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Kalman adaptive filtering was applied for the first time to the real-time simultaneous determination of water isotopic ratios using laser absorption spectroscopy at 2.73 µm. Measurements of the oxygen and hydrogen isotopologue ratios $\delta^{18}O$, $\delta^{17}O$, and $\delta^{2}H$ in water showed a 1-σ precision of 0.72‰ for $\delta^{18}O$, 0.48‰ for $\delta^{17}O$, and 0.84‰ for $\delta^{2}H$, while sampling the output of the tuned Kalman filter at 1-s time intervals. Using a standard running average technique, averaging over ~30-s is required to obtain the same level of precision. The Kalman filter has the advantage of a faster response to step-like changes in the input than the 30-s averaged output and is significantly less susceptible to outlier values ('spikes'). This is an important advantage for applications in which small but fast changes in the isotopic composition need to be resolved, such as, for example, in on-line breath analysis.

OCIS codes: 120.6200, 300.6260, 300.6340

Water (H_2O) isotopologue ratio measurements (in the vapor or liquid phase) are of great relevance to various research fields, such as climate and paleoclimate studies, geological surveys, hydrological studies (see, e.g. [1]), and clinical research for diagnosis ([2-4]). As an alternative to isotope ratio mass spectrometry (IRMS), laser absorption spectroscopy (LAS) is more and more frequently employed to determine stable isotope abundance ratios [1, 5]. The high measurement precision required by many applications represents a real challenge for isotopic composition analysis by means of LAS [6], especially in the case of water [7, 8]. Apart from instrument instability and measurement errors related to sample handing and injection (e.g. incomplete evacuation of the gas cell between two consecutive measurements will lead to memory effects and thus affect the measurement precision), the signal-to-noise ratio (SNR) is often the most important limiting factor for achieving high precision. In LAS, apart from reducing the intrinsic noise of the spectrometer, a high SNR can be achieved by selecting stronger absorption lines and using a multiple-pass cell or a high-finesse optical cavity to enhance the effective optical path length. Another possibility is to decrease the detection bandwidth by averaging N laser scans. In the common case of white noise, this will reduce the noise by a factor of $N^{1/2}$, until the limits of the spectrometer stability are reached. The optimal averaging time can be determined by an Allan variance analysis [9]. Alternatively, the individual spectral scans are processed, and the resulting isotope ratios are further averaged to obtain the desired level of precision (again limited by the system's stability). Though this "post-processing" technique permits one to obtain a high measurement precision that can be similar to that obtained by the IRMS method [5, 7], the drawback is a slower response of the system to fast changes in the isotopic ratios. For specific applications, such as the on-line monitoring of exhaled breath [4], it is highly desirable to be able to perform real-time measurements with high sensitivity and precision, while maintaining a fast system response. Kalman adaptive filtering has been applied before to real-time trace gas concentration measurements [10, 11], while adaptive filtering was discussed in a more general sense by Werle and co-workers [12]. In this letter, we report on the first implementation of Kalman filtering to real-time isotopic ratio measurements using LAS. The Kalman filtering technique shows superior performance compared to a fixed bandwidth filter. It will adjust to changes in the signal statistics and dynamic range, and in addition is computationally efficient [11]. Simultaneous measurements of the $H_2{}^{18}O/H_2{}^{16}O$, $H_2{}^{17}O/H_2{}^{16}O$, and HDO/H_2O isotopic ratios in liquid water have been performed with a precision of 0.72‰ for $\delta^{18}O$, 0.48‰ for $\delta^{17}O$, and 0.84‰ for $\delta^{2}H$ (the isotopic composition is conventionally

expressed as a δ-value giving the relative deviation of the isotope ratio with respect to the reference standard), by sampling the output of the tuned Kalman filter at 1-s time intervals. Using a standard running average technique, averaging over ~30 s is required to obtain the same level of precision.

The experimental set-up, mounted on a 50×70 cm^2 optical breadboard, is depicted in Figure 1. The laser source used was a cw room temperature distributed feed-back (DFB) diode laser emitting at 2.73 μm (nanoplus GmbH) with a single mode output power of up to 2mW. A Thorlabs ITC-502 diode laser controller provided temperature control and drive current for the laser. The output laser beam was collimated first by an off-axis parabolic mirror (PM1) with an effective focal length (EFL) of 25mm. The laser beam was then transformed into a quasi-parallel beam with a diameter of ~4 mm by the use of a combination of a coated CaF_2 lens F1 (EFL=200 mm) and a second off-axis parabolic mirror PM2 (EFL=50 mm). A fraction (~8%) of the laser beam was separated by a beam splitter (CaF_2) and coupled to a Fabry-Perot etalon consisting of two air-separated uncoated CaF_2 plates for frequency metrology. Positions of H_2O vapor absorption lines from the HITRAN 2004 database [13] provided an absolute frequency reference for frequency calibration. The frequency scale was linearized using the interference fringes of the etalon with a free spectral range of 0.0283 cm^{-1}. The main light beam was directed to a multiple-pass cell with an optical path length of 20-m. The emerging absorption signal from the cell was focused by a lens F2 (f=50 mm) onto a LN2-cooled HgCdTe detector (J15D22-M204-S01M-60). A home-built bridge circuit was employed to realize DC coupling of the detector to a low noise preamplifier (EG&G, Model 5113). A beam shutter (Thorlabs, SH05) was placed before the detector for zero background level acquisition at the beginning of each absorption spectrum scanning.

The temperature of the multiple-pass cell has been actively controlled. The temperature was set at 30°C by use of a heater band and maintained constant within ±0.1°C by a PID controller. The cell temperature was monitored with calibrated platinum resistors (Pt100) (with an accuracy of 0.03ºC and a precision of 0.01ºC). No temperature gradient along the cell axis has been observed within the measurement precision of the temperature sensors. As the molecular absorption strength is temperature-dependent, temperature changes in the water vapor sample may cause systematic deviations in the isotope ratio determinations. The temperature coefficients for the selected lines are listed in Table 1. The lines used here are the same as those used previously in the work by Kerstel et al. [14]. The temperature coefficients of the respective line intensities yield the following sensitivities of the isotope ratio

determinations: -3.1‰/K for $\delta^{18}O$, -6.0‰/K for $\delta^{17}O$, -8.0‰/K for $\delta^{2}H$. A sample temperature stabilization to better than ±0.1°K is thus required to insure a measurement precision < 1 ‰.

12 μL liquid water samples were injected into the pre-evacuated multiple-pass cell through a silicon membrane using a syringe, resulting in a pressure of ~4.5 mbar inside the absorption cell (the water saturated vapor pressure is ~42 mbar). Figure 2 (a) shows a portion of the H_2O isotopologue absorption spectrum near 2.73 μm recorded in this work. The H_2O absorption features were fitted to Voigt [15] or Galatry [16] profiles, in order to determine the integrated area under the absorption lines using a Levenberg-Marquardt multi-line fitting algorithm. The baseline was modeled with a fourth order polynomial to account for the laser intensity ramp. As indicated by the residuals of the Voigt (b) and the Galatry (c) fits shown in figure 2, the use of the Galatry profile fit leads to a 3-fold reduction in uncertainty in determination of the integrated area in comparison with the use of a Voigt line shape. In theory, with knowledge of the line intensities (provided by HITRAN 2004, for instance), the integrated areas can be used to determine the isotopic δ-value with respect to the water isotopic composition of the international standard material known as Vienna Standard Mean Ocean Water (VSMOW). Unfortunately, the line intensity is usually not accurate enough for isotopic ratio determination with high accuracy. For this reason, our laser instrument was calibrated against water standards obtained from the Center for Isotope Research (CIO) of the University of Groningen. It is noted that for this study, this calibration is not essential as we are predominantly interested in the precision of the measurement, and less in the correct absolute values of the isotope ratios. Bottled water (Vittel, France), instead, was used as a less-expensive, unknown sample. The 1-s raw measured δ values shown in Table 2 give 1σ precision of 2.7‰ for $\delta^{18}O$, 2‰ for $\delta^{17}O$, and 3.3‰ for $\delta^{2}H$, respectively. In order to further improve the measurement precision, we first used conventional averaging of n measured δ-values. The optimum number of measurements to average was determined from an Allan variance analysis. As can be seen in figure 3 (lower panel), the optimal averaging time for the present instrument was ~30-s. (i.e. an average of 30 δ-values). Herewith, the precision has been improved to 0.72‰ for $\delta^{18}O$, 0.46‰ for $\delta^{17}O$, and 0.82‰ for $\delta^{2}H$ with an equivalent measurement time of 30-s. This improvement in measurement precision, obtained by post-processing of the data, comes at the price of a slow, 30-s time-constant, system response.

We then applied the Kalman filtering technique to fast (1-s), real-time, high-precision isotope ratio determinations. In a recursive procedure, the true parameter to be determined by

a measurement system is estimated in real time based on the previously determined value by taking into account the process variability and measurement noise. Using a linear stochastic difference model, the true isotope ratio value at time k+1 is evolved from the value given at k according to:

$$x_{k+1} = x_k + w_k \ , \tag{1}$$

At time k, the measured isotope ratio value z_k of the true value x_k can be expressed as follows:

$$z_k = x_k + v_k \ , \tag{2}$$

where w_k and v_k are uncorrelated random variables related to the process variability and the measurement noise, respectively, with covariance of σ^2_w and σ^2_v, respectively.

In practice, the parameters σ^2_v (representing the measurement noise) and σ^2_w (representing the process variability due to real isotope abundance variation and real-time drifts resulting from laser frequency shift, thermal fluctuation, pressure variation, etc.) should be well defined. Information on σ^2_v is usually available, because it depends on the quality of the measurement instrument, while determination of the process variability variance σ^2_w is quite subjective. Whereas both σ^2_v and σ^2_w vary with real variations of the isotope abundance, once the measurement system has reached equilibrium, the ratio of σ^2_v to σ^2_w should be constant [11]:

$$q = \sigma^2_v / \sigma^2_w = \text{constant} \tag{3}$$

This ratio of variances can be used as a parameter to tune the filter.

In our experiment, σ^2_v was determined by the δ value variance deduced from the first 10 raw measurements of water samples. σ^2_w was then calculated by dividing σ^2_v by q. The selection of the value for q depends on the particular instrument and its application environment. The larger the q value, the longer time it will take for the system to follow large changes in the measured isotopic ratio. For a smaller q value, the filtering is less efficient in removing shot-to-shot variability related to the real-time noise. Figure 4 shows the standard deviations as a function of the q-value for our water isotope ratio determinations using Kalman filtering (the water vapor concentration remained constant during the measurement time of ~30 min). A value of q=150 was chosen, independent of the Allan variance result, as a compromise between fast temporal response and high filtering efficiency for the laser instrument. Not surprisingly, this value corresponds to a precision level that can be obtained by conventional 30-s averaging, where the 30 seconds correspond to the optimum averaging time as derived from an Allan variance analysis (Figure 3, bottom panel). The measurement precisions are summarized in Table 2. The 1-σ standard deviation has been improved from

2.7‰ to 0.72‰ for $\delta^{18}O$, from 2.0‰ to 0.48‰ for $\delta^{17}O$, and from 3.3‰ to 0.84‰ for $\delta^{2}H$, with a measurement time of 1-s at the output of the Kalman filter.

In conclusion, we demonstrated the potential of using Kalman filtering for real-time isotope ratio measurement, which permits for a significant improvement in measurement precision and temporal response. We are currently applying this adaptive filtering technique to on-line measurements of water isotope ratios in exhaled breath, where we expect to see a significant improvement in the ability to resolve small changes in the input isotope ratios, while maintaining a sufficiently fast response to observe rapid changes without distortion.

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Table captions

Table 1 List of the absorption lines used for the measurements in this work.

Table 2 Measurement precision comparison: Raw measured δ was determined from the average of 10 laser scans in 1-s. Optimal average time of 30-s leads to average of 30 δ-value, and q=150 was used for Kalman filtering.

Table 1

Isotopologue coef.	Frequency (cm^{-1})	Rotational assignment	Intensity ($10^{-23}cm \cdot mol^{-1}$)	Ground state energy (cm^{-1})	Temp. at 296K(K^{-1})
$H^{18}OH$	3662.9196	$5_{15} \leftarrow 5_{14}$	2.1	398.3	1.5 ‰
$H^{16}OH$	3663.0452	$6_{24} \leftarrow 7_{17}$	8.5	586.4	4.6 ‰
$H^{17}OH$	3663.3213	$3_{13} \leftarrow 4_{14}$	7.2	224.3	-1.4 ‰
$H^{16}OD$	3663.8419	$2_{12} \leftarrow 3_{13}$	1.2	100.4	-3.4 ‰

Table 2

Method / Time	Measurement precision		
	$\delta^{18}O$ (SD)	$\delta^{17}O$ (SD)	$\delta^{2}H$ (SD)
Raw measurement / 1s	2.7 ‰	2.0 ‰	3.3 ‰
Averaging 30-δ / 30s	0.72 ‰	0.46 ‰	0.82 ‰
Kalman filtering / 1s	0.72 ‰	0.48 ‰	0.84 ‰

Figure captions

Figure 1 Optical layout. PM: parabolic mirror; F: lens.

Figure 2 H_2O isotopologue absorption spectrum (a) measured in this work. Data were fitted to Voigt and Galatry profiles. Residuals resulting from each fit are shown : (b) from Voigt fit and (c) from Galatry fit, respectively.

Figure 3 The upper three panels show the raw measurements of $\delta^{18}O$, $\delta^{17}O$, and $\delta^{2}H$ (dots) and the corresponding Kalman-filter output for a q-value of 150 (lines). The Allan variances in the lower panel show an optimal averaging time of about 30-s for the present laser system: (a) $\delta^{18}O$, (b) $\delta^{17}O$, (c) $\delta^{2}H$.

Figure 4 Plots of the standard deviations in the measurement of the water $\delta^{18}O$ (a), $\delta^{17}O$ (b), and $\delta^{2}H$ (c) using Kalman filtering as a function of the q-value.

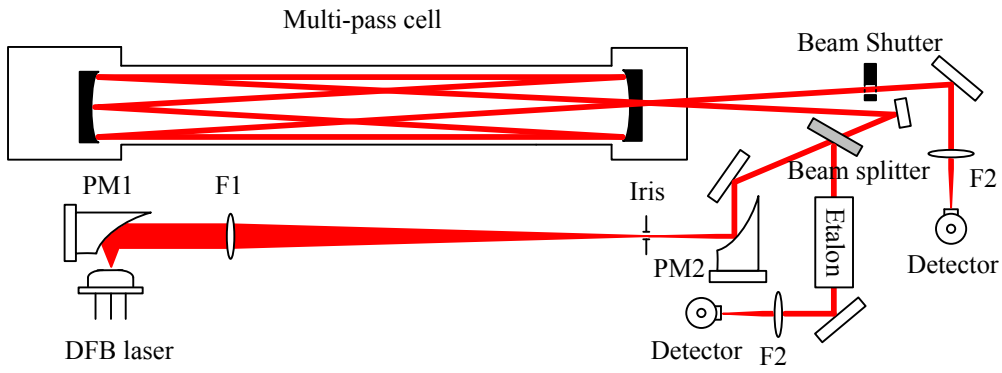
Multi-pass cell
Beam Shutter
PM1
F1
Iris
Beam splitter
F2
Etalon
Detector
PM2
DFB laser
Detector
F2

Figure 1

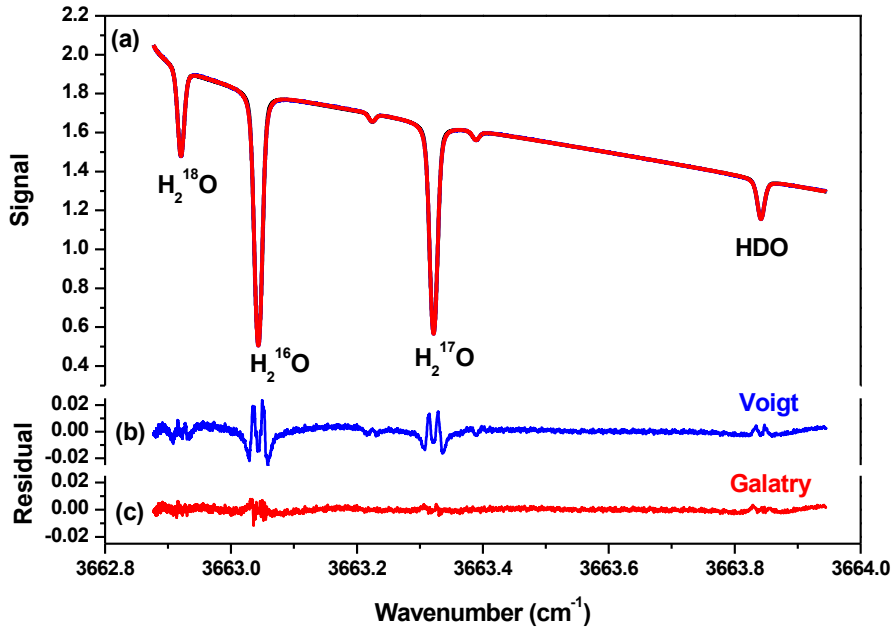
(a)
Signal
$H_2{}^{18}O$
$H_2{}^{16}O$
$H_2{}^{17}O$
HDO
(b)
Voigt
(c)
Galatry
Residual
Wavenumber (cm^{-1})

Figure 2

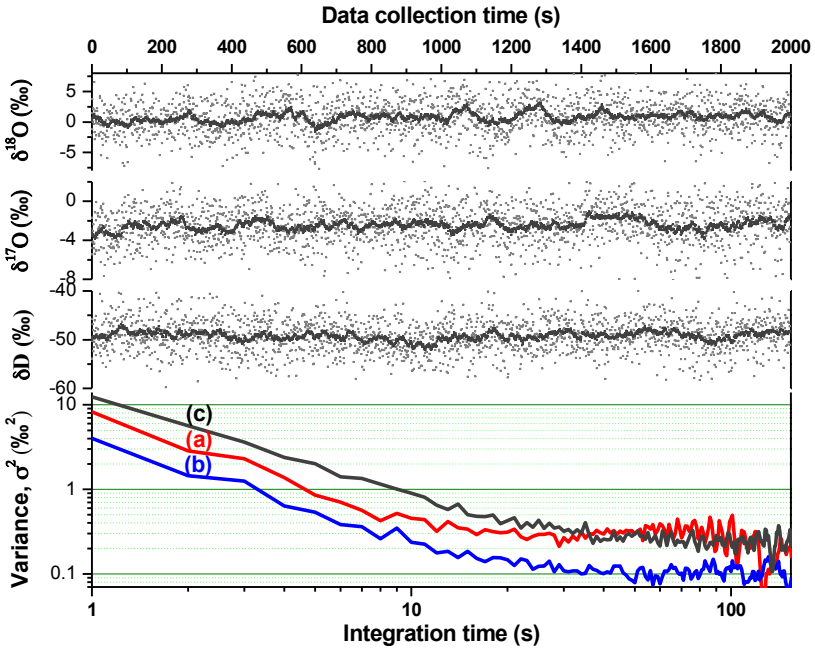
Data collection time (s)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
δ18O (‰)
5
0
-5
δ17O (‰)
0
-4
-8
δD (‰)
-40
-50
-60
Variance, σ2 (‰2)
10
1
0.1
(c)
(a)
(b)
1
10
100
Integration time (s)

Figure 3

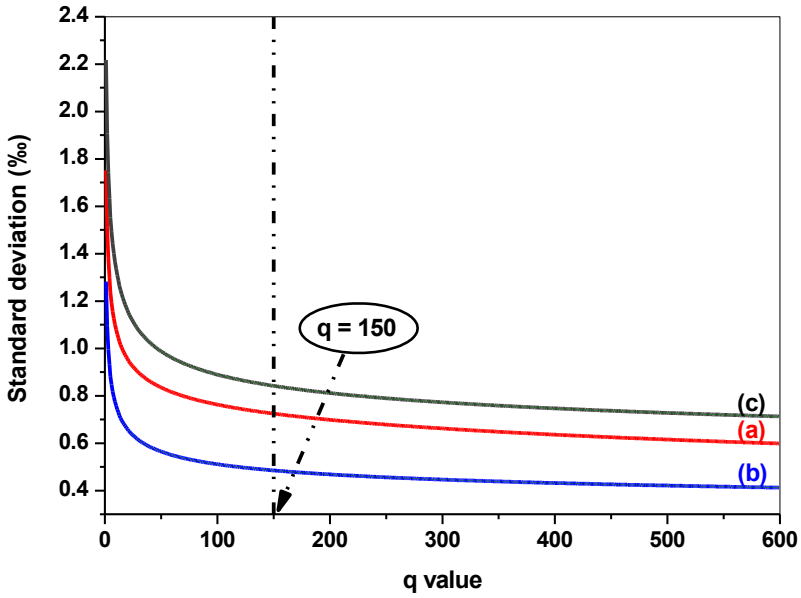
Standard deviation (‰)
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0
100
200
300
400
500
600
q value
q = 150
(c)
(a)
(b)

Figure 4