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Tunable diode laser atomic absorption spectroscopy for detection of potassium under optically thick conditions

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ABSTRACT: Potassium (K) is an important element related to ash and fine-particle formation in biomass combustion processes. In situ measurements of gaseous atomic potassium, K(g), using robust optical absorption techniques can provide valuable insight into the K chemistry. However, for typical parts per billion K(g) concentrations in biomass flames and reactor gases, the product of atomic linestrength and absorption path length can give rise to such high absorbance that the sample becomes opaque around the transition line center. We present a tunable diode laser atomic absorption spectroscopy (TDLAAS) methodology that enables accurate, calibration-free species quantification even under optically thick conditions, given that Beer-Lambert's law is valid. Analyte concentration and collisional lineshape broadening are simultaneously determined by a least-squares fit of simulated to measured absorption profiles. Method validation measurements of K(g) concentrations in saturated potassium hydroxide vapor in the temperature range 950-1200 K showed excellent agreement with equilibrium calculations, and a dynamic range from 40 pptv-cm to 40 ppmv-cm. The applicability of the compact TDLAAS sensor is demonstrated by real-time detection of K(g) concentrations close to biomass pellets during atmospheric combustion in a laboratory reactor.

In the quest for a sustainable energy production with reduced impact on climate, environment and health, biomass becomes increasingly important as a renewable, CO₂-neutral energy source. However, highly volatile and reactive inorganic compounds in biomass, such as alkali metals, can cause slagging and agglomeration, as well as fine-particle emission and corrosion in industrial reactors^{1,2}. Detailed knowledge of the release forms and primary gas-phase reactions during thermochemical conversion is needed to improve kinetic models, increase conversion efficiency and mitigate operational and environmental issues^{2,3}.

The most important and abundant inorganic element in this context is potassium (K), with potassium chloride (KCl) and potassium hydroxide (KOH) as the main intermediate gaseous species¹. Atomic potassium, K(g), is usually present in lower concentrations, but closely related to the main species. The relative contribution of each potassium species to the total gaseous K depends on the chemical composition of the fuel, the conversion conditions (stoichiometry, particle and gas temperature, humidity), and the conversion phase (devolatilization, char conversion).

Valuable experimental data on K release could be obtained from accurate measurements close to burning fuel particles and inside the reactor core of larger facilities. This, however, requires analytical techniques capable of in situ detection, reliable quantification in harsh and sooty environments with limited optical access, and the ability to distinguish between K species. Moreover, since concentrations can vary considerably and on short time-scales, fast and calibration-free techniques with wide dynamic range are desirable.

Online techniques for detection of potassium in combustion processes have been reviewed by Monkhouse⁴. The total amount of K can be measured with optical emission and mass spectrometric methods, including excimer laser-induced fragmentation fluorescence (ELIF)^{5,6}, laser-induced breakdown spectroscopy (LIBS)⁷, molecular beam mass spectrometry (MBMS)⁸, inductively coupled plasma mass spectrometry (ICP-MS)⁹ and surface ionization methods¹⁰. Of these, only LIBS allows for in situ detection. Conventional absorption techniques, such as atomic absorption spectroscopy

(AAS) with hollow-cathode lamps¹¹ and differential optical absorption spectroscopy (DOAS)¹² offer specificity for K compounds and in situ capability, but in a limited linear working range. All techniques mentioned above need calibration procedures and can be affected by stray light, self-absorption and the presence of soot.

Laser-based absorption spectroscopy (LAS), in particular tunable diode laser absorption spectroscopy (TDLAS), is a well-established technique for calibration-free detection of atoms, molecules and process parameters, such as gas temperature, in combustion applications¹³⁻¹⁵. For example, differential absorption light detection and ranging (DIAL)¹⁶ was developed for single-ended KCl(g) quantification, and direct TDLAS was employed to monitor low concentrations of K(g) in the flue gases of a coal combustion plant¹⁷. Fixed-wavelength laser-based AAS of K(g) in combination with collinear photofragmentation (CPFAAS) was successfully used to simultaneously measure K(g), KOH(g) and KCl(g), but only at low overall K(g) absorbance^{18,19}. Due to the strongly absorbing electronic K transitions, the upper detection limit for K(g) with conventional LAS instruments is usually below 1 parts per million by volume (ppmv) for 1 cm path length. In contrast, actual concentrations and path lengths encountered in biomass flames and reactors can by far exceed these values^{19,20}. Few groups have worked on extending the dynamic range of LAS techniques beyond the optical thin limit²¹⁻²³.

Here, we introduce a methodology based on tunable diode laser atomic absorption spectroscopy (TDLAAS) for accurate species quantification when optical thickness arises from a large product of linestrength and absorption path length, rather than from a high number density of absorbers. The TDLAAS lineshape fitting routine can be applied even when the sample is opaque around the transition line center. A sensor for K(g) detection over six orders of magnitude is presented and validated against equilibrium calculations by measuring in saturated KOH vapor. Further validation is provided by comparison to a fixed-wavelength approach, where the concentration is extracted at low absorbance from the wing of the absorption profile. The compact, inexpensive TDLAAS sensor is demonstrated by K(g) measurements directly above biomass pellets during combustion in a laboratory reactor.

METHODOLOGY

Tunable diode laser absorption spectroscopy. In TDLAS, the frequency ν of a tunable laser is rapidly scanned across a narrow region of the optical spectrum covering one or several electronic, vibrational or rotational-vibrational absorption lines. The intensity of the light, $I(\nu)$, impinging on a photodetector after passing a sample with absorbers can be described by Beer-Lambert's law according to

$$I(\nu) = I_C + I_{L0}(\nu) \exp[-\alpha(\nu)], \quad (1)$$

where I_C is the frequency-independent background in the absence of laser light, which can include detector noise, I_{D0} , and broadband emission, I_B , from a combustion process, $I_{L0}(\nu)$ is the transmitted laser intensity in the absence of the analyte, and $\alpha(\nu)$ is the frequency-dependent absorbance. The absorbance can be written as

$$\alpha(\nu) = S(\nu, T) \chi(\nu, c, P, T) c PL, \quad (2)$$

where $S(\nu, T)$ is the temperature-dependent line strength of the transition (cm^2/atm), χ the area-normalized lineshape function (cm), T the temperature (K), c the concentration of the analyte, P the pressure (atm) and L is the optical path length (cm). In atmospheric combustion applications, a Voigt profile with Doppler width $\nu_D(T)$ and collisional width $\nu_C(c, P, T)$ provides an adequate model for the absorption lineshape¹⁴.

The line-of-sight, path-averaged analyte concentration can be extracted using a single, fixed-wavelength lineshape value (usually the peak value), the lineshape-independent integrated absorbance, or a least-squares fit of a simulated to the measured spectrum. The laser background signal is recorded separately, extrapolated from the non-absorbing baseline of the spectrum in presence of the analyte, or included in the simulation of the spectrum.

A clear advantage of TDLAS compared to fixed-wavelength approaches is that lineshape fitting enables accurate species quantification even in the presence of spectral interference from neighboring absorption lines, unwanted frequency-dependent losses (such as from etalon effects) and background fluctuations. A typical TDLAS instrument is optimized for highest sensitivity and detection of molecules under optically thin conditions ($\alpha < 0.05$) using the integrated absorbance.

TDLAAS under optically thick conditions. Optical thickness is usually associated with high analyte concentrations and a violation of Beer-Lambert's law, which is only valid as long as the atoms or molecules act independently of each other²⁴. In this case, a single, low-absorbance value in the wings of the lineshape can be evaluated, but quantification requires calibration or knowledge of the line broadening²¹. According to Equation 2, a high absorbance may, however, not only originate from a high analyte concentration, but also from a large transition line strength, and a long absorption path. For a combination of the latter two cases at low analyte concentration, the requirements for Beer's law are fulfilled and the absorbance is directly proportional to the analyte concentration at arbitrary optical thickness²⁴. It was previously shown that the number density of rubidium atoms under optically thick and opaque conditions can be determined from the peak value of an absorption profile reconstructed by a fit to the lineshape wings²³.

Figure 1 shows examples of direct TDLAAS detector signals (measured light intensities) for scans across the potassium D1 line ($4s^2S_{1/2} \rightarrow 4p^2P_{1/2}$) centered at 12988.76 cm^{-1} (769.9 nm) under optically thick and partially opaque conditions. The data is taken from

a typical single biomass pellet combustion experiment at atmospheric conditions and flame temperatures around 1500 K. The figure also displays the separately measured laser background signal, $I_{D0} + I_{L0}(\nu)$, recorded with the flame off (round markers). The large line strength of the D1 line ($7.43 \times 10^6 \text{ cm}^2/\text{atm}$ at 296 K) allows K(g) detection limits in the low pptv range, but the sample becomes opaque already at a mole fraction of 10^{-6} and a path length of 2 cm. In that case, the contribution of the laser light to the detected signal is significantly smaller than I_C (dashed line) around the line center. At high concentrations, the maximum tuning range of the diode laser did not permit recording the full absorption profile. Therefore, to ensure a good measurement of at least one of the wings and the non-absorbing background, the transition was scanned off-center.

Figure 1. Laser background signal and direct TDLAAS detector signals for scans around the potassium D1 line and concentrations of 12 ppbv, 92 ppbv, 1.2 ppmv and 4.0 ppmv. The data set is taken from a typical biomass pellet combustion experiment, where $L=2 \text{ cm}$, $T=1500 \text{ K}$ and $P=1 \text{ atm}$. For concentrations above 900 ppbv, the sample becomes opaque near the transition center.

Figure 2. Measured absorbance spectra (markers) of the potassium D1 line together with least-squares curve fits (solid lines) yielding concentration of 12 ppbv, 92 ppbv, 1.2 ppmv and 4.0 ppmv. The profiles are truncated for concentrations above 900 ppbv. The arrows indicate the center wavenumber k_0 and the two wavenumbers in the wing (k_1 and k_2) used for the fixed-wavelength validation (see Figure 6).

Figure 2 presents absorbance spectra (markers) derived from the detector signals in Figure 1, together with least-squares fits (lines) performed using the TDLAAS fitting routine described below (Figure 3). At 12 ppbv and 92 ppbv, where full spectra could still be recorded, the concentrations agree to within 5% with the values obtained from the integrated absorbance. The collisional broadening determined by the fit was around 4 times larger than the Doppler broadening, and the total linewidth was similar for all spectra. Emission of thermally excited K and optical saturation¹⁷ were considered negligible.

Figure 3. Flow chart of the TDLAAS fitting routine. The scheme can accommodate for optical thick and partially opaque conditions with truncated absorption profiles at the line center due to a large product of linestrength and absorption path length.

The TDLAAS fitting routine is illustrated in the flow chart in Figure 3. First, an absorbance is calculated using the known values for temperature, path length and pressure, a Voigt lineshape with linestrength and Doppler width fixed according to the temperature, and initial values for concentration and collisional width. This absorbance is then used together with the measured laser background signal and the frequency scale, to calculate the simulated intensity $I^S(\nu)$ according to Beer-Lambert's law without approximation (Equation 1). If necessary, the background signal is corrected for broadband emission. At lower absorbance and optically thin conditions, the value of I_E is obtained by comparing the background signal to the non-absorbing baseline of the measured intensity, $I^M(\nu)$, which includes the emission. Under optically thick and opaque conditions, I_E is determined from the truncated region as the difference between I_C and the (independently measured) detector noise I_{D0} .

In order to account for a possible truncated region, the simulated intensity is set equal to I_{D0} , whenever smaller than I_{D0} . Finally, the simulated absorbance $\alpha^S(\nu)$, derived from $I^S(\nu)$, is least-squares fitted to the measured absorbance $\alpha^M(\nu)$, calculated from $I^M(\nu)$, with analyte concentration and collisional width as free fitting parameters. The fact that the simulated absorbance includes the truncated region facilitates the fit of the Voigt lineshape to the wings of the absorption profile and increases the robustness and speed of the fitting routine, in particular in the presence of fluctuations in I_E (emission) and I_{D0} (e.g. soot particles).

EXPERIMENTAL SECTION

TDLAAS setup. A schematic drawing of the experimental setup is shown in Figure 4A. A DFB laser (Nanoplus GmbH) with output power <10 mW and wide mode-hop-free tuning range (>4 cm⁻¹ or

120 GHz) was used to scan across the potassium D1 line. The laser injection current was supplied by a low-noise driver (ILX Lightwave, LDC-3724C), which also controlled the diode temperature. The scan was achieved by varying the laser current with an 80 Hz triangular wave generated by a function generation card (National Instruments, PXI-5402). After passing an optical isolator (OS, Isowave, I-80-3M), the light was coupled into a single mode optical fiber via two mirrors and a fiber collimator (Thorlabs, F240APC-780).

With the aid of a fiber splitter (FS, Newport, F-CPL-S12785), a part of the light was directed through the target region and then focused onto a photodetector (PD1, Thorlabs, PDA36A-EC). A narrowband optical filter (Thorlabs, FB770-10) was installed in front of the detector to ensure minimal influence of stray light and broadband emission from the combustion process. The detector signal was sampled at 250 kHz (National Instruments PXIe-6356) and averaged over ten scans. Once per measurement session, to record the relative frequency scale of the laser wavelength scan in response to the varying laser injection current, a part of the light was directed through an uncoated, solid, fused silica etalon with a free spectral range of 1.5 GHz (SLS Optics), and detected with photodetector PD2 (RedWave Labs, D101). Waveform generation and data acquisition were controlled via LabVIEW, whereas the curve fitting was performed using Matlab.

Figure 4. (A) Schematic drawing of the experimental TDLAAS setup. OI-optical isolator, M-mirror, C-collimator, FS-fiber splitter, L-lens, F-optical filter, PD-photodetector, FG-function generator card, DAQ-data acquisition card. Photographs of a biomass pellet combusted in the laboratory reactor, (B) flaming devolatilization (laser beam positions at 2 and 4 mm above the pellet indicated in blue) and (C) char conversion.

Laboratory reactor. An electrically heated, laboratory-scale reactor with optical access windows served as (i) furnace for the generation of K(g) in saturated KOH vapor for the main validation of the TDLAAS method, and (ii) as reactor for the combustion of biomass pellets for demonstration purposes. A thermocouple installed in the center of the reactor provided the overall temperature regulating the ceramic heating elements.

For the saturated KOH vapor measurements, a ceramic tube of length 20 cm was inserted between the optical access windows (Figure 4A). The ends of the tube were open to keep a constant pressure of 1 atm, but well isolated to ensure a uniform temperature distribution along the tube, and minimal gas exchange with ambient air. A separate thermocouple measurement of the temperature profile along the tube confirmed a variation <10 K.

To enable combustion of single pellets, the ceramic tube was removed from the reactor and an upwards-directed laminar flow of dry air (4 L/min) was introduced at the bottom of the furnace. A platinum net on a hook was employed to suspend a pellet in the center of the flow, just below the laser beam. The pellet holder was mounted

on a micrometer stage to allow fine tuning of the beam height above the pellet. A detailed description of the furnace used as single-pellet-reactor can be found in Qu et al.²⁵. Photographs of a typical pellet flame during the devolatilization phase, and of a glowing pellet during the char conversion phase are shown in Figures 4B and 4C, respectively.

Since the reactor thermocouple was located outside the ceramic tube (as well as outside the pellet flame) and only provided a point-measurement, its readings did not accurately represent the gas temperature inside the tube. Therefore, the actual, average gas temperature was measured with a second TDLAS instrument^{15,25} (not shown in Figure 4A) using the same beam path and sample volume as the K(g) sensor. This instrument also provided the ambient air H₂O concentrations inside the tube. The uncertainties of the sensor were 10 K for temperature and 0.1 % for H₂O. Although the line strength of the D1 potassium line has a weak temperature dependence, the TDLAS measured temperature was used to determine the correct line strength with the help of the partition function²⁶.

METHOD VALIDATION

K(g) in temperature controlled tube. In order to generate known concentrations of atomic potassium, 5 g KOH powder was evenly distributed in the ceramic tube and heated up to temperatures in the range 930-1200 K. Above the melting point of KOH (679 K), a saturated vapor pressure of KOH(g) was present in the ceramic tube, of which a fraction decomposed to K(g), H₂O(g) and O₂(g) following the reaction

The equilibrium constant k can then be written as

$$k = \left[p\text{K(g)}^2 \times p\text{H}_2\text{O(g)} \times p\text{O}_2^{1/2} \right] / p\text{KOH(g)}^2, \quad (4)$$

where p indicates the partial pressure of the species. The reactor temperature was changed in steps of 25 K. At each temperature, the K(g) signal was observed for around 20 minutes prior to conducting the TDLAS measurements, which took about 5 minutes. During these 25 minutes, the K(g) signal was stable, confirming thermodynamic equilibrium.

Thermodynamic equilibrium calculations were performed using the FactSage software package (FactSage 6.4, GTT Technologies)²⁷ and the associated database Fact PS with established thermodynamic data. FactSage operates by minimizing the Gibbs free energy of the system, and provides information on e.g. product species, balanced stoichiometry, vapor pressures and molar concentrations. The conditions in the ceramic tube were simulated with a system consisting of air (78.1% N₂, 20.9% O₂, 0.9% Ar and 0.039% CO₂), varying amounts of H₂O vapor (up to 10%) and sufficient solid KOH to assure saturated vapor pressure of KOH(g). The total pressure was set to 1 atm, and the temperature was varied in the range 900 K to 1250 K.

Figure 5A shows the K(g) concentrations (markers) measured at different temperatures in the ceramic tube. Three separate measurement series were conducted, two with increasing temperature (experiments 1 and 2), and one with decreasing temperature (experiment 3). The figure also shows the corresponding K(g) equilibrium concentrations (lines) in saturated KOH vapor in the presence of different amounts of water vapor. As expected from Equation 4, a minor change in H₂O concentration has a large effect on the amount of K(g). In Figure 5B, the measured K(g) concentrations are plotted

against the corresponding equilibrium values calculated using the actual TDLAS-measured temperatures and H₂O concentrations as input parameters for each point. In both panels, the data points with hollow markers indicate partially opaque conditions with truncated absorption lineshapes.

The measured K(g) concentrations are in excellent agreement with the equilibrium calculations (average accuracy within 9 %). This confirms the validity of Beer-Lambert's law under these conditions and verifies the TDLAS methodology up to concentrations of 40 ppm-cm. The spectra recorded at 940 K (50 pptv at 20 cm path-length) revealed a signal-to-noise ratio of 25, which yields a lower detection limit of 40 pptv-cm and thus a working range of 10⁶.

Figure 5. (A) Measured K(g) concentrations (markers) in saturated KOH vapor as a function of temperature in the ceramic tube. Calculated equilibrium K(g) concentrations (lines) for different amounts of H₂O are shown for comparison. (B) Measured versus equilibrium K(g) concentrations. The calculations were performed using TDLAS-derived temperature and H₂O values for each point. In both panels, the hollow markers indicate opaque conditions with truncated absorbance spectra.

Fixed-wavelength in the wing. Apart from the main validation presented above, further confirmation of the validity of the TDLAS method can be obtained by comparison to a fixed-wavelength evaluation at low absorbance in the lineshape wing. In general, as mentioned above, a fixed-wavelength approach has significant drawbacks, including the need for calibration (or knowledge of the line broadening), a limited working range, and the fact that a single absorbance value is difficult to interpret in the presence of a fluctuating background and spectral interference. Thus, a fixed-wavelength

evaluation cannot be recommended, especially in combustion applications, where gas matrices and background signals may be complex and subject to change.

Figure 6 shows $K(g)$ concentrations determined with the TDLAAS fitting routine plotted against those derived from evaluation of the same raw data (taken from a typical biomass pellet combustion experiment, as shown in Figure 7) at the line center (k_0) and two wavenumbers (k_1 and k_2) in the lineshape wing (see Figure 2). Here, to enable quantification at the fixed wavelengths, the lineshape broadening parameters known from TDLAAS fits of low-absorbance spectra were used to calculate the linestrengths at 12989.60 cm^{-1} (k_1) and 12990.90 cm^{-1} (k_2), which, in turn, were used to extract the concentrations from the high-absorbance spectra. The fixed-wavelength evaluation also benefited from the low flame emission, negligible etalon effects and lack of spectral interference in this particular case. The result of the comparison again confirms the capability of the TDLAAS methodology to accurately measure concentrations under high absorbance and partially opaque conditions.

Figure 6. $K(g)$ concentrations retrieved via the TDLAAS fitting routine plotted against concentrations obtained from a fixed-wavelength evaluation at the peak (k_0) and two wavenumbers in the wing (k_1 and k_2), as indicated in Figure 2. The raw data was taken from a typical biomass pellet combustion experiment (as in Figure 7).

SENSOR DEMONSTRATION

Combustion of pelletized biomass. The applicability of the TDLAAS sensor is demonstrated by measuring $K(g)$ close to biomass pellets during atmospheric combustion in the laboratory reactor at 1123 K. Panels A and B in Figure 7 show $K(g)$ concentrations detected 2 and 4 mm above pelletized Energy Wood (EW) and Wheat Straw (WS), respectively, as a function of combustion time. According to wet chemical analysis, the total amount of K is significantly higher (at least by a factor of ten) in WS than in EW²⁸. The black dashed line indicates the onset of opaque conditions, and thus the maximum concentration that could have been measured using a fixed-wavelength approach at the transition line center.

Devolatilization was considered from the time when the pellet was inserted in the hot reactor to the moment the flame disappeared. Therefore, this first phase includes heating, drying before ignition as well as release of the volatiles. The char conversion phase was defined from the moment the flame was extinct until the char stopped glowing. The absorption path length during flaming devolatilization (3.4 cm for EW and 2.1 cm for WS) was estimated from a photograph such as shown in Figure 4B, and the same path length was used for the char conversion phase. Assuming thermodynamic equilibrium, the actual K linestrengths were calculated based on the average

(flame) temperature above the pellet measured with the second TDLAS sensor²⁵. The sample was assumed homogenous along the beam path with respect to temperature and species concentration.

For both EW and WS, the measured $K(g)$ concentrations were significantly higher in the flame than during char combustion and decreased sharply at the end of devolatilization. This has previously been observed above burning biomass particles^{19,29}, and is most likely a consequence of the large difference in gas temperature and oxidizing conditions above the pellets during these two phases. Similar and rather constant concentrations (around 3 ppmv) were recorded for the two types of biomass during devolatilization, which appears to be in contrast to the difference in total K content and initial weight. Possible explanations lie in the release mechanism or gas-phase chemistry, e.g. the high chlorine content in WS favoring KCl formation²⁸. During char combustion, the $K(g)$ concentrations are again comparable, but the peak, indicating high total K release, occurs at different combustion time points and shifts to later times with increasing distance from the pellet.

Figure 7. $K(g)$ time histories measured in situ at heights-above-pellet (HAPs) of 2 mm and 4 mm for Energy Wood (A) and Wheat Straw (B) during atmospheric combustion in the laboratory furnace. The flaming devolatilization and char combustion phases are indicated. The dashed line indicates the onset of opaque conditions.

Outlook. Although only a minor part of the volatile potassium in biomass is released as $K(g)$ ²⁹, continuous in situ measurements of the atomic species on various process scales with high accuracy, precision and temporal resolution can be useful for validation and improvement of particle³⁰ and kinetic³¹ models. Future investigations should involve a variety of biofuels and conversion conditions (stoichiometry, additives), complemented by conventional ash, flue gas

and particle analysis as well as 1D and 2D reacting flow simulations^{30,32}.

The upper detection limit of the TDLAAS sensor could be further extended by employing a laser with wider mode-hop-free tuning range, whereas the sensitivity could be improved by implementing (calibration-free) wavelength modulation absorption spectroscopy^{15,25}. Photofragmentation in combination with TDLAAS may be a promising approach for simultaneous detection of K(g), KOH(g) and KCl(g) in the presence of high K(g) absorbance. Since the methodology presented here applies also to molecules, as long as Beer-Lambert's law is valid, the technique could be useful for long path length measurements in the atmosphere and remote sensing applications.

CONCLUSIONS

We present a novel TDLAAS methodology for measurements in the optical thick regime, when high absorbance arises from a large product of linestrength and absorption path length. The technique is validated and demonstrated by detection of atomic potassium in saturated KOH vapor and close to single biomass pellets during combustion, respectively. The K(g) sensor enables fast, robust and calibration-free in situ measurements over six orders of magnitude, needs little optical access, can operate in the presence of soot, and can be realized in a portable and affordable setup. Thus, the sensor is particularly well suited for diagnostics and process monitoring in combustion and gasification applications. Detailed, systematic investigations on various process scales can be performed, which will lead to a better understanding of the role of potassium in thermochemical conversion of biomass.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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