

HIGH TEMPERATURE *IN-SITU*-DETECTION OF ATOMIC POTASSIUM WITH NIR-DIODE LASERS

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A laser-based *in-situ* spectrometer using near infrared diode laser at 767 and 770 nm to detect potassium atoms in high-temperature environments is described. The device was used to investigate the thermal dissociation of KCl and to monitor K behind the flue gas filter (300mm diameter, 1000°C) of a 250kW-coal combustor, without the necessity of error prone gas sampling. With a response time of 2 s we achieved detection sensitivities in the order of 10^7 atoms/cm³. The spectrometer should therefore be fast and sensitive enough to detect a malfunction of the flue gas filters via the release of potassium atoms.

1 Introduction

Since the combustion of fossil fuels will remain an important energy source over the next decades, it becomes an urgent task to minimize CO₂-emission by maximizing the total efficiency of combustion. Coal in contrast to natural gas and crude oil is supposed to last at least another two hundred years. Hence it is most important to improve the conversion efficiency of coal combustion (up to 60%) by the development of modern high-temperature combined-cycle power plants, where an additional expansion turbine is included directly after the main combustion chamber. However, the high process temperatures needed lead to an increased release of alkali and heavy metal compounds, which cause severe corrosion problems in the flue gas turbines. Hence, many turbine producers impose strict limits (6.5 ppbw for K/Na [7]) for these metals at the turbine entrance. To maintain long turbine lifetimes innovative high temperature filters, reliable diagnostic techniques and detailed knowledge of the high temperature chemistry of the alkali compounds are needed. The usefulness of conventional probe sampling techniques to study these systems is in doubt due to the high process temperatures and the high reactivity of the flue gas constituents, so that a direct *in-situ* detection for the relevant species is required to allow on-line monitoring of the high temperature filters. For this purpose we developed a compact, diode-laser based absorption spectrometer capable of highly sensitive *in-situ* detection of atomic species. To demonstrate its usefulness for industrial applications we investigated the possibility to detect atomic potassium from dissociated alkali compounds right behind a high temperature filter of an atmospheric coal-combustor.

2 Experimental

Potassium (K) atoms can be detected via strong electronic dipole transitions: the well known D1 ($4s^2S_{1/2} \rightarrow 4p^2P_{1/2}$) and D2- line ($4s^2S_{1/2} \rightarrow 4p^2P_{3/2}$) at 769,90 nm and 767,49 nm. These lines can be recovered with special wavelength selected Fabry-Perot-type AlGaAs-Diode lasers. These lasers can then be tuned coarsely over several nm by variation of the diode

temperature. The absorption profile is then detected within less than a millisecond via wavelength modulation achieved by current modulation.

Laser-based *in-situ* absorption spectroscopy has the advantage of completely omitting the sampling processes and allowing *in-situ* measurements directly in the probe volume. For industrial applications it is very favorable to use tuneable near infrared diode lasers (NIR-DL) as a laser source, because they are inexpensive, compact, rugged, relatively simple to operate and allow room temperature operation. Their fast tunability and high spectral resolution offers the opportunity for non-intrusive and fast chemical sensors with high sensitivity and specificity. Even simultaneous multi-species and temperature measurements have been shown [1-4]. The basic measurement principle is based upon a direct measurement of the absorption losses of a wavelength tuned laser beam propagating through the measurement volume. The major advantage is that absolute absorber densities can be determined without calibration, if only the absorption path length and the absorption cross section is given. However, especially for in-situ measurements it is necessary to correct for additional broad band absorption effects, which modify the overall transmission of the measurement path. Such disturbances may be caused by dust particles or by beam steering effects. Additionally it is often required to suppress thermal background radiation from particles or furnace walls. Methods to suppress such disturbances are described in detail elsewhere [3-6]. A typical set-up (Figure 1) consists of the temperature stabilized and collimated laser and a bending mirror on the "sender"-side of the absorption path and a collecting mirror, an interference filter and a photo detector on the "receiving" side.

3 Results

In preparation for the in-situ measurements we tested the linearity and resolution of the laser spectrometer by detection of the K vapor pressure above solid and liquid K in a low-pressure water-cooled glass cell. Despite the short absorption path of 8 mm we achieved - over a temperature range from 40°C to 75°C - excellent agreement with a calculation based on tabulated data. Over solid K the maximum deviation was below $3 \cdot 10^8$ atoms/cm³.

Further we realized the in-situ detection of K atoms under high temperature conditions by thermally dissociating KCl in a multi-section oven. The first section set the evaporation temperature in the quartz cell thereby controlling the amount of KCl in the gas phase via the vapor pressure. This low-temperature part was connected via a heated capillary to the high temperature dissociation section, which had a diameter of 6 cm and was optically accessible. As expected the plot of log(number density) vs. reciprocal temperature showed a nice linear behavior. The detection limit we achieved under these conditions was better than 10^7 atoms/cm³. With the same set up we also studied the effect of foreign gas collisions on the spectral line shape of the D2 line for Ar, N₂ and CO₂. In addition to the expected pressure broadening in the range of 2.4 to 3.4 MHz/mbar, we also found a significant pressure induced line shift (2.0 to 2.7 MHz/mbar). A detailed publication of this study is in preparation.

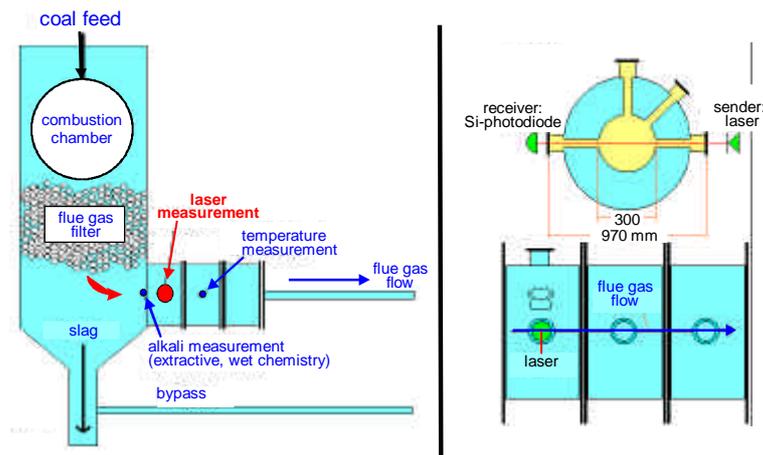


Figure 1: Left: Schematics of the 250 kW-atmospheric coal combustor with flue gas filter and sampling location of the in-situ laser spectrometer for the detection of atomic potassium. Right: Cross-section of the flue gas duct and location of the laser measurement path.

Finally we used the in-situ spectrometer under industrial conditions to detect K atoms in the flue gas channel (300 mm diameter, 1000°C) of an atmospheric 250 kW-coal combustor (Figure 1). Laser, optics and detectors were attached to steel platforms and directly connected to the channel walls. The frequency and amplitude behavior of the transmission of the *in-situ* path and of the thermal emission was analyzed and used to adapt the data processing scheme. The laser was scanned with a repetition rate of 1 kHz across the absorption line. 100 successive scans were averaged. A fitting algorithm extracted the line area used to calculate the K concentration. A time resolution of 2 s was achieved. Typical K number densities found under standard combustion conditions were around $8 \cdot 10^9$ atoms/cm³ corresponding to $2 \mu\text{g}/\text{Nm}^3$, while the total range of the observed number densities covered $50 \text{ ng}/\text{m}^3$ to $30 \mu\text{g}/\text{m}^3$. We achieved a detection limit of about $10 \text{ ng}/\text{Nm}^3$. A typical K concentration trace over a time period of 8 hours is depicted in figure 2 in combination with the oxygen concentration in the flue gas. A, B and C correspond to time periods where the combustor was cofired with oil. The amount of oil which was used with respect to A was twofold in B and fourfold in C. A close anti-correlation between the oxygen and the K-signal is observed, which was expected since excess O₂ reacts with K to form K₂O, shifting the equilibrium concentration further towards the reaction products. This could be corrected if the equilibrium constant and its temperature behavior are known and a precise oxygen signal with the same time response like the laser signal would be available. This was not the case. It has been shown however, that a simultaneous in-situ oxygen and temperature measurement is possible with NIR-DL, so that a correction might be possible in the near future [3,4]. During severely O₂ depleted and thus chemically reducing situations the K-concentration can increase within very short time scales by a ten or a hundred fold to more than $30 \mu\text{g}/\text{m}^3$ and even lead to complete absorption of the laser light. It is expected that the K signal increases: a) with rising flue gas temperatures due to stronger dissociation, b) with higher alkali content of the coal, and c) according to the amount of reaction partners of K in the flue gas (O₂, H₂O, CO₂). Further studies are planned to

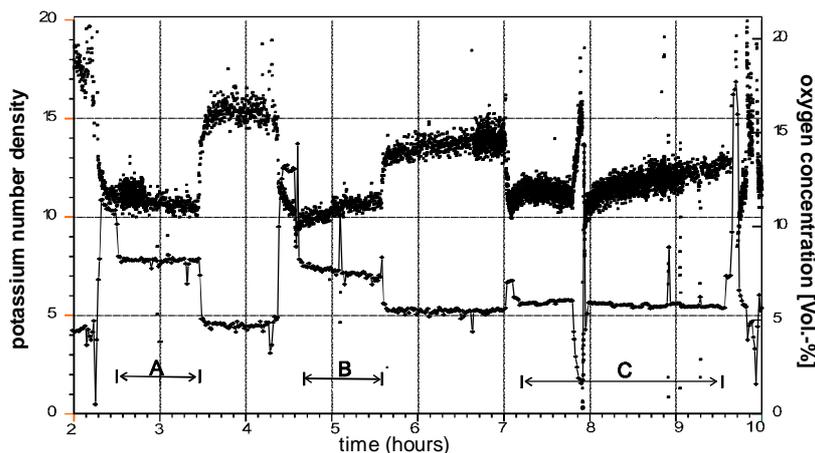


Figure 2: In-situ detection of the concentration of atomic potassium (Black squares, top) in the flue gas duct of a 250kW-coal-combustor by a laser in-situ spectrometer. Black line: O₂-concentration as determined by an extractive O₂-sensor.(Further explanations in the text).

investigate the chemistry and the corrosion effects of the K-release. In addition it is planned to extend the ability of the *in-situ* spectrometer to other species like heavy-metals. In conclusion we demonstrated the *in-situ* detection of K-atoms with high sensitivity and proved that the *in-situ* K-sensor is fast and sensitive enough to detect a malfunction of the flue gas filters.

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