E. SCHLOSSER¹ J. WOLFRUM¹ L. HILDEBRANDT² H. SEIFERT³ B. OSER³ V. EBERT^{1,}⊠

Diode laser based *in situ* detection of alkali atoms: development of a new method for determination of residence-time distribution in combustion plants

¹ Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

² Sacher Lasertechnik, Hannah-Arendt-Str. 3–7, 35037 Marburg, Germany

1

³ Institut f
ür Technische Chemie, Forschungszentrum Karlsruhe GmbH, Postfach 3640, 76021 Karlsruhe, Germany

Received: 29 April 2002/Revised version: 21 June 2002 Published online: 2 September 2002 • © Springer-Verlag 2002

ABSTRACT The residence-time of the flue gas in a furnace is an important parameter for a complete and clean combustion. A new method to determine the residence-time has been developed and is presented for the first time. It is based on the injection of alkali compounds as a tracer. Alkali atoms that are produced by thermal decomposition of the tracer are detected in the hot flue gas after passage of the combustion facility. This is done without any gas sampling using direct tunable diode laser based absorption spectroscopy. Different diode laser (DL) types (Fabry-Pérot DLs, external-cavity DLs, and vertical-cavity surface-emitting lasers) were analyzed and used to develop several spectrometers for the in situ detection of lithium (671 nm), potassium (770 nm), and rubidium (780 nm). Various spectrometers were built for single- or multi-species detection using a single laser, for time-multiplexed multi-species detection using two lasers, and for multi-path detection at two different locations along the flue-gas duct. To evaluate the system performance the potassium atom background caused by the fuel was continuously monitored in the post-combustion chamber (PCC) for several weeks. A typical concentration range of 1 ng to 1 µg at STP (800 ppq to 800 ppt; ppq = 10^{-15}) was observed. By averaging 100 individual absorption scans the response time was 2.7 s. The minimum detectable absorption was about 10^{-4} optical density, corresponding to a detection limit of 4×10^{11} K atoms/m³ at 1200 K instead of "K'. (K(D2) absorption line; 1.9-m absorption path). This is equivalent to a detection limit of 0.1 ng/m^3 at STP or 80 ppq. The fastest response time (0.16 s) was achieved by evaluating single absorption scans. Two combustion facilities at the Forschungszentrum Karlsruhe (a batch combustor and a 3-MW special waste incinerator with a rotary kiln followed by a PCC) were investigated. Alkali chlorides were added to the combustion chamber in different forms, of which short spray pulses of an aqueous salt solution was the method of choice for the residence-time measurement. Flow-time distributions were measured and the mean residence-time was calculated for various operation conditions. A simultaneous flow-time measurement at two different locations (8.4 m/17.0 m from the tracer discharge location) was realized with a binary K/Rb tracer and a multi-species spectrometer. Mean residence-times of $(15 \pm$ 1) s and (26 ± 1) s were observed and met the expected values. PACS 39.30.+w; 42.62.cf; 42.62.fi; 07.20.ka; 32.70.jz

Introduction

One of the most important parameters for the design of continuously working reactors is the residence-time. Combined with the reaction velocity, it determines the turnover rate or, respectively – at a given turnover rate – it determines the size of the facility. In Germany several parameters have to be monitored and kept above the limits according to the 17th BImSchV for waste-incineration plants (1990). These are: the temperature (850 °C, for halogenated materials 1200 °C), the residual oxygen content (6 vol. %), and the residence-time of the flue gas (2 s in the post-combustion chamber – PCC). Similar requirements exist in the US and Canada (US Rule 1989/91, CCME Guidelines 1992) [1]. Therefore, r esidence-time measurements in combustion plants are of great relevance.

We propose to measure alkali atom concentrations, generated by thermal dissociation of tracers like alkali salts (especially the chlorides of lithium, rubidium, and potassium), in order to determine the residence-time distribution of flue gas in the high-temperature zone of combustion plants or other high-temperature processes. Because K is usually present in fossil fuels, we expect a permanent offset in the atom signal above a certain minimum temperature. Li and Rb are usually not present in fuels and can be used to avoid this offset.

An extractive measurement technique cannot be used to monitor the alkali atoms due to the extreme reactivity of the atoms, but optical detection is possible using direct tunable diode laser based absorption spectroscopy (TDLAS). This technique has been proven to be a versatile and robust method for the *in situ* detection of gaseous species in technical environments [2–5].

Due to the high oscillator strengths (f = 0.25 to 0.73) of the electronic transitions of the alkali atoms from the ground state (${}^{2}S_{1/2}$) to the first excited state (doublet: ${}^{2}P_{1/2}$, ${}^{2}P_{3/2}$), TDLAS allows a highly sensitive detection (in the order of 10⁶ atoms per cm³) of alkali metals. Other important facts are the possibility of a direct determination of absolute absorber number densities without the need for calibration and the compact, inexpensive, and robust instrument design possible with near-infrared diode lasers (NIRDLs). Diode lasers with emission wavelengths suitable for all but one (Na) alkali metals are available: Li (670.8 nm), K (769.9 nm, 766.5 nm), Rb (794.8 nm, 780.0 nm), and Cs (894.5 nm, 852.1 nm).

[🖾] Fax: +49-6221/5450-50, E-mail: volker.ebert@pci.uni-heidelberg.de

We employed and compared several diode laser types to measure Li, K, and Rb: Fabry-Pérot diode lasers (FPDLs), external-cavity diode lasers (ECDLs) and vertical-cavity surface-emitting lasers (VCSELs). All lasers are wavelengthtuned for acquiring continuous absorption profiles of the atoms. Several laser absorption spectrometers have been constructed based on these laser types and were used for the time-resolved in situ detection of Li, K, and Rb. Various measurement scenarios were realized: (A) single-species measurement in a single path, (B) multiple-species measurements in a single path, and (C) simultaneous multi-species measurements at different measurement locations. The multi-species detection was realized as a dual-species measurement with a single laser and by time-multiplexing multiple lasers in a composite multi-color beam. Finally - to assess the capabilities of these spectrometers - we conducted tracer experiments at two combustion facilities of the Forschungszentrum Karlsruhe (FZK), Germany.

2 Method

Direct TDLAS is based upon a detection of the spectrally resolved losses of wavelength-modulated nearmonochromatic diode laser light of initial intensity $I_0(\lambda)$ propagating through the measurement volume containing a number density, N, of absorbers. An extended Beer's law can be used to describe *in situ* absorption measurements:

$$I(\lambda, T, t) = I_0(\lambda) e^{-S(T)g(\lambda - \lambda_0)Nz} Tr(t) + E(t),$$
(1)

where $I(\lambda, T, t)$ – with λ = wavelength, T = temperature, and t = time – is the resulting intensity after passage through a probe volume of thickness z. The absorption line is characterized by the temperature-dependent, spectrally integrated line strength S(T) and by the line-shape function $g(\lambda - \lambda_0)$ centered at the wavelength λ_0 .

Two major problems have to be taken care of to perform *in situ* measurements: the first is the time-dependent background transmission Tr(t) of the measurement path. These losses in laser light are caused by broadband absorption/scattering by soot or particles, or refractive-index gradients. The high-speed wavelength-tuning capabilities of diode lasers allow the laser to be tuned much faster than typical fluctuations in Tr(t), so that Tr(t) can be assumed to be constant within a single wavelength scan and corrected by a simple division through the baseline of the absorption signal. Another disturbance common for *in situ* measurements is background (Planck) radiation, which gives rise to an offset E(t) that can be largely minimized by narrow-band optical filters. Furthermore, it is compensated for by mathematical calculations using the amplitude modulation of the laser [3].

3 Diode laser characterization

Three diode laser types were used for these studies: FPDLs at 670 nm, 770 nm, and 780 nm, ECDLs at 670 nm and 780 nm, and VCSELs at 767 nm and 770 nm.

For a precise determination of the absolute absorber density and to achieve high stability, several laser parameters had to be determined which were not supplied by the manufacturer: static wavelength tuning properties – with regard to laser current, temperature, or piezo voltage. These were measured using a wavemeter (Burleigh WA-1000). By modifying this wavemeter to allow an evaluation of the interference pattern of the Michelson interferometer inside with a selfmade electronic circuit based on a Fourier transformation and a mathematical compensation of the non-linear mirror movement, we could simultaneously measure the emission spectrum and hence the side-mode suppression. 1-cm and 10-cm air-spaced etalons served to determine the dynamic wavelength tuning properties and their deviation from linearity, which are needed to determine absolute number densities from the detected absorption profiles. For the line-fitting process the deviation from linear tuning needs to be small or it has to be compensated for by calibrating the 'local' tuning rate within the scan. To extract this parameter the number and temporal positions of the maxima on the etalon transmission signal are determined (see Figs. 1 and 3). This is done with a LABVIEW program, which counts the maxima by detecting the zero crossings with a negative slope of the first derivative of the etalon trace. The dynamic tuning curve of the laser can be depicted by plotting the time at each zero crossing ver-



FIGURE 1 Dynamic tuning behavior of the 780-nm Littman ECDL during an up-scan across the Rb(D2) line measured with a 10-cm air-spaced etalon with 0.05-cm⁻¹ FSR. The wavelength of the laser was modulated via the piezo element with a 120-Hz triangular signal. A tuning coefficient of (0.213 ± 0.007) cm⁻¹/ms = 0.043 cm⁻¹/V was found. Mode hops marked with '#' occur near the end of the wavelength swing and limit the tuning range to 0.65 cm⁻¹



FIGURE 2 Side-mode suppression of our Littman ECDL at 670 nm measured with an optical spectrum analyzer



FIGURE 3 Fringe pattern created by sending the radiation of a injection current modulated VCSEL (for K(D2), 767 nm) through an air-spaced 1-cm etalon with a free spectral range of 0.5 cm^{-1} . The separation of the fringes is used to determine the dynamic tuning coefficient of the laser, which is necessary for a calibration free measurement of absolute absorber densities. The fringe pattern also serves to determine the non-linear tuning behavior and to calibrate the wavelength scale on the raw data. For a modulation frequency of 1.3 kHz we determine an average tuning coefficient of $(41.9 \pm 1.2) \text{ cm}^{-1}/\text{ms}$ or $(5.51 \pm 0.15) \text{ cm}^{-1}/\text{mA}$

sus the fringe index number multiplied by the free spectral range of the etalon $(0.05 \text{ cm}^{-1} \text{ or } 0.5 \text{ cm}^{-1})$. Finally, a first-and a second-order polynomial were fitted to the tuning curve.

3.1 FPDLs

FP-type AlGaAs lasers are conventional edgeemitting diode lasers. The FPDL used by us (Mitsubishi-ML4405 for K, ML4402 for Rb) showed a significant scatter in the wavelength emitted by the individual laser and a discontinuous, staircase-like wavelength tuning ('mode hops'). Therefore, all lasers had to be tediously selected with regard to high spectral quality, i.e. single-mode-emission behavior, and coverage of the desired absorption line. This selection became even more complicated since some lasers showed only erratic mode hopping (1 in 100 to 1 in 1000 scans), which would falsify the signal if the scans were averaged. 100 s of singlewavelength scans had to be analyzed to identify lasers which show this behavior and to correct for occasional mode hops. So, despite being relatively inexpensive, the cost of ownership is largely increased for FPDLs by the need to select a suitable laser. For example, out of 60 ML4405 pre-selected by the manufacturer for the 760- to 770-nm interval, 28 lasers emitted between 764 and 770 nm at room temperature and only 12 lasers near 769.9 nm and 15 near 766.5 nm by choosing different operating temperatures and currents. Just three (5%) of them had a suitable mode map that allowed a mode-hopfree, single-mode scan of the K absorption line (1 for the D1 and 2 for the D2 line of K) [6]. For comparison, the selection yield to find a ML4405 for a randomly chosen O₂ line within the A-band was about 30% [7]. Experiments to alter the mode map of a FPDL (Hitachi HL6712, 670 nm) by temperature stressing the laser were time consuming and not rewarding.

The wavelength of the selected ML4405 could be temperature-tuned by 108 cm⁻¹. But more than 75% of this spectral interval is not accessible because of mode hops. The typical static continuous tuning range in between mode hops was only \sim 1.9 cm⁻¹. This range was further reduced under dynamic current-tuning conditions to be 1 cm⁻¹ at 1-kHz modulation frequency.

3.2 ECDLs

To avoid the selection process mentioned above, an external resonator can be used to force FPDLs to emit at the target wavelength. To suppress the longitudinal modes of the laser diode chip, which are caused by the high reflectivity (30% to 40%) of the cleaved facets of the laser chip, the front facet has to be antireflection-coated. Otherwise the single-mode behavior is disturbed by the presence of three competing cavities [8]. Several dielectric layers coated on the facets will result in a residual reflectivity of typically R < 0.02%. Two different ECDL types are common.

- In the Littrow configuration [9–11] the collimated laser light is directed onto a holographic grating and the firstorder beam is reflected back directly into the laser diode, while the light diffracted in the zeroth order is coupled out. Wavelength tuning is achieved by tilting the grating. The disadvantage is that this also results (A) in a tilt of the output laser beam or (B) in a parallel shift when implementing a beam-correction mirror.
- 2. The second external cavity concept is the Littman configuration [12]. Here the first diffraction order from the grating is not directly reflected into the laser but onto a planar tuning mirror or a 90° prism, which closes the external resonator. The tilting angle of this mirror selects which light is reflected back into the laser via the grating. Again the zeroth diffraction order is coupled out. Since the grating is fixed and the mirror is used for tuning, the beam orientation remains unchanged. Furthermore, Littman lasers can be tuned further without mode hops because higher-order changes in the cavity round-trip length can be corrected via the position of the turning point of the mirror.

ECDLs provide a very low line width in the order of several hundred kHz (compared to 1 to 100 Mhz for monolithic lasers) and a side-mode suppression of 30 to 40 dB as depicted in Fig. 2 for the ECDL Littman laser at 670 nm. Wavelength tuning of ECDLs is - in contrast to monolithic laser diodes like FPs, DFBs (Distributed feedback), or VCSELs accomplished by mechanical variation of the spectrally selective feedback. While monolithic lasers can be tuned by injection current and temperature changes only over relatively narrow spectral ranges [13], it may be as much as 240 nm for ECDLs [14]. Compared to monolithic DLs, the tuning speed is limited (below 1 kHz) because of the necessary mechanical movement of the tuning element. Linear periodic (triangular) modulation may cause excitation of higher-order mechanical vibrations that reduce the emission quality. A sinusoidal mechanical movement is smoother for fast (1 kHz) modulation but requires the linearization of the frequency axis of the absorption profile. Despite the Littrow ECDL being easy to align, cost effective, and having a larger output power than the Littman ECDL, it is not suitable for our setup because of the reduced beam-pointing stability.

Two ECDLs (Sacher Lasertechnik, TEC 500-675-5, TEC 500-780-20) in Littman configuration [15] were used for Li and Rb(D2). No temperature or current tuning is needed be-

cause of the external cavity. Thus the emitted laser power is almost constant under small wavelength excursions. Wide tuning however reveals periodically structured amplitude modulation (AM) due to the residual reflectivity of the AR-coated facet. Rapid wavelength tuning over roughly 1 nm is achieved via a piezo-electrical element. Figure 1 shows the dynamic tuning behavior of the 780-nm Littman ECDL during an upscan across the Rb(D2) line measured with a 10-cm air-spaced etalon with 0.05-cm⁻¹ FSR. A 120-Hz triangular function was used to drive the piezo element. A dynamic tuning coefficient of $(0.213 \pm 0.007) \text{ cm}^{-1}/\text{ms} = 0.043 \text{ cm}^{-1}/\text{V}$ was found. The deviation from linearity is very low (1%). However, mode hops marked with "#" occur near the end of the wavelength swing and limit the tuning range to 0.65 cm⁻¹.

3.3 VCSELs

VCSELs are, in contrast to edge-emitting lasers, pumped along the resonator axis by an annular contact. The ring contact, with an inner diameter between 2 µm and 20 µm, forms the emitting aperture. This leads to a circular, relatively weakly diverging (~ 12°) beam that is free of astigmatism. Due to their very thin gain region and short resonator length they are longitudinally single-mode. However, they can emit higher transverse modes if pumped too hard or if their emitting aperture is too large. They have very low threshold currents (1–6 mA), which is good for battery-powered systems. But they provide only rather low output power (100 µW to 1 mW), which is one limitation for using VCSELs for *in situ* measurements in strongly scattering or absorbing environments with substantial light losses ($I/I_0 < 10^{-3}$).

They offer two major spectroscopic advantages: (1) their small AM to wavelength tuning ratio (= $dP/d\lambda$), also termed specific amplitude modulation (sAM), which determines the power variation during a wavelength scan and thus the dynamic range needed to recover a small absorption signal [7] and (2) an extremely wide, continuous, single-mode tuning range of 20–30 cm⁻¹ accessible by rapid current modulation. They are therefore ideal for fast wavelength sweeps across several or very broad absorption lines, e.g. in industrial high-pressure environments [6] and under laboratory conditions for the detection of oxygen [7, 16, 17].

VCSELs are commonly available as multi-mode lasers for telecommunication purposes (850 nm) or as single-mode lasers (for Cs, Rb, K/O₂, and Li) for spectroscopic purposes. We used two different VCSELs (CSEM) for the detection of K(D1) at 769.9 nm and K(D2) and O₂ at 767.5 nm. Their emission line width is in the order of several 10 MHz so that they can be used for high-resolution spectroscopy [18]. The fringe pattern used to determine the dynamic tuning coefficient of the 767-nm VCSEL using an air-spaced 1-cm etalon and the associated tuning plot is shown in Fig. 3. For a modulation frequency of 1.3 kHz we determine an average tuning coefficient of $(41.9 \pm 1.2) \text{ cm}^{-1}/\text{ms}$ or $(5.51 \pm$ (0.15) cm⁻¹/mA. The errors given for these two numbers are mainly governed by the deviation from linearity. The accuracy of this method using the 1-cm etalon is $0.01 \text{ cm}^{-1}/\text{mA}$, and respectively 10 times better with the 10-cm etalon (FSR 0.05 cm^{-1}). The lower graph in Fig. 3 indicates the small deviation from linearity of only 0.6% of the tuning range $(12.5 \,\mathrm{cm}^{-1}).$

Selected laser properties that we determined for the lasers used in our experiments are listed for comparison in Table 1.

4 Atomic absorption profiles

The detailed line shapes of the alkali atoms are governed by the fine structure and hyperfine splitting of the transitions. The fine-structure splitting of Li is small ($\Delta \lambda =$ 0.015 nm = 10 GHz), so that the doublet is not resolved for atmospheric combustion conditions. The D1 and D2 lines are clearly separated however in K ($\Delta \lambda = 3.4$ nm) and Rb ($\Delta \lambda = 14.7$ nm). Furthermore, the hyperfine splitting broadens the Doppler absorption profile of K slightly (HWHM is 0.45 GHz instead of 0.39 GHz at 298 K), while it is in Rb large enough to even distort the pressure-broadened absorption lines at 1 bar (Figs. 4 and 5).

Usually, no other lines are found near the absorption lines of most alkali metals. But parts of the P-branch of the A-band of oxygen, which belongs to vibrational subtransitions of the $b^{1}\Sigma^{+}{}_{g} \leftarrow X^{3}\Sigma^{-}{}_{g}$ magnetic dipole transition [19, 20], are found in the vicinity of the K(D1) and (D2) lines. The O₂-lines in this spectral range occur in pairs ($\Delta \nu = 1.7 \text{ cm}^{-1}$), which are separated by 9.7 cm⁻¹. The width (HWHM) of each line is 0.03 to 0.05 cm⁻¹ (300 K, 1 atm). The maximum line strength

	FPDL K(D2)	FPDL Rb(D2)	ECDL Rb (D2)	VCSEL K(D2)	VCSEL K(D1)
Wavelength (nm)	766.49	780.03	780.03	766.49	769.90
Emission power (mW)	3	3	25	0.6	1.0
Continuous tuning (cm ⁻¹) I (threshold) (mA) Amplitude modulation coefficient (mW/mA)	1-2 44 0.26 ± 0.01	$\begin{array}{c} 36\\ 0.302\pm0.001\end{array}$	0.7–3.3 32 n.a.	$10 \\ 5.6 \\ 0.20 \pm 0.01$	$20 \\ 1.7 \\ 0.24 \pm 0.01$
Static current-tuning coefficients (cm^{-1}/mA)	-0.24 ± 0.01	-0.246 ± 0.001	n.a.	6.2 ± 0.3	6.2 ± 0.3
Static temperature-tuning coefficient (cm ⁻¹ /K)	$-1.01 \pm 0.01 \ (-3.37 \pm 0.05,$ incl. mode hops)	-0.944 ± 0.002	n.a.	0.96 ± 0.05	
Dynamic current-tuning coefficient (cm^{-1}/mA)		0.157	$\begin{array}{c} 0.043 \ \mathrm{cm^{-1}/V_{piezo}} \\ \mathrm{at} \ 120 \ \mathrm{Hz} \end{array}$	5.4–5.7	5.0-6.8
Beam profile	Elliptic	Elliptic	Elliptic 1:3	Circular	Circular

 TABLE 1
 Properties of the diode laser types used



FIGURE 4 Absorption lines of Rb(D2) (780 nm) simultaneously measured in situ in the batch reactor KLEAA (at 1 bar and 1273 K) (single broad feature, *gray*) and in a low-pressure (< 1 mbar), room-temperature Rb cell (narrow, multi-line feature, because of hyperfine splitting). Both features were measured simultaneously with a FPDL. The difference between the fit of four lines (relative position locked, but shifted by -0.047 cm^{-1}) and the measured absorption line is shown in the *lower trace*



FIGURE 5 Same line as in Fig. 4, but measured with the Littman ECDL. Four Lorentzian lines were used for the fit. The absorption line scan recorded using the ECDL is – compared to the FPDL – more disturbed by the slower sweep rate and variations of the laser power because of the wide tuning

at 300 K is about 2×10^{-4} cm⁻¹ atm⁻¹. As a result of this coincidence it is advantageous at low K concentrations to use the K(D1) line for diagnostics even though the K(D2) absorption line (Fig. 6) is twice as strong. Using the K(D2) line, which coincides with the P21P21 O₂ absorption line, we could realize at moderate K absorptions a simultaneous detection of both species (K and O₂) by using the P21Q20 O₂ absorption line that was close to the K line but isolated.

A Voigt profile is most suitable as a line-shape function. Nevertheless, we used a Lorentzian line shape as an approximation, because it allowed a faster linear fitting scheme. The error caused by this simplification was rather small, justifying our choice. At our measurement conditions, e.g. atmospheric pressure and temperatures of about 1200 °C leading to line-broadening contributions of $\gamma_L = \sim 2.6$ GHz and $\gamma_D = 0.8$ GHz, we overestimated the total line area by $\sim 1.5\%$. For the Doppler-broadened absorption lines of the low-pressure reference cells we used Gaussian line profiles.

Due to the extremely high line strength of the electric dipole transitions of the alkali atoms it is known that absorp-



FIGURE 6 Simultaneous in situ detection of potassium and oxygen with a single VCSEL in the PCC of a rotary kiln waste incinerator THERESA (at p = 1 bar and T = 1400 K). The absorption scan, which was selected for a rather low K signal, shows two O₂ lines (P21Q20, P21P21, separated by 1.82 cm⁻¹) and the K(D2) line at 767 nm, coinciding with the weaker P21Q20 O₂ line. The residual is shown between a fit of three independent Lorentzians and the measured profile, indicating a fringe-associated noise of less than 10^{-3} and an electronic noise level of below 10^{-4} fractional absorption

tion measurements of alkali atoms may be severely influenced by power broadening. The effect of this saturation depends on the line-broadening mechanism: for homogeneous broadening (e.g. by collisions), which dominates in our application, the line shape will remain the same - and can therefore not be detected in the residual of the fit – but the total area will be reduced and the line width will be larger, whereas for inhomogeneous broadening line shape, area, and width will be affected. In both cases the total area will be reduced, so that a quantitative measurement would have large systematic errors depending on laser power. However, for our measurement conditions power broadening need not be included due to our high total pressure and low beam power density (relatively large beam diameter and low laser power). The high pressure effectively quenches the upper transition state and repopulates the initial state. A rough estimate indicates that we are about a factor of 20 000 below the saturation intensity.

By comparison of the absorption signals in the flue gas and in the low-pressure reference cells, we could also determine the pressure-induced line shift of the atomic lines. Furthermore, it was also possible to determine the collisional widths of the lines and derive the broadening coefficient for a typical combustion flue gas. To minimize the effects of Doppler broadening we performed these measurements at a high-pressure combustion facility with up to 13 bar. Here we found the pressure-induced broadening coefficient for the flue gas from coal combustion to be (0.09 ± 0.01) cm⁻¹/atm (halfwidth) while the line shift was (-0.060 ± 0.003) cm⁻¹/atm (measured at 1540 K and 11.2 bar, statistical error given as 1σ). These measurements are described in more detail in [6].

Using the standard deviation (1σ) of the residual noise and the etalon structures in the absorption profile, which can be separated from the measured scan via the fitting routine, it is possible to determine a minimum detectable absorption (MDA) of the *in situ* spectrometer. The MDA is 3.3×10^{-4} for the K(D2) absorption line using a VCSEL (Fig. 6, z = 1.9 m, 100 averages). For Rb(D2) we found an identical value of 9.6×10^{-4} for a FPDL (Fig. 4, z = 0.22 m, single scan), and a ECDL (Fig. 5, z = 0.22 m, 10 averages). Depending on the laser type used for the measurements, various effects limit the sensitivity: FPDLs suffer from a mode-hop-limited tuning range, while erratic mode hops can generate the necessity to record single scans. The use of ECDLs is limited by the slow tuning speed, so that fast *in situ* disturbances might not be corrected completely. In addition, their periodic AM at wide wavelength scans cannot be isolated by simple polynomials, but requires separate measurements for scan correction. The VCSELs on the other hand have only one drawback: their low emission power. However wider spectral scans possible with a VCSEL and their low sAM compensate to a certain extent for that disadvantage by enhancing the reliability of the background determination and the precision of the measurement.

5 In situ measurements of alkali atoms

5.1 Test facilities (combustors)

We reported already on measurements of potassium in the flue gas of two pulverized-coal-fired plants (1 bar/250 kW and 10-16 bar/1 MW) [6, 21, 22]. The experiments for determination of residence-times by measurement of the flow times of alkali tracers, which are presented here, were conducted at two facilities at the FZK:

(1) KLEAA (Fig. 7) is a laboratory scale test combustor for batch incineration [23]. The experiments were performed without the use of a fuel, but by electrical heating only and by pumping air/N₂ mixtures through the oven.

(2) THERESA (Fig. 8) is a semi-technical, experimental plant built to investigate the combustion of special types of industrial waste. It is a test facility on the pilot scale, equipped with a 1.5-MW rotary kiln and a post-combustion chamber (0.5 to 1.5 MW) [24]. Oil and natural gas were used as fuel,



FIGURE 7 Simplified scheme of KLEAA. The locations of the tracer injection and the laser detection are indicated



FIGURE 8 Simplified cross-section scheme of THERESA, a rotary kiln waste incinerator with a PCC (post-combustion chamber) showing the location of the tracer injection, the first measurement path after the rotary kiln, and the second path in the upper PCC

co-fired with mixtures of wood chips, glass, PVC, or waste during our experiments.

Atomic alkali metals (Li, K, Rb) were measured *in situ* at different locations in these high-temperature combustion facilities.

The optical access to the flue-gas channels was possible via pressurized, air-purged windows. For the simultaneous measurement of O_2 the access tubes with a length of 64 cm were purged by nitrogen. Laser, optics, and detector were attached to small steel platforms that were rigidly connected to the walls on both sides of the flue-gas channel.

5.2 Setup

5.2.1 Single-species measurements. The following optical setup was chosen during the tests at KLEAA for singlespecies measurements. The laser was collimated and coupled into the combustion zone via a plane mirror and a tilted window. Behind the exit window a focusing mirror ($f \sim 20 \text{ cm}$) directed the collected light through a narrow-band interference filter onto a silicon photodiode. Exploiting the 4% reflection from the tilted entrance window, we generated a reference beam. This secondary beam was directed through a lowpressure reference cell (filled with metallic K or Rb) that was used for line identification, line-locking, and spectral laser characterization purposes only. A calibration of the direct TD-LAS signal was not necessary since all required parameters (absorption strength, the path length, and the dynamic tuning coefficient) were known. For Li a small burner and traces of Li salt were used as reference 'gas'.

The electronic setup consisted of a combined laser/peltierelement driver (Profile, LDC 1000), which provided a lownoise (< 0.4 μ A rms, 10 Hz – 6 MHz) current source for the laser, and a temperature-control loop ($\Delta T = 10$ mK) for the peltier elements. Laser current (respectively laser wavelength) was modulated via a function generator (SRS DS345) using a symmetric triangular signal with a repetition rate of 1.3 kHz.

The photocurrents were preamplified (Femto DLPCA 100) and digitized at 1.25 Msamples/s by an eight-channel, simultaneously sampling 12-bit A/D converter on a PCI plugin board (T112-8, Imtec). Typically 100 consecutive scans with a length of 1024 samples each were averaged for further noise reduction and stored on a hard disk within 2.7 s (= 0.37 Hz) for offline evaluation. For flow-time measurements we collected usually 10-fold averages or even single scans, leading to response times of 0.4 s (2.5 Hz) or 0.16 s (6.1 Hz).

The scans were corrected for variations in transmission and background emission [3, 6]. A second-order background polynomial and a Lorentzian line-shape function were fitted to the scans, using a linear regression algorithm. For very strong absorption lines a non-linear curve fit using the Levenberg–Marquard algorithm was used. The line position could be extracted from the fit to the *in situ* signal or from the reference cell absorptions in the case of weak *in situ* signals. Finally the absorption line area determined by the fit was converted into absolute number densities using the tabulated absorption cross sections [20, 25, 26], the dynamic tuning coefficient of the laser, the absorption path length, the pressure, and the gas temperatures (assuming an ideal gas).

5.2.2 Simultaneous multi-species measurements: multiplexing setup. The simultaneous measurement of spectrally wellisolated species has been demonstrated recently under laboratory [27-29] and industrial conditions [2-4]. Here the laser beams are combined to form a composite beam, which is split into its initial components after the passage through the absorber by a grating [28] or a combination of dichroic beam splitters and interference filters [2-4]. This spectral multiplexing becomes more and more impossible the smaller the spectral distance between the species is, e.g. O₂, K(D1) and (D2), or Rb(D2). Dichroic filters do not have a steep enough filter function, whereas a grating separation would need too much space to spatially separate the beams. Here frequency modulation [29] or time-multiplexing [27] techniques can be employed to the best advantage, but have not been used in industrial combustion processes. Time-multiplexing takes advantage of the rapid amplitude and wavelength tuning properties of diode lasers by combining multiple laser beams and directing them onto a single detector, but turning them on and off one after the other to realize a consecutive quasi-simultaneous measurement of the species. The individual lasers are distinguished by their temporal [27] or modulation frequency [29] properties.

We modified our single-species *in situ* setup for time multiplexing and tested it at THERESA to perform a two/three species measurement of Rb, K, and O₂. Using a single widescanning VCSEL we could simultaneously measure K and O₂ (Fig. 6). But to determine both K D-lines or K and Rb we had to combine two individual laser beams (Rb: FPDL/K: VCSEL) by reflecting them via small mirrors onto a larger one to couple them into the flue-gas channel (Fig. 9). After the flue-gas passage both beams are collected by the same focus-



FIGURE 9 Simplified optical setup for multiplexing

ing mirror and directed onto a common photodiode without using an interference filter. A reference beam was again accomplished using the reflection from the entrance window but placing two reference cells into the reference-beam path.

For phase-locked modulation of the lasers, two arbitrary function generators (SRS DS345) were programmed with the identical but phase-shifted saw-tooth-shaped modulation function: the first laser was linearly tuned across the absorption line within 383 µs and then its injection current was kept at a constant level just below the threshold while the sequence was repeated for the other laser and vice versa. Turning the laser off it was possible to determine the offset, E(t), necessary to perform an emission correction. An external pulse generator triggered the function generators. The modulation signals were phase-shifted in such a way that a complete sawtooth signal is observed at the detector. The repetition frequency of a complete scan with both lasers was 1.3 kHz. Typical in situ signals (at 1 bar, 1200 °C) and reference cell signals (< 1 mbar, ambient temperature) of K and Rb are shown in Fig. 10. The more powerful FPDL laser had an intentionally



FIGURE 10 Directly measured absorption profiles (*upper trace*) during quasi-simultaneous, time-multiplexed detection of Rb (with a FPDL at 780 nm) and K and O₂ (with a VCSEL at 766 nm). The raw data of the in situ absorption profiles (in the PCC of THERESA, at 1 bar, 1200 °C) show two strong absorption lines of Rb (*left*) and K (*right*) and four weaker O₂ lines (indicated by *black arrows*). The raw data from the two reference cells (*lower trace*) show Rb with hyperfine splitting and K (at less than 1 mbar and ambient temperature)

slightly diverging beam to match the power reaching the detector by the VCSEL. The same setup but with two VCSELs was used for a simultaneous detection of the K doublet. By monitoring the same species with two lasers we could separate the fast concentration fluctuations from noise and errors generated by the *in situ* spectrometers.

5.3 Multi-location setup: residence-time measurements

For a simultaneous detection of the flow times at different locations, we monitored at THERESA two independent measurement paths separated by 8.6 m. One measurement path (2.60-m absorption length within the flue gas) was located at the end of the rotary kiln (800 to $1200 \,^{\circ}$ C), the other one (1.90-m absorption length) was in the PCC (900 to $1300 \,^{\circ}$ C) above the two PCC burners. By time-multiplexing two lasers, multiple species were monitored simultaneously at each absorption path.

For a flow-time measurement we added alkali-metal salts to the combustion chamber at a well-defined injection time t_0 . For our very first experiments we inserted the tracer in the process stream by dropping polyethylene bottles filled with the salt into the combustion chamber using the solid-fuel dosage of the plant. The salts were pure, mixed, dissolved in water or impregnated on wood.

Later we developed a technique with much more precise timing properties by generating short concentration spikes with well-known temporal structure by injection of an aqueous (or partially alcoholic) salt solution into the combustion chamber from a spray nozzle using a water-cooled lance. The solution was delivered from a reservoir using a pump unit, which kept the fluid at a constant pressure by pumping the solution continuously though a circular bypass. The pneumatic valves could be electronically activated by applying a constant voltage for the desired duration of the pulse. The control unit closed the valve for the bypass and opened the valve for the lance. A DA plug-in board (NI AT-MIO) generated the trigger signal. An AD plug-in board inside the same PC was used for data acquisition. In this way the injection time and duration could be remotely computer-controlled from the same location as the data acquisition. The amount of solution delivered was determined by weighing the solution reservoir. Usually a pulse duration between 300 ms and 2 s was chosen. By comparing 35 pulses we found that, for example, (835 ± 11) ms corresponded to (2.3 ± 0.5) g solution.

To demonstrate the effect of different injection locations, two injection ports were realized: one at the head of the rotary kiln next to the main burner and the other one at the exit of the rotary kiln adjacent to the PCC. During the injection in the upstream port we could realize a simultaneous detection of atomic species at the rotary kiln exit and in the PCC. To determine the flow times inside the PCC only, the two signals are compared, or we injected in the port at the exit of the rotary kiln and measured at the end of the PCC.

The solution is discharged into the furnace as a fine spray and rapidly vaporized. Alkali atoms are released by thermal dissociation of the salts. The temporal progression of the tracer concentration is detected by means of TDLAS of the free alkali atoms. The time and duration of the injection as well as the absorption scans are stored on a PC for offline evaluation. After correction of the raw scans and converting the line area to concentration units, the time scale is referenced to the injection time, and a Gaussian fit modified with an exponential decay (2) can be fitted to the detected concentration trace:

$$f(t) = y_0 + \frac{A}{\tau_0} \exp\left(\frac{1}{2}\left(\frac{\omega}{\tau_0}\right)^2 - \frac{t - t_c}{\tau_0} \int_{-\infty}^{z} \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{t^2}{2}\right) dt\right)$$

with $z = \frac{t - t_c}{\omega} - \frac{\omega}{\tau_0}.$ (2)

Three of the resulting parameters are times that characterize the concentration profile: t_c , the center of the Gaussian distribution, represents the progression of the initial injection; ω the broadened width of the injection pulse; and τ_0 , the decay time. For species like K that have a natural background, an offset (y_0) has to be allowed. The integrated concentration equals the peak area (A).

The mean residence-time (\bar{t}) is calculated using (3), where t is the time in seconds after the injection time, c the tracer concentration, n the number of concentration measurements used for evaluation, and i the index number of the discrete measurements:

$$\bar{t} = \frac{\sum_{i=1}^{n} t_i \cdot c_i}{\sum_{i=1}^{n} c_i}.$$
(3)

5.4 Potassium-atom background

We measured at THERESA continuously for several weeks (18 days) under various operation conditions the potassium-atom background concentration, originating from the combustion of fossil fuels, wood, and added glass to evaluate the performance of the *in situ* spectrometer.

The K density in the flue gas varied greatly with temperature (Fig. 11), the O₂ concentration (anticorrelated), and the K-salt concentration. Correcting for the temperaturedependent density changes, assuming an ideal gas, we calculate a normalized potassium density whose remaining temperature dependence is a result of the thermal dissociation, which is determined by the free enthalpy (ΔG_{diss}). These dependences indicate that flow-time measurements have to be corrected for the process parameters or have to be performed under constant process conditions. Since a typical flow-time experiment at THERESA lasts only 30 s to 120 s the last condition can easily be met.

Usually we measured a K background absorption at the D2 line between 2% and 10% (extreme values 0% to 80%). Converted into typical K concentrations and densities at STP in the flue gas this corresponds to 1 ng/m³ (0.8 ppt) to 1 μ g/m³ (0.8 ppb) (lower limit ~ 3.5 × 10¹² potassium atoms/m³ at 1200 K) depending on the type of fuel, the temperature inside the PCC, and the oxygen content of the flue gas. Using



FIGURE 11 The background potassium concentration (*bottom trace*, at 273 K, 1.023 bar) in the flue gas of the PCC of THERESA changes sensitively with the flue-gas temperature (*top trace*, digitization steps visible) because of thermal dissociation and release. The oxygen concentration was constant at 9.5 vol. %. The in situ potassium density equals $(1.3-3.4) \times 10^{13}$ atoms/m³. Measured in situ with a VCSEL to access the K(D2) line at 766 nm

an absorption path of 1.9 m within the flue gas and acquiring/averaging 100 scans for each line fit, we achieved a time resolution of 2.7 s and a detection limit of 0.1 ng/nm³ at STP (0.08 ppt = 80 ppq). Under these conditions the detectivity corresponded to a minimum detectable absorption in the order of 10^{-4} .

 O_2 could also be detected and led to a total absorption of about 1.2% (P21P21); half of which was caused by the ambient O_2 outside the flue-gas channel (path length outside 1.2 m). The residual O_2 absorption is assigned to the O_2 inside the flue gas (1.90 m). The influence of the access pipes (1.34 m) to the flue gas was minimized by purging with nitrogen. Assuming a MDA of only 10^{-3} OD, we estimate at 1200 K flue-gas temperature the minimum detectable O_2 concentration to be ~ 1.5 vol. %, mainly limited by the disturbance from ambient O_2 and by the low-gain amplifier settings needed for the detection of alkali atoms.

5.5 Addition of alkali salts to the combustion chamber

The concentration of the alkali atoms detected in the flue gas can be varied by adding alkali salts to the process stream. Numerous experiments with different injection scenarios and injection parameters have been performed, but only a few typical experiments are shown here: (1) adding solid (a), dissolved KCl (b), or KCl impregnated on wood (c) via the solid-fuel dosage port and (2) spray injection of KCl and binary KCl/RbCl solutions via the water-cooled lance.

(1a) The upper graph in Fig. 12 shows the response of the potassium density measured in the PCC at 12.6-m height. 35 g of crystalline KCl were added to the rotary kiln of THERESA using the solid-fuel dosage. The fuel composition at that time was chipped wood, glass, and polyvinyl chloride pellets, co-fired with natural gas or light oil. The flue gas traveled a total distance of 17 m from the location of the dosage. The K concentration is scaled logarithmically, so the exponential decay of the average signal is linearized. A 1/e decay time of 125 s was determined. In addition to the decay, periodic



FIGURE 12 Upper graph: in situ measurements of the temporal evolution of the potassium density in the PCC of THERESA after adding 35 g of solid KCl. The two *lines* show the slope of the background and of the decay. The peak heights of the maxima show a decay time of 125 s. *Lower graph*: K-atom density after adding 69 g of KCl dissolved in 300-ml water. Slow eminently periodic variations $(\Delta t = 5 \min, 8 \text{ s})$ are visible. The decay time of the peak maxima is 37 min

variations in the K density are observed $(1/\omega = 31.3 \pm 0.2 \text{ s})$, which show the same periodicity as the batchtype addition of the solid fuels. A possible cause for these periodic changes might therefore be the variation in the combustion temperature and/or the oxygen concentration initiated by the addition of solid fuels.

- (1b) In another experiment shown in the lower graph of Fig. 12, 69 g of KCl solved in 300-ml water were added in a PE container again via the solid-fuel dosage port. During the combustion of the PE bottle the water seems to evaporate more rapidly and allows the KCl to be more finely distributed, generating a much stronger initial rise in the K concentration. On the other hand the decay thereafter is slower. This might be an indication that the salt became part of the rotating slag film on the inside of the kiln. The decay was mono-exponential for more than 3.5 h and the decay time was measured to be 37 min. Again we found the same fast periodic variations, but we also found much wider spaced, very periodic lowfrequency fluctuations at $1/\omega = 5 \min 8.5 \text{ s} \pm 0.3 \text{ s}$. One prominent periodic event in the rotary kiln is the rotation of the rotary kiln itself, which had a rotation frequency of 0.29 turns per minute, $1/\omega = 3 \min 27$ s. However the periodicity of the signal could not be linked directly to the rotation speed (two peaks per three turns). If the delayed rotation is a consequence of the liquid slag film on the inside of the rotary kiln being unable to follow the rotation of the rotary kiln and therefore lagging behind, this has to be investigated further. Either way, the decay is caused by evaporation and dissociation of the KCl. Additionally, the slow movement of the slag on the inside of the rotary kiln and chemical absorption/diffusion into the slag may contribute to the decay.
- (1c) In a third experiment 70 g of wood chips impregnated with 20 wt. % KCl caused one large peak only with a following exponential decay. No obvious periodicity was observed afterwards. This behavior might indicate that

the salt has disappeared completely during combustion of the wood chips, before becoming part of the slag.

While these experiments show very rich structures in the time-dependent release of the injected potassium salts, the mechanisms behind the delayed release and the cause for the extremely periodic variations of the signal are still under investigation.

5.6 Residence-time measurements

As the previous experiments show, a direct injection of the tracer into the gas phase has to be accomplished to avoid contact and adsorption effects within the slag. It is also necessary to know the exact time of the release. This can be ensured by spraying diluted alkali-salt solutions into the furnace in the vicinity of the main burner with a remote-controlled injection lance. Various solution concentrations (0.02%, 1%, 5%) were used for such experiments (2) mentioned above.

Figure 13 shows the effect of a 836-ms injection of 2.3 g of a 5% aqueous KCl solution with a small amount $(\sim 0.02\%)$ of RbCl. Rb atoms of the tracer pass the rotary kiln and are detected at the end of the kiln, 8.5-m downstream of the injection site. 8.6-m further downstream in the PCC (Fig. 8). K atoms are detected. The result of the line fit using (2) for Rb at the kiln exit and K in the PCC is $y_0 = (Rb = 0/K = 4.0 \pm 0.1) \times 10^{13} atoms/m^3 s; A = (2970 \pm 0.1) \times 10^{13} atoms/m^3 s$ $80/444 \pm 11$ × 10^{13} atoms/m³ s; $t_c = (5.0 \pm 0.1/8.6 \pm 0.1)$ s; $\omega = (1.79 \pm 0.2/2.59 \pm 0.1)$ s; and $\tau_0 = (11.4 \pm 0.5/19.6 \pm 0.1)$ 0.6) s. It is expected that the Rb-atom concentration is higher at the exit of the kiln because of the lower O₂ concentration (3 vol. %). The broadening and shift of the time parameters is in agreement with the gas flow and flue-gas volume. The mean residence-time of the tracers is 15 s for the rotary kiln (Rb) and 26 s for the PCC and the rotary kiln combined (K). The residence-time distributions calculated from the measured data lie, as expected, in between the two idealized reactor models of a plug-flow and a perfectly stirred vessel.



FIGURE 13 Simultaneous flow-time measurements at THERESA using a binary tracer made from a mixture of K and Rb salts: the tracer mixture was injected at t = 0 over a period of 836 ms at the head of the rotary kiln (see Fig. 2). The two species were measured at two locations within the plant: Rb atoms at the end of the rotary kiln – 8.5 m from the injection site (*left peak* at t = 9 s); K atoms (peak to the *right* at t = 15 s) in the PCC – 8.6 m down-stream of the first measurement location. Since K is part of the fuel of the kiln the signal has – in contrast to Rb – an offset even without a tracer injection. Concentration distribution functions are fitted to the two traces

Conclusions

6

We propose a new method to determine the residencetime in combustion plants and high-temperature processes: using sensitive *in situ* detection of free alkali atoms (Li, K, Rb) based on direct TDLAS at their strong D lines at 670, 767, 770, and 780 nm it is possible to detect the flow of an alkali-salt tracer.

Three different diode laser types were used for in situ measurements and compared with regard to their spectroscopic capabilities: FPDLs were successfully used to detect K and Rb; however their use is hampered by the necessity to select and characterize suitable individual lasers. The efficiency of the selection was found to be only in the order of 5% for lasers suitable for the detection of the K D1 or D2 line. ECDLs, which could avoid this selection process, were also successfully used for in situ detection of Li and Rb. However, they proved to be less suitable for environments with large and rapid transmission changes because of the relatively slow mechanical wavelength tuning (100 Hz). Finally, VCSEL-based spectrometers for the in situ detection of K and O₂ were successfully realized by taking advantage of the extremely wide current-tuning range of 20 cm⁻¹. Their only drawback was a low output power, which restricts their use to applications with good to moderate transmission conditions and low background radiation.

We conducted tracer experiments at two different test facilities at the Forschungszentrum Karlsruhe, a small batch reactor and a 3-MW special waste incinerator with a rotary kiln. Various spectrometers were realized and tested: (1) a singlelaser setup for the detection of one species, which could be extended to a simultaneous detection of K and O₂, and (2) a time-multiplexed setup involving two spectrally adjacent lasers, for the quasi-simultaneous detection of multiple spectral features like the D1 and D2 lines of K or of K and Rb. And, finally, (3) a multi-path setup, using two of the previous setups simultaneously at two different sites along the flue-gas channel.

The fastest response time achieved was 0.16 s using single scans. By averaging 100 scans a response time of 2.7 s was possible. The minimum detectable absorption by averaging 100 scans corresponded to an optical density in the order of 10^{-4} . The best results were achieved using a VCSEL to detect K in the PCC, with a detection limit of 4×10^{11} atoms/m³ at 1200 K using the D2 absorption line and a 1.9-m absorption path. This is equivalent to 0.1 ng/m^3 at STP or a mixing ratio of 80 ppq (ppq = 10^{-15}). The background K concentration was measured to be between 1 ng/m^3 (800 ppq) and $1 \,\mu g/m^3$ (800 ppt). No background was observed for Rb or Li. We verified that the concentration of the alkali atoms in the flue gas depend significantly on the temperature, the oxygen concentration, and the amount of the tracer, indicating that the conditions during one residence-time measurement (typical duration 120 s) should be kept constant.

The placement of tracers in the gas stream was accomplished in different ways: addition of solid alkali salts or aqueous solutions thereof in polyethylene bottles to the solid fuel leads to complicated adsorption effects and long decay times. Using a water-cooled lance to inject small amounts of tracer solutions into the process stream ensured a much better control of the injection timing and completely avoided the adsorption effects of the solid-fuel dosage port. As an example, we presented the simultaneous measurement of Rb at the exit of the kiln and K in the PCC, from which mean residencetimes could be extracted.

ACKNOWLEDGEMENTS Funding by the Land Baden-Württemberg is acknowledged. The assistance of the staff at the Institute of Technical Chemistry, Forschungszentrum Karlsruhe, especially Dr.H. Dittrich, and Mr.R. Siegel is greatly appreciated.

REFERENCES

- 1 R. Seeliger: 'Konvergenz oder Divergenz? Sonderabfallpolitik in Deutschland, Kanada und den USA, 1970 bis 1996'. Dissertation, Eberhard-Karls-Universität, Tübingen, 2001 [in German]
- 2 V. Ebert, T. Fernholz, C. Giesemann, H. Pitz, H. Teichert, J. Wolfrum, H. Jaritz: J. Proc. Combust. Inst. 28, 423 (2000)
- 3 H. Teichert, T. Fernholz, V. Ebert: In: Laser Applications to Chemical and Environmental Analysis (OSA Trends Opt. Photon. (TOPS) 64, OSA Tech. Dig., Post-Conf. Edn.) (Optical Society of America, Washington DC 2002) ThB3-1
- 4 T. Fernholz, H. Pitz, V. Ebert: In: Laser Applications to Chemical and Environmental Analysis (OSA Tech. Dig.) (Optical Society of America, Washington DC 2000) pp. 77-79
- 5 J. Wolfrum, T. Dreier, V. Ebert, C. Schulz: 'Laser-based Combustion Diagnostics'. In: Encyclopedia of Analytical Chemistry, ed. by R.A. Meyers (Wiley, Chichester 2000) pp. 2118-2148
- 6 E. Schlosser, T. Fernholz, H. Teichert, V. Ebert: Spectrochim. Acta 58, 2347 (2002)
- 7 P. Vogel, V. Ebert: Appl. Phys. B 72, 127 (2001)
- 8 J.R. Sacher, D. Baums, P. Panknin, W. Elsässer, E.O. Göbel: Phys. Rev. A 45, 1893 (1992)
- 9 W. Demtröder: Laser Spectroscopy, 2nd edn. (Springer, Berlin 1996); or Laserspektroskopie, 4. Aufl. (Springer, Berlin 2000)
- 10 T.W. Hänsch: Appl. Opt. 11, 895 (1972)
- 11 K.B. MacAdam, A. Steinbach, C. Wieman: Am. J. Phys. 60, 1098 (1992)
- M.G. Littman, H.J. Metcalf: Appl. Opt. **17**, 2224 (1978)
 C.E. Wieman, L. Hollberg: Rev. Sci. Instrum. **62**, 1 (1991)

- 14 H. Tabichi, H. Ishikawa: Electron, Lett. 26, 742 (1990)
- 15 L. Hildebrandt, R. Knispel, J. Sacher: Tech. Mess. 68, 374 (2001) [in Germanl
- 16 S.T. Sanders, J. Wang, J.B. Jeffries, R.K. Hanson: Appl. Opt. 40, 4404 (2001)
- 17 J. Wang, S.T. Sanders, J.B. Jeffries, R.K. Hanson: Appl. Phys. B 72, 127 (2001)
- 18 C. Affolderbach, A. Nagel, S. Knappe, C. Jung, D. Wiedenmann, R. Wynands: Appl. Phys. B 70, 407 (2000)
- 19 K.J. Ritter, T.D. Wilkerson: J. Mol. Spectrosc. 121, 1 (1997)
- 20 L.S. Rothman, R.R. Gamache, R.H. Tipping, C.P. Rinsland, M.A.H. Smith, D.C. Benner, V.M. Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S.T. Massie, L.R. Brown, R.A. Toth: J. Quant. Spectrosc. Radiat. Transfer 48, 469 (1992)
- 21 E. Schlosser, T. Fernholz, H. Pitz, W. Christmann, V. Ebert: 'High Temperature In-situ-Detection of Atomic Potassium with NIR-Diode Lasers'. In: Proc. 10th Int. IUPAC Conf. High Temp. Mater. Chem., Forschungszentrum Jülich, Germany, 10–14 April 2000; Reihe Energietechnik/Energy Technology, Vol. 15, Part I (Schriften des Forschungszentrums Jülich, 2000) pp. 27-30 [ISSN 1433-5522]
- 22 E. Schlosser, T. Fernholz, H. Teichert, V. Ebert, J. Wolfrum, W. Christmann, D. Hourfar: 'Hochtemperatur-In-situ-Nachweis gasförmiger Spezies am Beispiel von atomarem Kalium'. In: K. Hannes (Eds.): Proc. 2. Druckflamm-Statusseminars "Entwicklung eines kohlegefeuerten Gas- und Dampfturbinenprozesses mit Flüssigascheabscheidung", Aachen, 2000, pp. 210-215 [in German]
- F. Schumacher, H. Meichelböck, A. Merz, H. Vogg: 'Entwicklung 23 und Inbetriebnahme eines Laborofens zum Studium der Verbrennung von Reststoffen auf Rostsystemen'. In: GVC Symp. Abfallwirtsch., Würzburg, 1994 [in German]
- 24 H. Dittrich, L. Malcher, H. Seifert: VDI Ber. 1629, 397 (2001) [in German]
- 25 D.R. Lide (ed.): CRC Handbook of Chemistry and Physics (CRC, Boca Raton, FL 1999) CD-ROM
- 26 A.A. Radzig, B.M. Smirnov: Reference Data on Atoms, Molecules, and Ions (Springer, Heidelberg 1985)
- 27 M.G. Allen: Meas. Sci. Technol. 9, 545 (1998)
- 28 S.T. Sanders, J.A. Baldwin, T.P. Jenkins, D.S. Baer, R.K. Hanson: J. Proc. Combust. Inst. 28, 587 (2000)
- 29 D.B. Oh, M.E. Paige, D.S. Bomse: Appl. Opt. 37, 2499 (1998)