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Published in:
Applied Spectroscopy

DOI:
[10.1177/0003702818763819](https://doi.org/10.1177/0003702818763819)

2018

[Link to publication](#)

Citation for published version (APA):
Weng, W., Leffler, T., Brackmann, C., Aldén, M., & Li, Z. (2018). Spectrally Resolved UV Absorption Cross-Sections of Alkali Hydroxides and Chlorides Measured in Hot Flue Gases. *Applied Spectroscopy*, 72(9), 1388-1395. <https://doi.org/10.1177/0003702818763819>

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Title page:

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This is the peer reviewed version of the following article: [W. Weng, T. Leffler, C. Brackmann, M. Aldén, Z.S. Li, 'Spectrally resolved UV absorption cross-sections of alkali hydroxides and chlorides measured in hot flue gases', **Applied Spectroscopy** **72**, 1388-1395 (2018).], which has been published in final form at: <https://doi.org/10.1177/0003702818763819>

Spectrally Resolved UV Absorption Cross-sections of Alkali Hydroxides and Chlorides Measured in Hot Flue Gases

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Abstract Spectrally resolved ultraviolet (UV) absorption cross-sections of gas-phase sodium chloride (NaCl), potassium hydroxide (KOH) and sodium hydroxide (NaOH) were measured, for the first time, in hot flue gases at different temperatures. Homogenous gas-phase NaCl, KCl (potassium chloride), NaOH and KOH at temperatures 1200 K, 1400 K, 1600 K and 1850 K were prepared in the post-flame zone of laminar flames by seeding nebulized droplets out of aqueous solution of corresponding alkali species. The amount of droplets seeded into the flame was kept constant, so the relative concentration of different alkali species can be derived. The broadband UV absorption cross section of KCl vapor reported by Leffler et al. (Rev. Sci. Instr. 88, 023112, 2017) was adopted to derive the absorption cross-section curves of NaCl, NaOH and KOH with the corresponding measured spectrally resolved absorbance spectra. No significant changes in the spectral structures in the absorption cross-sections were found as the temperature varied between 1200 K and 1850 K, except for NaOH at around 320 nm. The difference between the absorption spectral curves of alkali chlorides and hydroxides is significant at wavelengths above 300 nm, which thus can be used to distinguish and obtain the concentrations of alkali chlorides and hydroxides in the broad band UV absorption measurements.

Key words: alkali chlorides; alkali hydroxides; absorption cross-section; laminar flame; UV absorption spectroscopy

1. Introduction

Alkali species, mainly alkali chlorides can cause severe problems, e.g. corrosion, slagging and fouling in boilers when combusting biomass fuels¹⁻³ and coals.^{4, 5} The release of alkali species from burning biomass and coal has been widely studied using different optical measurement techniques, such as planar laser-induced fluorescence,^{6, 7} laser-induced breakdown spectroscopy,⁸⁻¹¹ excimer laser-induced fragmentation,¹² photofragmentation and atomic absorption spectroscopy,¹³ tunable diode laser absorption spectroscopy^{14, 15} and spontaneous emission.¹⁶ All these techniques have mainly been applied in lab-scale measurements, and the determinations of the concentrations of alkali species in large-scale boilers and furnaces¹⁷⁻¹⁹ are still a challenge. Ultraviolet (UV) differential optical absorption spectroscopy (DOAS) can be a reliable and practical method for alkali-chloride (KCl and NaCl) monitoring in boilers.²⁰ Quantitative measurements, however, require accurate and precise UV absorption cross-section data obtained at well-defined conditions.²¹ This data is also required for other online measurements techniques, such as laser-induced photofragmentation spectroscopy²² and differential absorption LIDAR.²³ Previous works have targeted on the measurements of UV absorption cross-section of alkali chlorides. Davidovits et al.²⁴ have measured the UV absorption cross-section for gas-phase alkali halides in the wavelength range between 200 nm and 400 nm. Forsberg et al.²⁰ obtained the UV absorption cross-section of KCl and NaCl at a temperature of 1133 K using an open calibration cell. In addition, Daminelli et al.²⁵ have investigated the spectral shape of different alkali halides. Related to the UV absorption spectra, photolysis cross-section spectra of alkali chlorides have also been investigated.¹³ Recently, a more reliable measurement of the spectrally resolved UV absorption cross-sections of KCl at temperatures between 973 K and 1073 K was reported

by Leffler et al.²¹ In their work, a novel quartz calibration cell was developed, which was characterized by a closed design with accurate control of the temperature homogeneity to ensure well-defined and reproducible alkali vapor pressure. The cell was made with a relatively large diameter to avoid wall effects. The absorption path length was determined by the requirement of temperature homogeneity and the desire to make it as long as possible to enhance absorption sensitivity.

During combustion of biomass fuels, alkali species can be released both as chlorides and hydroxides, depending on the ratio of alkali and chlorine in the fuel, the combustion temperature, and the fuel-oxidizer ratio.²⁶ Alkali chlorides can be transformed into alkali hydroxides at high temperatures, e.g. >1000 K.²⁷ The UV absorption cross-sections of alkali hydroxides are rarely available or in the case of KOH absent,¹³ which hinders accurate quantitative measurement of these compounds. In addition, this limits the accurate measurements of alkali chlorides due to the fact that there is substantial spectral overlap between alkali chlorides and alkali hydroxides. Therefore, the insufficient knowledge of the hydroxide cross-sections makes it difficult to assess the relative contribution of chlorides and hydroxides from the UV absorption spectrum. Obtaining accurate spectrally resolved absorption cross-sections for alkali hydroxides is thus crucial in UV absorption measurements.²⁸ Compared with alkali chlorides, alkali hydroxides melt at a lower temperature and the vapor pressures for solid-gas equilibrium are lower than for chlorides. The typical temperatures needed for calibration in the previously mentioned cell are therefore much higher than the melting points: 591 K for NaOH and 679 K for KOH,²¹ which presents a challenge for the quartz cell, since the hydroxides are very reactive in liquid phase. The only report on absorption measurement of alkali hydroxide at high temperature was conducted in a flame with seeding of NaOH by

Daidoji²⁹ (Self and Plane³⁰ have measured the photolysis cross-section of NaOH at 300 K). Its cross-section was calculated by Rowland et al. with an uncertainty of $\pm 25\%$.³¹ No report for UV absorption cross-section of KOH has been found in literatures so far. Sorvajärvi et al.¹³ have obtained the photolysis spectral structure of KOH qualitatively, and the cross-section of NaOH was adopted to estimate the concentration of KOH. Hence, accurately determined UV absorption cross-sections for NaOH and KOH are necessary for quantitative measurements of alkali hydroxides.

In the present work, laminar flames from a specially designed burner were used to prepare NaCl, KCl, NaOH and KOH in the hot flue gases with known temperature and concentrations. The absorption cross-sections were determined for NaCl, KOH and NaOH in the hot flue gas at temperatures ~ 1400 K. Their absolute cross-section values were calibrated based on the results for KCl reported by Leffler et al.²¹ In addition, the temperature dependence of the absorption spectra was investigated between 1200 K and 1850 K.

2. Measurement object and setup

A hot flue gas environment was simulated using a laminar flame burner, which has been described in detail in a previous work³² and only a brief description is given here. The burner is composed of two plenum chambers, a jet-flow chamber and a co-flow chamber. There are 181 jet tubes connected to the jet-flow chamber to form an array of laminar conical flames. The burned gas from these conical flames is mixed with the gas from the co-flow chamber to provide a hot gas environment with a well-controlled and evenly-distributed temperature above the burner³². The size of the outlet of the burner is $110 \text{ mm} \times 60 \text{ mm}$. A flame stabilizer was installed 35 mm above the burner (Fig. 1a) to

maintain a stable flow field. In this study, six flame cases (detailed parameters shown in Table 1) were used to produce hot flue gas environments at temperatures 1200, 1400, 1600 and 1850 K.

Table 1. Conditions of the premixed flames used in this work.

Case	Equivalence ratio (Φ)	Jet-flow composition (l/min)				Co-flow composition (l/min)	Hot flue gas composition (%)				Temperature (K)
		CH ₄	H ₂	O ₂	N ₂		N ₂	CO ₂	H ₂ O	O ₂	
Flame 1	0.7	0.66	3.74	4.55	22.54	9.90	1.67	12.80	3.44	82.09	1400
Flame 2	0.7	1.83	1.83	6.52	21.31	9.90	4.52	13.54	4.84	77.12	1600
Flame 3	0.7	1.80	0	5.15	13.30	9.90	5.97	11.94	5.14	76.95	1600
Flame 4	0.9	2.26	0	5.02	12.97	9.90	7.50	14.99	1.66	75.85	1850
Flame 5	0.7	0	3.97	2.84	13.33	13.20	0	12.66	2.74	84.60	1200
Flame 6	1.6	0	5.96	1.86	12.30	13.20	-	-	-	-	1200

Aerosols of aqueous solution of KCl, NaCl, K₂CO₃ and Na₂CO₃ were generated by a fog generator and seeded into the jet-flow chamber by an N₂ flow. Gas-phase KCl, NaCl, KOH and NaOH were distributed homogeneously in the hot gas environment of the post-flame zone (see a photo shown in Fig. 1a). The seeded K₂CO₃ and Na₂CO₃ decompose and transform into KOH and NaOH in the hot flue gases to avoid using corrosive alkali hydroxide solutions directly. The concentration of aqueous solutions of KCl and NaCl was kept at 1.0 mol/l, while that of K₂CO₃ and Na₂CO₃ was kept at 0.5 mol/l to maintain equal amounts of alkali elements seeded into the hot gas environment for each investigated alkali seeding.

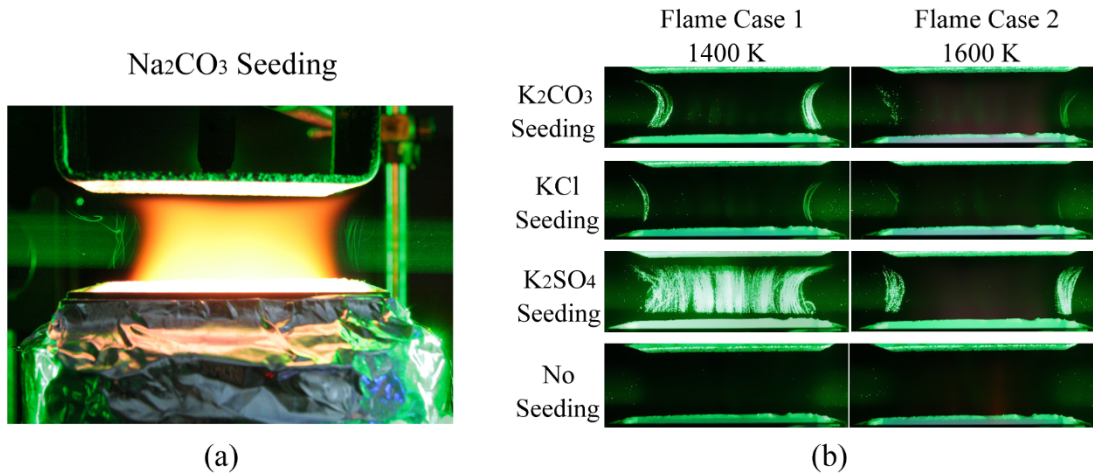


Figure 1. (a) Photo of the chemiluminescence of the hot flue gas above the burner with Na_2CO_3 seeding (side view); (b) photos of Mie/Rayleigh scattering from the post-flame zone, illuminated by a green Nd:YAG laser beam (532 nm), above the burner with different seeding species in different hot gas environments (side view).

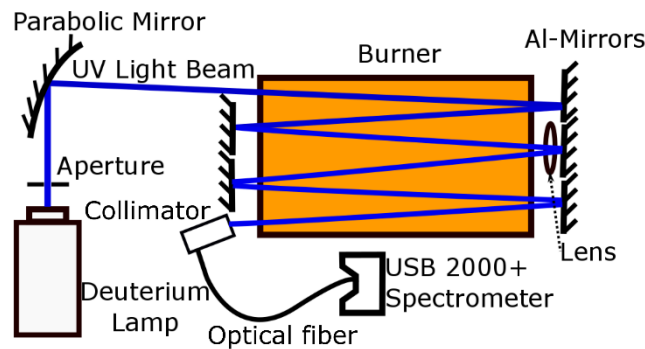


Figure 2. A schematic of the UV absorption setup for measurement in hot flue gas above the burner (top view).

A schematic of the UV absorption setup is shown in Fig. 2. The UV light was generated by a deuterium lamp and passed through the hot flue gas containing gas-phase KCl, NaCl, KOH or NaOH to measure the absorption spectra. The light was kept at the same height (~ 2 mm) above the burner. Five UV enhanced aluminum mirrors were used to increase the absorption path length to 0.57 m. The transmitted UV light was finally analyzed by a USB 2000+ spectrometer (Ocean Optics) with a resolution of 0.3 nm/pixel.

The spectrally resolved absorbance spectra of the hot gas with different seeding were analyzed using the Beer-Lambert law.

$$\text{Absorbance}(\lambda) = -\ln\left(\frac{I_s(\lambda)}{I_0(\lambda)}\right) = N_A\sigma_A(\lambda)L \quad (1)$$

where λ indicates the wavelength in units of nm, $I_0(\lambda)$ and $I_s(\lambda)$ are the intensity of the UV light source and UV light after the hot gas with seeding, respectively. N_A is the number density of the alkali species in the hot gas, σ_A is the absorption cross-section of alkali species, and L is the absorption path length. Since the flames have significant effect on the UV light propagation direction, the UV light after the hot gas without seeding was adopted as the light source intensity in Equation (1). For each measurement, the data were collected and averaged for ~2 minutes. Nine measurements were performed for each case and a standard deviation of ~10% of the absorption peak value was obtained for those absorption peaks (as shown in Fig. 3a). The deviation is mainly attributed to the instability of the seeding system and the UV lamp.

3. Results and discussion

To obtain absorption cross-sections of NaCl, NaOH and KOH, the following strategies were adopted: vapors of NaCl, NaOH, KCl and KOH were prepared in the homogenous hot gas environments at known concentration; spectrally resolved absorbance spectra of corresponding species were obtained through UV absorption measurements; the cross-sections of NaCl, NaOH and KOH were derived using the known cross-sections of KCl from Leffler et al.²¹ with using the Beer-Lambert law. To achieve this, the following preconditions should be fulfilled:

- (a). The effect of temperature on the cross-sections of KCl should be small, which is supported by the finding of Leffler et al.²¹ for temperature up to 1073 K.
- (b). The same amount of alkali elements should be introduced into the flue gas regardless of the seeding of different alkali species.
- (c). Alkali species are completely vaporized in the flame at the investigated region.
- (d). KCl (NaCl) and KOH (NaOH) are the only form of alkali species in the hot flue gas.

Alkali species were found to be completely vaporized as the flue gas has a temperature above 1400 K. A 532 nm laser beam from the second harmonic of a Nd:YAG laser (Brilliant B, Quantel) was used to detect Mie scattering from aerosol particles that were not vaporized after the flame. The laser beam was shaped into a vertical laser sheet passing through the hot gas region as shown in Fig. 1b. Outside the hot flow, one can see the Rayleigh and Mie scattering from ambient air and aerosols in the lab atmosphere. No Mie scattering was observed in the center of the hot gas at 1600 K (cf. Fig. 1b), which indicates that the salt particles were fully vaporized. Some Mie scattering appeared at the cooler edge regions of the hot flow due to the condensation of salt vapor. Once the temperature was reduced to 1400 K, some scattering started to appear with the seeding of K_2SO_4 . Scattering from the cases with KCl and K_2CO_3 seeding appeared negligible. Therefore, the quantitative measurements were only made in the hot gas environment with temperatures above 1400 K to assure the fully vaporized of the seeded alkali species to meet precondition (c). For the case at 1200 K, the weak flame with low temperature could not quickly vaporize the alkali species from the nebulized droplets and some aerosol particles were observed in the flue gas. At 1200 K only the shape of the absorption spectrum was used to compare with the results from the cases with higher temperatures

and with the results from previous work obtained at low temperatures ($\sim 1200\text{K}$)^{21, 24} to verify any potential temperature dependence of the spectral shape of the absorption spectra.

To check preconditions (b) and (d), absorption measurements in the flue gases of flame 3 (1600 K) were performed with seeding of NaOH/Na₂CO₃/K₂CO₃. Typical absorption spectral curves are shown in Fig. 3a. The spectra obtained for the seeding with Na₂CO₃ show perfect overlap with the spectra obtained for the seeding with NaOH, which indicates that alkali carbonates decompose and the same amount of alkali hydroxides are formed in the hot flue gases (precondition (d)). It is also proved that the same amount of alkali elements can be introduced into the flue gas regardless of the seeding of different alkali species (precondition (b)).

The absorbance spectrum of NaOH obtained in the present study was compared to the one obtained by Rowland et al.³¹ as shown in Fig. 3a. Both have two main peaks at around 230 nm and 320 nm, but the intensity difference between these two peaks is smaller in the present work than in the results from Rowland et al.,³¹ which might be attributed to the different measurement temperature. Similarly, the absorption spectrum of KOH can be obtained with seeding of K₂CO₃. Comparing the absorption spectra from NaOH and KOH, differences are observed both in intensity and structure. For KOH, the two absorption peaks occurred at 244 nm and 327 nm and its absorbance was almost the half that of NaOH.

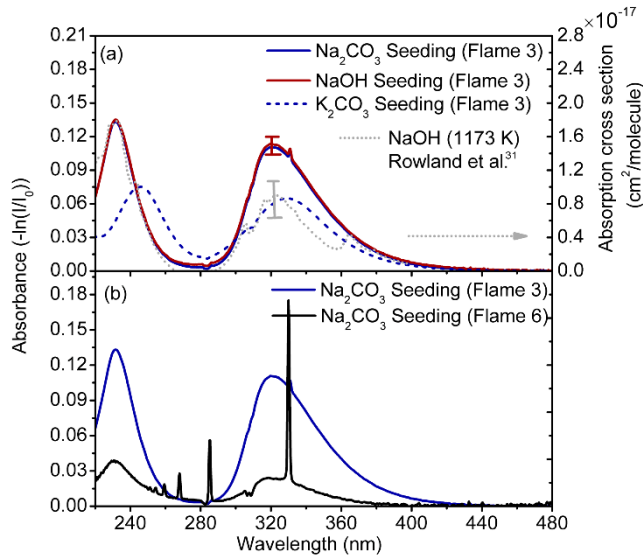


Figure 3. (a) Absorbance spectra measured in the hot flue gases of flame 3 seeded with Na_2CO_3 , NaOH and K_2CO_3 compared with the absorption cross-section curve of NaOH from Rowland et al.;³¹ (b) Absorbance spectra for Na_2CO_3 seeding in the hot flue gas of flame 3 and flame 6 to verify the influence of different flame conditions. (For interpretation of the references to color in the figure legend, the reader is referred to the web version of this article.)

The chemical reactions between the gas-phase alkali species and the hot flue gas should be considered regarding precondition (d). When alkali chlorides and alkali carbonates are seeded into the hot flue gas, alkali species are mainly in the form of alkali chlorides, alkali hydroxides and alkali atoms according to chemical reaction simulation using a mechanism containing alkali species.³³ High temperature and rich flame conditions can increase the percentage of alkali atoms.²⁶ For the fuel-lean conditions investigated in the present work ($\Phi=0.9$ and $\Phi=0.7$) the percentage of alkali atoms of the total alkali species is less than 1%, which can be neglected considering the measurement uncertainty. For the rich flame ($\Phi=1.6$), as shown in Fig. 3 (b), a larger amount of sodium atoms were produced in the hot flue gas and strong atomic absorption lines were observed at wavelengths 330 nm, 285 nm, 268 nm, 259 nm and 254 nm. For the lean condition, even though the number of atoms is small, there is still some interference from the absorption of alkali atoms on the spectra of alkali chlorides and alkali hydroxides at

wavelength 405 nm for potassium and 330 nm for sodium (Fig. 4 (a) and (c)). This is because the absorption cross-section of alkali atoms is about three orders of magnitude greater than those of alkali chlorides and hydroxides.

Fig. 4 (a) and (c) present absorbance spectra obtained in the hot flue gas from flame 1 with K_2CO_3 , KCl, Na_2CO_3 and NaCl seeding. Besides the broad-band absorption of alkali chloride and alkali hydroxide and the atomic absorption mentioned above, some dips on the spectrum near 283 nm and 310 nm were observed, which was induced by the change in concentration of OH with alkali species seeding. The dips mean that the consumption of OH radicals was enhanced by the seeded sodium and potassium³⁴ in the hot flame. Fortunately, the absorption spectrum of OH radical is restricted to small wavelength regions near 310 nm and 280 nm, and the interference to the broad-band spectra of alkali species can be removed.

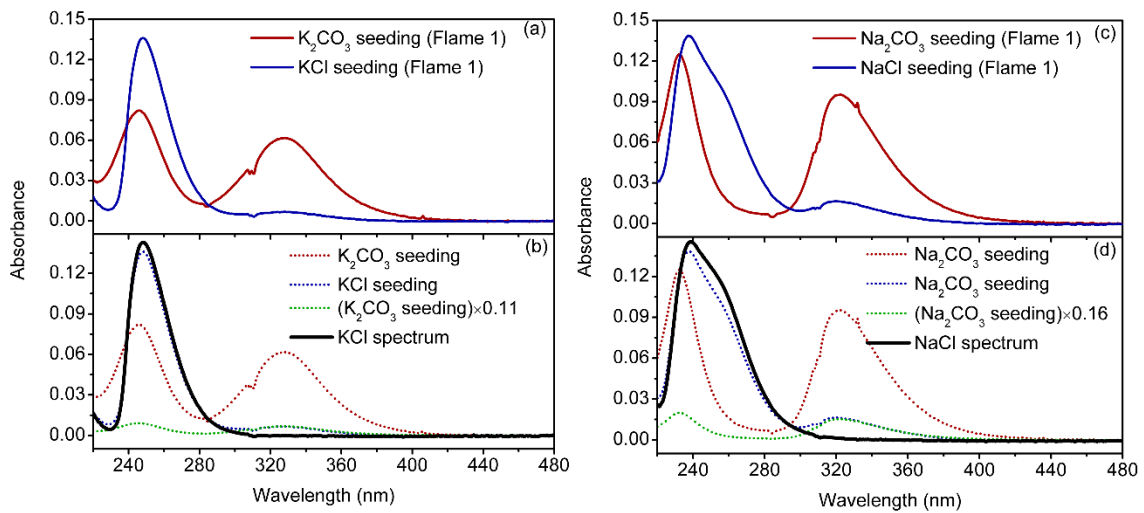


Figure 4. Absorbance spectra in the hot flue gas from flame 1 with K_2CO_3 and KCl seeding (a) and Na_2CO_3 and NaCl seeding (c); curves representing the process to get the pure KCl spectrum in case of all the seeded K elements exist as KCl (b) and the pure NaCl spectrum (d) through excluding the influence from absorption of KOH and NaOH: $A_{Cl \text{ spectrum}} = (A_{Cl \text{ seeding}} - A_{2CO_3 \text{ seeding}} \times Ratio) / (1 - Ratio)$. Pure KOH and NaOH spectrum in (a) and (c) with K_2CO_3 and Na_2CO_3 seeding referring to precondition (d). (For interpretation of the references to color in the figure legend, the reader is referred to the web version of this article.)

As shown in Fig. 4 (a) and (c), the absorbance spectral curves are quite different for seeding with alkali chlorides (ACl) and alkali carbonates (A_2CO_3). Alkali hydroxides (AOH) are produced when ACl are injected into the flame, and more AOH can be formed in an environment with higher temperature according to chemical reaction simulation³³. To separate spectral contributions from chlorides and hydroxides, some data processing was conducted, using the following equations to obtain the absorption spectra of KCl, KOH, NaCl and NaOH. Here, the seeded alkali elements are all converted to AOH in case of A_2CO_3 seeding, and AOH and ACl in case of ACl seeding, while the total amount of the seeded alkali elements is the same, described as precondition (b).

$$Absorbance_{A_2CO_3}(\lambda) = N_{AOH}\sigma_{AOH}(\lambda)L \quad (2)$$

$$Absorbance_{ACl}(\lambda) = (N_{ACl}\sigma_{ACl}(\lambda) + N'_{AOH}\sigma_{AOH}(\lambda))L \quad (3)$$

$$N_{total} = N_{ACl} + N'_{AOH} = N_{AOH} \quad (4)$$

$$Ratio = N'_{AOH}/N_{total} \quad (5)$$

$$Absorbance_{ACl}(\lambda) - Absorbance_{A_2CO_3}(\lambda) \times Ratio = (1 - Ratio) \times N_{total}\sigma_{ACl}(\lambda)L \quad (6)$$

$Absorbance_{A_2CO_3}$ and $Absorbance_{ACl}$ are the absorbance of the hot gas with seeding of alkali carbonates and alkali chlorides, respectively, while σ_{ACl} and σ_{AOH} are the absorption cross-section of alkali chlorides and alkali hydroxides, respectively. N_{total} is the total number density of the alkali species while N_{ACl} and N'_{AOH} are the number densities of alkali chlorides and alkali hydroxides in the hot gas with seeding of alkali chlorides. N_{AOH} is the number density of alkali hydroxides in the hot gas with seeding of

alkali carbonates and *Ratio* is the percentage of alkali chlorides that were transformed into alkali hydroxides in the hot gas.

The absorbance resulting from the seeding of alkali chlorides includes the absorbance of alkali chlorides and hydroxides as expressed in Equation (3) and shown in Fig. 4 (a) and (c). The absorbance with the seeding of alkali carbonates is expressed in Equation (2), which comes from the absorbance of alkali hydroxides as shown in Fig. 4 (a) and (c). It is necessary to separate the contributions of ACl and AOH to obtain the correct spectra of KCl and NaCl. It was observed that there was no absorption at wavelengths between 320 nm and 400 nm for both KCl and NaCl according to cross-section measurements of KCl and NaCl from previous research^{20, 21, 24} and also shown in Fig 5a. Hence, for the cases with seeding of ACl, the absorption at wavelengths above 320 nm in Fig. 4 (a) and (c) is attributed to AOH. The *Ratio* can then be obtained when the right-hand side of Equation (6) is set to zero, i.e. $\sigma_{ACl} = 0$, as the wavelength is over 320 nm. The *Ratio* for the cases (flame 1) with seeding of KCl and NaCl is 12% and 16%, respectively. As the *Ratio* is known, the product $N_{total}\sigma_{ACl}L$ was obtained, and pure KCl and NaCl spectra could be obtained as shown in Fig. 4 (b) and (d). Thereby, the spectrally resolved absorbance spectra of NaCl, KCl, NaOH and KOH with the same absorption path length and species concentration were obtained, as shown in Fig. 4. Using the known cross-sections of KCl, the cross-sections of the other three can be derived.

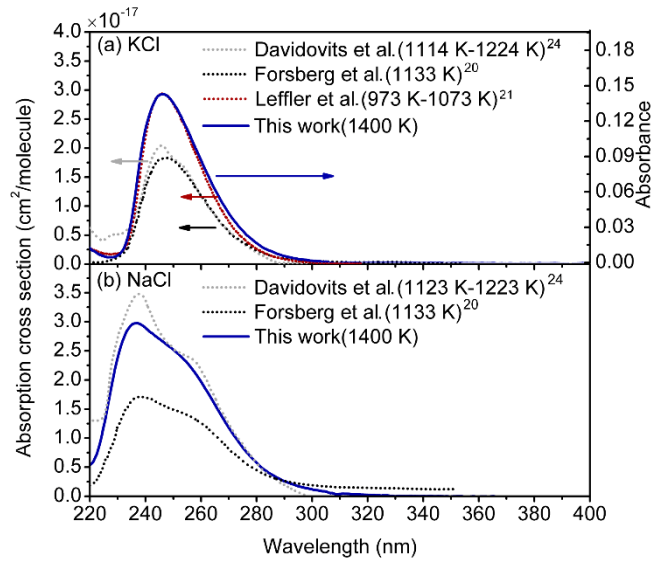


Figure 5. Comparison of the spectrally resolved absorbance spectra of KCl obtained in the present measurement with previous absorption cross-section curves^{20, 21, 24} (a), and comparison of the absorption cross-section curve of NaCl derived in this study with previous results^{20, 24} (b). (For interpretation of the references to color in the figure legend, the reader is referred to the web version of this article.)

The KCl absorption data performed between 973K and 1073 K reported by Leffler et al.²¹ was used here to quantify the absorption cross-section values. One should notice that the present measurements were performed at 1400 K. However, the effect of temperature on the cross-section of KCl is reported to be small.²¹ As shown in Fig. 5 (a), the spectra of KCl obtained in the present work in the hot flue gas overlap well with the one from Leffler et al. measured in the sealed quartz cell. The concentration of the alkali species in the hot gas of flame 1 was calculated to 15 ppm. The cross-sections for NaCl, KOH, and NaOH can then be obtained with the corresponding absorbance spectra of pure NaCl, KOH and NaOH in Fig. 4. The cross-sections of NaCl obtained in the present work are shown in Fig. 5 (b) together with the results from the previous studies.^{20, 24} All the spectra present similar shapes. The cross-sections obtained in the present study are closer to the results from Davidovits et al.²⁴ than those from Forsberg et al.²⁰ The KCl absorption

cross-section (1400 K) for wavelength $\lambda = 246.2$ nm was 2.9×10^{-17} cm²/molecule referring to the results of KCl reported by Leffler et al.²¹ The NaCl absorption cross-section (1400 K) for wavelength $\lambda = 237.1$ nm was found to be 3.0×10^{-17} cm²/molecule.

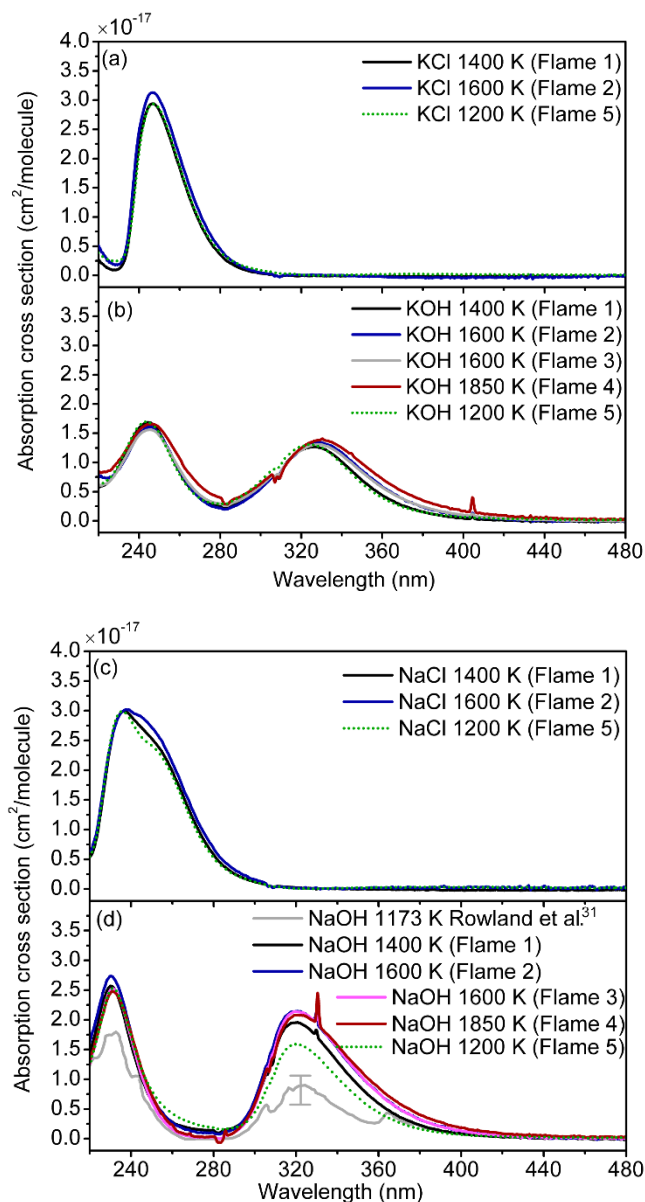


Figure 6. The absorption cross-sections of KCl (a), KOH (b), NaCl (c) and NaOH (d) at different temperatures. For cases at 1200K, only the shape of the absorption spectrum was valuable. (For interpretation of the references to color in the figure legend, the reader is referred to the web version of this article.)

The absorption cross-sections of alkali chlorides and hydroxides obtained at different temperatures for different flame cases are summarized in Fig. 6. The data can be found in Supplementary Material. The absolute uncertainty for the cross-sections at 1400 K can mainly be originated from their small temperature dependence since the referring data from Leffler et al.²¹ was performed between 973K and 1073 K. For the cross-sections at temperature of 1600 K and 1850 K, the absolute uncertainty can also come from the temperature measurement of the flue gas and the gas flow control system for the burner. The uncertainty of the temperature measurement is around 50 K, which can induce ~5% of uncertainty in cross-sections calculation. The uncertainty from the gas flow control was estimated to be ~2.5% with the mass flow controllers with an accuracy of $\pm 0.8\%$ of the reading value plus $\pm 0.2\%$ of the full scale value. The total error was estimated to be ~7.5%.

When the temperature for KCl and NaCl was changed from 1400 K to 1600 K, the change of their cross-section is small, which is within the measurement deviation and the estimated absolute uncertainty. The shape of the spectra also shows to be independent of temperature between 1200 K and 1600 K, except for a small change in the spectra of NaCl at wavelengths around 250 nm. The KOH absorption cross-section (1400 K) for wavelengths $\lambda = 244.3$ nm and $\lambda = 327.3$ nm was 1.7×10^{-17} cm²/molecule and 1.3×10^{-17} cm²/molecule, respectively. For NaOH the absorption cross-sections (1400 K) for wavelengths $\lambda = 230.0$ nm and $\lambda = 320.6$ nm were 2.6×10^{-17} cm²/molecule and 2.0×10^{-17} cm²/molecule, respectively. The change of the hydroxide absorption cross-sections is not significant with varying temperature from 1400 K to 1850 K, except for NaOH at around 320 nm, where the absorption can be temperature-sensitive since the absorption of vibrationally excited NaOH starts to appear.³⁰ As a comparison, the absorption cross-

sections of NaOH at 1173 K estimated by Rowland et al.³¹ based on the experimental data from Daidoji²⁹ are also presented in Fig. 6 (d). The spectrum has a similar structure to the one from the present study, but with different values. The difference is acceptable considering the uncertainty of $\pm 25\%$ estimated by Rowland et al.³¹ and the temperature effect caused by hot-band absorption.³⁰ If comparing the spectrum of AlCl with that of AOH, however, the difference is significant, especially for the absorption band at around 330 nm. This difference can be used in the distinction of KCl/NaCl from KOH/NaOH, especially when they co-exist in hot environments.

4. Conclusion

Gas-phase KCl, NaCl, KOH and NaOH at temperatures between 1400 K and 1850 K were prepared in laminar flames with known amounts through seeding fogs of water solution of different alkali salts. The concentration of KCl was obtained using the absorption cross-section measured in a previous work.²¹ Consequently, the spectrally resolved UV absorption cross-sections of NaCl, KOH and NaOH were obtained, using direct absorption spectroscopy in the present work. In agreement with previous observation, the dependence of the absorption cross-sections on the temperature was found to be weak. There are significant differences between the absorption cross-sections of alkali chlorides and alkali hydroxides, especially in the wavelength region between 300 nm and 400 nm, where a strong absorption band exists for alkali hydroxides, while alkali chlorides show no absorption. This can be used in the distinction of alkali chlorides and alkali hydroxides in concentration measurements with broadband UV absorption spectroscopy.

Supplementary material

See supplementary material for the data of the UV absorption cross-sections of KCl, KOH, NaCl and NaOH from 220 nm to 480 nm at temperature of 1400 K, 1600 K and 1850 K, including the interference from the absorption of OH radical, Na and K atom.

Acknowledgements:

The work was financially supported by the Swedish Energy Agency, the Knut & Alice Wallenberg foundation, the Swedish Research Council (VR), the European Research Council (Advanced Grant TUCLA program) and the Danish Council for Strategic Research (the GREEN project).

References:

1. H.P. Nielsen, F.J. Frandsen, K. Dam-Johansen, L.L. Baxter. "The implications of chlorine-associated corrosion on the operation of biomass-fired boilers". *Prog. Energy Combust. Sci.* 2000. 26(3): 283-298.
2. F. Jappe Frandsen. "Utilizing biomass and waste for power production—a decade of contributing to the understanding, interpretation and analysis of deposits and corrosion products". *Fuel.* 2005. 84(10): 1277-1294.
3. L.A. Hansen, H.P. Nielsen, F.J. Frandsen, K. Dam-Johansen, S. Hørlyck, A. Karlsson. "Influence of deposit formation on corrosion at a straw-fired boiler". *Fuel Process. Technol.* 2000. 64(1): 189-209.
4. G. Li, C.a. Wang, Y. Yan, X. Jin, Y. Liu, D. Che. "Release and transformation of sodium during combustion of Zhundong coals". *J. Energy Inst.* 2016. 89(1): 48-56.
5. X. Wang, Z. Xu, B. Wei, L. Zhang, H. Tan, T. Yang, H. Mikulčić, N. Duić. "The ash deposition mechanism in boilers burning Zhundong coal with high contents of sodium and calcium: A study from ash evaporating to condensing". *Appl. Therm. Eng.* 2015. 80: 150-159.
6. P.J. van Eyk, P.J. Ashman, Z.T. Alwahabi, G.J. Nathan. "Quantitative measurement of atomic sodium in the plume of a single burning coal particle". *Combust. Flame.* 2008. 155(3): 529-537.
7. Z. Wang, Y. Liu, R. Whiddon, K. Wan, Y. He, J. Xia, K. Cen. "Measurement of atomic sodium release during pyrolysis and combustion of sodium-enriched Zhundong coal pellet". *Combust. Flame.* 2017. 176: 429-438.

8. L. Hsu, Z.T. Alwahabi, G.J. Nathan, Y. Li, Z.S. Li, M. Aldén. "Sodium and Potassium Released from Burning Particles of Brown Coal and Pine Wood in a Laminar Premixed Methane Flame Using Quantitative Laser-Induced Breakdown Spectroscopy". *Appl. Spectrosc.* 2011. 65(6): 684-691.
9. Y. He, J. Zhu, B. Li, Z. Wang, Z. Li, M. Aldén, K. Cen. "In-situ Measurement of Sodium and Potassium Release during Oxy-Fuel Combustion of Lignite using Laser-Induced Breakdown Spectroscopy: Effects of O₂ and CO₂ Concentration". *Energy Fuels.* 2013. 27(2): 1123-1130.
10. H. Fatehi, Y. He, Z. Wang, Z.S. Li, X.S. Bai, M. Aldén, K.F. Cen. "LIBS measurements and numerical studies of potassium release during biomass gasification". *Proc. Combust. Inst.* 2015. 35(2): 2389-2396.
11. Z. Zhang, Q. Song, Z.T. Alwahabi, Q. Yao, G.J. Nathan. "Temporal release of potassium from pinewood particles during combustion". *Combust. Flame.* 2015. 162(2): 496-505.
12. B.L. Chadwick, G. Domazetis, R.J.S. Morrison. "Multiwavelength Monitoring of Photofragment Fluorescence after 193 nm Photolysis of NaCl and NaOH: Application to Measuring the Sodium Species Released from Coal at High Temperatures". *Anal. Chem.* 1995. 67(4): 710-716.
13. T. Sorvajärvi, N. DeMartini, J. Rossi, J. Toivonen. "In Situ Measurement Technique for Simultaneous Detection of K, KCl, and KOH Vapors Released During Combustion of Solid Biomass Fuel in a Single Particle Reactor". *Appl. Spectrosc.* 2014. 68(2): 179-184.
14. Z. Qu, E. Steinvall, R. Ghorbani, F.M. Schmidt. "Tunable Diode Laser Atomic Absorption Spectroscopy for Detection of Potassium under Optically Thick Conditions". *Anal. Chem.* 2016. 88(7): 3754-3760.
15. W. Weng, Q. Gao, Z. Wang, R. Whiddon, Y. He, Z. Li, M. Aldén, K. Cen. "Quantitative Measurement of Atomic Potassium in Plumes over Burning Solid Fuels Using Infrared-Diode Laser Spectroscopy". *Energy Fuels.* 2017. 31(3): 2831-2837.
16. P.E. Mason, L.I. Darvell, J.M. Jones, A. Williams. "Observations on the release of gas-phase potassium during the combustion of single particles of biomass". *Fuel.* 2016. 182: 110-117.
17. K.T. Hartinger, P.B. Monkhouse, J. Wolfrum, H. Baumann, B. Bonn. "Determination of flue gas alkali concentrations in fluidized-bed coal combustion by excimer-laser-induced fragmentation fluorescence". *Symp. (Int.) Combust.* 1994. 25(1): 193-199.
18. U. Gottwald, P. Monkhouse, N. Wulgaris, B. Bonn. "Simultaneous detection of nickel and potassium in the flue gas of a fluidised bed coal combustor by excimer laser-induced fragmentation fluorescence". *Fuel Process. Technol.* 2003. 80(2): 143-153.
19. U. Gottwald, P. Monkhouse, B. Bonn. "Dependence of alkali emissions in PFB combustion on coal composition". *Fuel.* 2001. 80(13): 1893-1899.
20. C. Forsberg, M. Broström, R. Backman, E. Edvardsson, S. Badiei, M. Berg, H. Kassman. "Principle, calibration, and application of the in situ alkali chloride monitor". *Rev. Sci. Instrum.* 2009. 80(2): 023104.
21. T. Leffler, C. Brackmann, M. Berg, M. Aldén, Z. Li. "Developments of an Alkali Chloride Vapour-generating Apparatus for Calibration of Alkali-measuring Devices.". *Rev. Sci. Instrum.* 2017. 88(2): 023112.
22. C. Erbel, M. Mayerhofer, P. Monkhouse, M. Gaderer, H. Spliethoff. "Continuous in situ measurements of alkali species in the gasification of biomass". *Proc. Combust. Inst.* 2013. 34(2): 2331-2338.
23. T. Leffler, C. Brackmann, A. Ehn, B. Kaldvee, M. Aldén, M. Berg, J. Bood. "Range-resolved detection of potassium chloride using picosecond differential absorption light detection and ranging". *Appl. Opt.* 2015. 54(5): 1058-1064.
24. P. Davidovits, D.C. Brodhead. "Ultraviolet Absorption Cross Sections for the Alkali Halide Vapors". *J. Chem. Phys.* 1967. 46(8): 2968-2973.
25. G. Daminelli, D.A. Katskov, R.M. Mofolo, P. Tittarelli. "Atomic and molecular spectra of vapours evolved in a graphite furnace. Part 1. Alkali halides". *Spectrochim. Acta, Part B* 1999. 54(5): 669-682.

26. K. Schofield. "The chemical nature of combustion deposition and corrosion: The case of alkali chlorides". *Combust. Flame*. 2012. 159(5): 1987-1996.
27. B. Li, Z. Sun, Z. Li, M. Aldén, J.G. Jakobsen, S. Hansen, P. Glarborg. "Post-flame gas-phase sulfation of potassium chloride". *Combust. Flame*. 2013. 160(5): 959-969.
28. T. Leffler, C. Brackmann, W. Weng, Q. Gao, M. Aldén, Z. Li. "Experimental investigations of potassium chemistry in premixed flames". *Fuel*. 2017. 203: 802-810.
29. H. Daidoji. "Molecular absorption spectra of some sodium salts in flames". *Bunseki Kagaku*. 1979. 28(2): 77-82.
30. D.E. Self, J. M. C. Plane. "Absolute photolysis cross-sections for NaHCO₃, NaOH, NaO, NaO₂ and NaO₃: implications for sodium chemistry in the upper mesosphere". *Phys. Chem. Chem. Phys.* 2002. 4(1): 16-23.
31. F.S. Rowland, Y. Makide. "Upper stratospheric photolysis of NaOH". *Geophys. Res. Lett.* 1982. 9(4): 473-475.
32. W. Weng, J. Borggren, B. Li, M. Aldén, Z. Li. "A novel multi-jet burner for laminar flat flames of wide range of temperatures and oxygen concentrations: Applicable for quantitative optical diagnostics of biomass gasification/combustion processes". *Rev. Sci. Instrum.* 2017. 88(4): 045104.
33. L. Hindiyarti, F. Frandsen, H. Livbjerg, P. Glarborg, P. Marshall. "An exploratory study of alkali sulfate aerosol formation during biomass combustion". *Fuel*. 2008. 87(8-9): 1591-1600.
34. P.J. Padley, T.M. Sugden. "Photometric Investigations of Alkali Metals in Hydrogen Flame Gases. IV. Thermal and Chemiluminescent Effects Produced by Free Radicals". *Proc. R. Soc. London, A*. 1958. 248(1253): 248-265.