is total partition function at reference temperature, $Q(T)$ is the total partition function at arbitrary temperature, $h$ is Planck constant, $K$ is Boltzmann constant and $c$ is speed of light in vacuum [15].

### 2.1.2 Lineshape functions

Each transition has a frequency dependent shape that is called line profile or lineshape function. It originates from the fact that transitions are not infinitely narrow line in frequency,
2.1 Laser absorption spectroscopy

but they are a distribution of frequencies over a spectral range. This area can have Lorentzian or Gaussian shape which has a width, $\delta \nu$ and depth, $\Delta I$ (Fig. 2).

![Fig. 2 The absorption line with width $\delta \nu$ and depth $\Delta I$ having Lorentzian, Gaussian or Voigt shape.](image)

The area under the lineshape shows how much light is absorbed and it depends on transition probability. It also depends on concentration of the gas and path length of the laser beam through the gas. If we have more atoms, we have more absorption. Longer sample would have more absorption also.

There are many parameters that influence this width, e.g. collision and velocity of molecules:

**Collision broadening**

Atoms and molecules move with respect to each other, so they have elastic and inelastic collision. Elastic collisions only interrupt the oscillation of atoms and molecules and do not change the energy and amplitude of the radiation. But inelastic collisions damp radiation energy with the rate of $\exp(-\gamma t)$, where $\gamma$ is damping coefficient and can be calculated as:

$$\gamma = B_p P,$$

where $B_p$ is pressure broadening coefficient.

These collisions cause excitation of the atoms and molecules to excited state and broadening the transition. Since these broadening is due to collisions, it is known as collision broadening. It is also called pressure broadening due to dependency of the collisions on the pressure of the gas. Collision broadening is the most important broadening mechanism in gases at
atmospheric pressure. It has a Lorentzian shape which can be calculated as:

\[ \chi_c(\nu) = \frac{\delta \nu_L}{2\pi} \left( \frac{\nu - \nu_0}{\delta \nu_L/2} \right)^2, \]  

(2.5)

where \( \nu_0 \) is the center frequency of the transitions and \( \delta \nu_L \) is the full width at half maximum (FWHM) of the Lorentzian lineshape which is determined by [16]:

\[ \delta \nu_L = \frac{\gamma}{2\pi}. \]  

(2.6)

**Doppler broadening**

Even if atoms and molecules are very weakly influenced by collisions and they have undamped oscillations, the absorption lines will be wider due to Doppler broadening. According Doppler effect, atoms and molecules moving in different directions with velocity, \( v \), experience the laser beam with different frequencies:

\[ \nu_{\text{exp}} = \nu \left( 1 \pm \frac{v}{c} \right), \]  

(2.7)

where + is used when atoms and molecules move with the velocity \( v \) towards the laser beam and − is used for that of move with the velocity \( v \) away from the laser beam.

Since atoms and molecules of the gas can have a wide variety of velocities, there will be a broad range of different resonance frequencies for a given absorption line. Therefore the absorption line will be broadened. This broadening has Gaussian shape and can be calculated as

\[ \chi_D(\nu) = \frac{2\sqrt{\ln 2}}{\delta \nu_D\sqrt{\pi}} \exp \left( - \frac{2\sqrt{\ln 2}(\nu - \nu_0)^2}{\delta \nu_D^2} \right), \]  

(2.8)

where \( \delta \nu_D \) is the FWHM of the Gaussian lineshape and can be determined as:

\[ \delta \nu_D = 7.16 \cdot 10^{-7} \nu_0 \sqrt{\frac{T}{M}}, \]  

(2.9)

where \( T \) is the temperature of the gas in Kelvin and \( M \) is molecular mass in gram [16].
2.2 Tunable diode laser absorption spectroscopy

**Voigt lineshape**

In many situations, and for atmospheric pressure samples, collision broadening and Doppler broadening exist at the same time because if atoms and molecules move, they collide. Therefore, to describe the lineshape, the convolution of a Lorentzian and a Gaussian function is used, known as Voigt lineshape:

\[
\chi_V(\nu) = \frac{1}{\pi \delta \nu_L} \int_{-\infty}^{\infty} \frac{e^{-y^2}}{(y+a)^2 + b^2} \, dy,
\]

(2.10)

where \( a \) and \( b \) are defined as [16]:

\[
a = 2\sqrt{\ln 2} \left( \frac{\nu_0}{\nu_D} - \nu \right)
\]

(2.11)

\[
b = 2\sqrt{\ln 2} \left( \frac{\delta \nu_L}{\delta \nu_D} \right)
\]

(2.12)

The Voigt lineshape can be calculated via convolution of a Lorentzian and Gaussian function [17], and the FWHM of the Voigt lineshape, \( \delta \nu_V \), can be approximated as [18]:

\[
\delta \nu_V = 1.0692 \delta \nu_L + \sqrt{0.86639 \delta \nu_L^2 + \delta \nu_G^2}
\]

(2.13)

2.2 Tunable diode laser absorption spectroscopy

Diode lasers are made of semiconductor materials and are available in different types, but all have a contact which enables sending an electronic current through them. They have very short cavities, in the range of a few hundred micrometers, which are formed by polishing the two ends of the semiconductor chip. Therefore, the cavity modes are well separated and only one mode can lase within the gain profile.

The applied current is a kind of pumping mechanism for the diode laser since it causes transition of electrons in n-type material to valance band and recombination with holes in conduction band and emit radiation which is the laser light. A wide spectral working range from visible to infrared is achieved for diode laser by bandgap engineering.

Diode lasers have a possibility to be tuned around their center frequency via current or
temperature. This property allows for recording continuous absorption profile of atoms when the emission frequency of the laser is scanned across a target transition. In this way, a decrease in laser intensity of the laser will be seen as the laser light hits the transition of the target species.

In order to increase the wavelength tuning range of a semiconductor laser, a wavelength selective element, like a grating can be added to the chip. The grating disperses different frequencies in different directions which allows for choosing particular frequency. The grating can be completely out of the laser, like external cavity diode laser, or inside the laser, like distributed feedback lasers (DFB) and distributed Bragg reflector lasers (DBR). The difference between the two latter is that the DFB lasers has a grating inside the chip, along the entire length of the active medium, but in DBR laser, the grating is placed outside the active medium.

If such tunable diode lasers are used in absorption spectroscopy, the technique is called tunable diode laser absorption spectroscopy (TDLAS) [12]. As any other absorption technique, it is very sensitive when the sample under study has a high oscillator strength as is the case for electronic transitions from the ground state to the first excited state (as the potassium D1 transition) [4].

2.2.1 Fabry-Perot etalon and relative wavelength scale

Tuning the laser frequency enables recording the lineshape function of the transition. In order to analyze the acquired lineshape, a frequency scale is required. When there is no absolute frequency scale, instead a relative frequency scale works properly. In TDLAS the relative frequency scale is created using a solid Fabry-Perot etalon (FP etalon). A solid FB for this kind of application consist of typically a piece of glass with very well known thicknesses.

![Fig. 3 Incident light, A_in to Fabry-Perot etalon is reflected from the first surface (S_1) with a phase shift of π, but it is reflected from the second surface (S_2) without any phase shift.](image-url)
The frequency scale is generated when the light is reflected on both surfaces of the glass, which has a higher refractive index $n$ than air ($n > n_{\text{air}}$). The reflected light from the first surface ($S_1$) $A_0$ has phase shift of $\pi$, due to the reflection at a surface between a optical thinner and a thicker medium, while reflected light from the second surface ($S_2$) $A_1$ does not have any phase shift. Also there is an optical path difference between $A_0$ and $A_1$, which will give rise to a thickness dependent phase shift as given by $\frac{4\pi nd}{c}$. The reflected light from both surfaces interfere destructively when the sum of these phase differences is an odd integer of $\pi$. The modes obeying $v_q$ condition, would experience destructive interference:

$$v_q = q \frac{c}{2nd},$$

where $d$ is the thickness of the etalon.

Destructive interference means low reflection and low reflection means high transmission, therefore, these frequencies would be the resonance frequencies of FP. They are equally spaced and the separation knowing as free spectral range (FSR), is determined by:

$$FSR = \frac{c}{2nd}$$

These equally spaced frequencies can be used as a ruler to provide the wavelength scale of the recorded absorption profile of the diode laser tuned across the sample transition [16].

### 2.3 TDLAS for detection of atomic potassium

Since atomic potassium has strong electronic transitions, it can be easily detected by TDLAS [3]. Potassium has two strong absorption lines, $D_1$ and $D_2$ at 769.9 nm and 767 nm, respectively. There are diode laser with emission wavelength at 769.9 nm and 766.5 nm, but at low concentration it is better to use $D_1$ line to avoid spectral interference from oxygen (O$_2$) [4]. The selected transition of potassium has line strength of $7.43 \times 10^6 \text{ cm}^2 \text{ atm}^{-1}$ at 296 K. The wide tuning range of the diode laser allows for recording the full absorption profile at low concentrations (approx. mole fraction of $10^{-7}$ or lower). But this strong transition leads to optically thick and opaque condition at higher concentrations of potassium (approx. mole fraction of $10^{-6}$ or higher) [3], according equation 2.2. In opaque condition, the intensity of the transmitted light is below the detector threshold. In general, the detection limit can be affected by broadband emission from the flame and by emission from K(g).
Figure 4 shows an example of potassium opaque spectrum in ppm range of concentration. Even in this conditions, the Lambert-Beer law is valid since atoms and molecules do not still influence each other, however, the center frequency should be scanned off-center to enable measuring at least one of the wings of the absorption profile. This allows for measuring the concentration of the gas by a least-squares fit of a simulated spectrum to the wing of the spectrum under optically thick condition [3].
Chapter 3

Experimental setup and procedure

3.1 Experimental setup

A schematic drawing of the experimental setup is shown in Fig 5. A DFB laser at 770 nm is run with a high compliance current source which also controls the laser temperature. The current source varies with a 80 Hz triangular wave generated by a function generator card. It enables scanning the the laser wavelength (770 nm) across the potassium D1 line.

Fig. 5 Schematic drawing of the experimental setup consisting a DFB laser (769 nm), a burner [19] and an etalon. M, flat mirror; C, fiber collimator; f, Lens; PD, photo detector; FG, function generator; DAQ, data acquisition card. Real photos of the setup can be seen in Appendix A, figure 18.
An optical isolator is placed in front of the laser to avoid optical feedback. Two flat mirrors, M₁,₂ are then used to couple the laser light to a single mode optical fiber via a fiber collimator, C₁. A fiber splitter is then used to send half of the light via another fiber collimator, C₂ to a flat mirror, M₃. The mirror directs the laser beam to a premixed methane/air flame.

The burner, which is adapted from the design of Hartung et al. [19], is used to simulate the biomass combustion and generate K(g) released from burning KOH. It has a diameter of 4 cm and was operated at stoichiometric ratio with flow rates 1.045 and 9.955 l/min for methane and air, respectively. It is mounted on a translation stage which enables the movement of the burner vertically and horizontally with precision of 0.01 mm and 2 mm, respectively. The burner body is cooled with flow of water when it is on. The transmitted light through the flame is focused by lens f₁ to photo detector PD₁. A narrowband filter is placed in front of the detector.

The other half part of the light is also directed via a fiber collimator C₃ though an etalon with a free spectral range of 1.5 GHz. The transmitted beam is detected by a photo detector PD₂ after being reflected by coupling flat mirrors M₃,₄ and lens f₂. This provides the frequency scale of the measurement. Both PDs are connected to a PC through a data acquisition card (DAQ) and data is acquired using a LabView program.

### 3.2 Experimental procedure

#### 3.2.1 Sample preparation

A round plate made of platinum with a diameter of 5 mm was used as a holder for potassium hydroxide (KOH) in all measurements. The plate was first weighted and then was placed on a heating plate (initially turned off). After putting a drop of the KOH solution (one molar of KOH in water) on the platinum plate, the heater was turned on. Drying the water contained in the solution, an evenly distributed layer of KOH was formed on the surface of the plate. The plate was weighted again before being used in the experiment. This procedure was done for all measurements. The amount of KOH salt on the plate was $0.9 ± 0.3 \, \mu g$.

#### 3.2.2 Measuring atomic potassium concentration

A stand with a height of 2.2 ± 0.1 mm was placed on the center of the burner surface when the flame was off. The plate was mounted on the stand as it can be seen in the magnified view shown in figure 6. The real photo of the burner is shown in appendix A, figure 19. The laser
beam was aligned parallel to the surface of the plate at the closest possible height above the plate (HAP). This height was determined where the full diameter of the beam was detected by the detector without being blocked by the plate surface. This height is known as zero height of the measurements and the signal was recorded as background (BG) signal of the laser light.

Running the experiment, broadband emission from the flat flame and potassium plume was a source of error for the measured transmitted laser intensity. To address this issue: first, the photo detector PD$_1$ was placed as far as possible to the flame and second, a narrowband optical filter was mounted in front of the detector to filter the emissions. The data was sent via a DAQ to a computer with a LabView program and were acquired by the program with the rate of 250k sample/second. In order to reduce the data file size, 1/10 of the points were saved.

For measuring the distribution of atomic potassium in the plume of KOH, the measurement was done in 4 sets at 75 other measurement points: First set was done in 15 different HAPs at the center of plume, Second set was done in 20 radial positions at HAP of 1.5 mm, Third set was done in 20 radial positions at HAP of 8 mm and the last set was done in 20 radial positions at HAP of 18 mm. The measurement points are shown in figure 6.

![Diagram showing KOH plume and measurement points](image_url)

Fig. 6 KOH salt was put on a plate located on a stand at height $2.2 \pm 0.1$ mm and was burned in a premixed methane/air flat flame (blue part). KOH plume is shown with orange color. Measurement points are from HAP of 1.5 mm to 24 mm in 15 marked points. At HAPs of 1.5 mm, 8 mm and 18 mm; 10 radial measurements to the right and 10 radial measurements to the left of the center point were also done.
3.2.3 Relative frequency scale

A fused silica etalon with a length of L=6.9 cm, which corresponds to a free spectral range of 1.5 GHz, was used to provide the relative frequency scale of the scanning range. They were detected by PD$_2$ and be recorded with LabView program with the rate of 250k sample/second. This measurement was done before each of 4 measurement sets explained in section 3.2.2.

3.2.4 Subtraction of the flame emission

Although a narrowband optical filter was used in front of the detector, the acquired spectra were clearly affected by the strong emission of the released K(g), specially when opaque condition arises. As can see in figure 7, the minimum intensity of the opaque spectra (spectra having cut off in transmitted intensity) is shifted with respect to that of the non opaque spectra, due to this additional emission of the flame.

To address this issue, the difference between the minimum intensity of the first non-opaque spectrum (first spectrum after the opacity ends) and each opaque spectrum at the center frequency of the transition was calculated and the result was subtracted from the corresponding opaque spectrum. Figure 8 shows the spectra after this correction.

By taking the logarithm of the ratio of the detector signal to the BG signal, absorbance will be calculated for all the corrected corrected spectra. Some of these measured absorbance spectra at measure point +4 mm/HAP 8 mm are plotted in figure 9.
3.2 Experimental procedure

Fig. 8 Corrected spectra for the flame emission in opaque condition at measurement point +4 mm/HAP 8 mm.

Fig. 9 Five measured absorbance spectra at measurement point +4 mm/HAP 8 mm, yielding concentrations of 15 ppm, 12 ppm, 7 ppm, 0.6 ppm and 0.3 ppm.

3.2.5 Curve fitting

A theoretical absorption spectrum was modeled by using equation 2.1, a Voigt line shape function and the BG signal in the absence of K(g) absorption. The absorption line data was taken from existing literature and databases [4, 14]. The path length of the laser light through the sample was considered to be 40 mm according to the diameter of the burner. The transition line strength was also calculated for the estimated average temperature in the
plume (T= 1770 K) using equation 2.3. The theoretical absorption spectra was then fitted with the corrected experimental spectra for each measurement points.

Theoretical absorption line had 2 free parameters: concentration of the gas and air width. They are allowed to change in a narrow range till the experimental and theoretical spectra fit together. Figure 10 shows two examples of this fitting at +4 mm/HAP 8 mm measurement point. As explained in section 2.3, both low (none opaque spectrum, Fig.10-a) and high concentration (opaque spectrum, Fig.10-b) of the potassium could be measured with this technique.
Chapter 4

Result and Discussion

4.1 Time-resolved K(g) concentration during KOH conversion

The concentration of the atomic potassium was one of the free parameters of the fit explained in subsection 3.2.5. It was extracted for all spectra of each measurement points. This results is shown for 3 measurement points in figure 11.

From the graphs it can be seen that the concentration is changing with time and, of course, this change is very fast before starting the conversion and during the final decay. The most stable part of the graph is at plateau where rate of this change is slower. The plateau situation is considered as steady-state where layer-by-layer evaporation of KOH under similar conditions happens. The absolute plateau value was found to be independent of KOH amount on the plate; but plateau time/length depends on the initial KOH amount on the plate. It can be proven by looking at the correlations.

4.2 Distribution of atomic potassium in the plume

In order to determine the K(g) distribution of the flame, the average concentration at the plateau of each measurement points was estimated. The results are tabulated in Appendix B, tables B.1 and B.2 for 60 radial and 15 vertical positions, respectively.
In figure 12, the acquired concentration values for radial measurements at HAPs 1.5 mm, 8 mm and 18 mm are plotted. It can be seen that the these values approximately fit a Gaussian shape. By increasing the HAP, the peak of the Gaussian fit decreases and the width increases due to the diffusion of K(g) out of the plume. Also the peaks are not always at the center of the burner in all 3 HAPs. It may be due to fluctuation of the flame during the measurements. To avoid this, one could either use a nitrogen flow around the flame to isolate the flame from the ambient or check ventilation.

The acquired concentration values for vertical measurements at the center of the burner are plotted in figure 13. This can be seen that the maximum value of concentration is measured at HAP 3 mm and then it decays exponentially to around 3 ppm at HAP 22 mm. It is
4.2 Distribution of atomic potassium in the plume

where all reactions are completed and concentration approaches the predicted equilibrium level, which can be estimated to around 2-4 ppm, depending on temperature and initial KOH.

Fig. 12 Radial concentration profiles measured in 60 points at HAPs: (a) 1.5 mm (b) 8 mm (c) 18 mm.

Fig. 13 Vertical concentration profiles measured in 15 points at the center of the plume.
At the center of the burner, there was difference between the concentrations measured at HAPs 1.5 mm, 8 mm and 18 mm in the first three set of the measurements and that of in the forth set. It can be counted as the uncertainty of the measurement which may arise by difference in preparation of the sample or placing the plate on the stand in the mentioned measurement points. To avoid this issue, the distribution measurement may be done with only one sample with much higher concentration of KOH. Very high concentration of KOH and consequently very long plateau part allows for moving the plate sample in different points of the plume and do continuously measurements in the same condition.

The path length of the laser light was considered as 40 mm, while it is clear from figures 12 and 20 that the path length of the laser beam varies by the position of the plate in the plume. To compensate the concentration values for the real path length at 60 radial measurement points, first the real path length for center point at HAPs 1.5 mm, 8 mm and 18 mm was estimated from the plots in figure 12 as 20 mm, 28 mm and 40 mm, respectively. These values were read from the plot where there was no measurable K(g) in the plume [8]. The other path lengths were estimated by calculating the sections of the circular surface at each HAP. Figure 14 shows an example of this section calculation for measurement points of +4 mm/HAP 8 mm.

The new concentrations after path length correction are plotted in figure 15. It can be seen that the concentrations increase considerably but still they obey the Gaussian fit. Also the height of this Gaussian fit decrease and the width increases with HAP.
4.2 Distribution of atomic potassium in the plume

Fig. 15 Radial concentrations being measured in 60 points with path length correction at HAPs: (a) 1.5 mm (b) 8 mm (c) 18 mm.

Since section calculation does not work to find the real path length for vertical measurement points, they were reevaluated from the corrected radial profiles by a second order polynomial fit to the real path length at HAPs 1.5 mm, 8 mm and 18 mm. The fit is shown in figure 16.

Fig. 16 Polynomial fit to 3 vertical path length at HAPs 1.5 mm, 8 mm and 18 mm.
Using the polynomial fit, other vertical concentrations were corrected as it can be seen in figure 17.

![Graph showing concentration vs. HAP](image)

**Fig. 17** Vertical concentrations measured at the center of the plume with path length correction

As it can be seen, the concentrations increased considerably but the general behavior is the same: still there is maximum concentration at HAP 3 mm and then it decays exponentially to reach close to the thermodynamic equilibrium at HAP 22 mm.
Chapter 5

Summery and conclusions

An existing TDLAS sensor for K(g) setup with a wide dynamic range was used to measure the atomic potassium K(g) during thermodynamical conversion of potassium hydroxide (KOH) in a premixed methane/air flat flame. The simple and compact setup was able to measure the concentration of potassium even under optically thick conditions which was a consequence of a large product of line strength, path length and K(g) concentration.

The measurement was done in one vertical set of 15 positions above the plate and three radial sets of 60 positions at selected heights. There was discrepancy between two of three common positions in vertical set with that of in radial sets, which can be counted as uncertainty of the measurements. Therefore the repeatability of the measurement should be checked before deciding about reliability of the setup in distribution measurement.

The radial concentration profiles obey a Gaussian fit with a peak close to the center point. In vertical measurements, for low heights above the plate (HAP) there are high concentrations due to chemical reactions. For larger HAPs, the concentration decays exponentially approaching equilibrium at 2-3 cm above plate for total flow rate 11 l/min.
References


Appendix A

Setup photos

Fig. 18 TDLAS set up starts from photo (a) at (1) DFB laser (769 nm). Then (2) Optical isolator, (3) and (4) coupling flat mirror M₁ and M₂ to (5) fiber collimator C₁. It continues to photo (b) after passing a 50/50 fiber splitter which is not shown in the photos to (6) fiber collimator C₂ and (7) reflecting flat mirror M₃ to (8) the burner [19] on a translation stage and (9) focusing lens f₁ and end at (10) photo detector PD₁. Air and methane flow of the burner is controlled by (11) two flow controllers. Frequency scale set up is shown in photo (a) where laser light comes from (12) fiber collimator C₃ to (13) etalon and couples with (14) flat mirror M₄, (15) lens f₂ and flat mirror M₅ to (17) photo detector PD₂.
The burner [19] (item 8) in a closer view:

Fig. 19 (a) The plate stand on the burner (b) The platinum plate on the stand

The plume of KOH in a closer view:

Fig. 20 KOH plume above the plate.
## Appendix B

### Average concentrations at plateau

Table B.1 Average concentrations at plateau in radial positions

<table>
<thead>
<tr>
<th>Radial Pos. [mm]</th>
<th>HAP 1.5 [mm]</th>
<th>HAP 8 [mm]</th>
<th>HAP 18 [mm]</th>
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Table B.2 Average concentrations at plateau at different HAPs

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