Aging studies on micro-fabricated alkali buffer-gas cells for miniature atomic clocks

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We report an aging study on micro-fabricated alkali vapor cells using neon as a buffer gas. An experimental atomic clock setup is used to measure the cell’s intrinsic frequency, by recording the clock frequency shift at different light intensities and extrapolating to zero intensity. We find a drift of the cell’s intrinsic frequency of $(−5.2 ± 0.6) \times 10^{−11}$/day and quantify deterministic variations in sources of clock frequency shifts due to the major physical effects to identify the most probable cause of the drift. The measured drift is one order of magnitude stronger than the total frequency variations expected from clock parameter variations and corresponds to a slow reduction of buffer gas pressure inside the cell, which is compatible with the hypothesis of loss of Ne gas from the cell due to its permeation through the cell windows. A negative drift on the intrinsic cell frequency is reproducible for another cell of the same type. Based on the Ne permeation model and the measured cell frequency drift, we determine the permeation constant of Ne through borosilicate glass as $(5.7 ± 0.7) \times 10^{−22} \text{ m}^2 \text{s}^{−1} \text{Pa}^{−1}$ at 81 °C. We propose this method based on frequency metrology in an alkali vapor cell atomic clock setup based on coherent population trapping for measuring permeation constants of inert gases.

Micro-fabricated alkali-atom vapor cells with volumes of few mm$^3$ are of interest for applications in instruments such as miniature atomic magnetometers, gyrosopes, imaging of microwave fields, and atomic clocks. Particular applications like Chip Scale Atomic Clocks (CSAC) based on Coherent Population Trapping (CPT) were first reported by NIST. Subsequent studies on the long term clock frequency drifts by NIST and Symmetricom identified possible sources of the frequency drifts and suggested remedies. Considerable work has been reported on the fabrication and characterization of miniature vapor cells, but only few studies addressed the long term frequency drifts in miniature atomic clocks induced specifically by the vapor cell itself. Certain studies suggest that the buffer gas pressure change inside the vapor cell causes the long term clock frequency drift; however, no quantitative treatment of the buffer gas pressure change nor a systematic evaluation of other contributions was given. The concept of the buffer gas pressure change as the possible cause of the in-orbit frequency equilibrium of space clocks has been studied by Camparo et al. in view of the He buffer gas permeation through the cell walls. The quantitative treatment of the He buffer gas permeation through the cell walls by Camparo points at the importance of the buffer gas pressure change as one of the crucial parameters to be considered, but the observed clock frequency drift could not be explained by this process. Note that all these studies were performed in clock operation conditions, i.e., under conditions where the light shift, in general, is non-zero and can be a dominant contributor to the clock frequency drift. Furthermore, they could neither link the observed clock frequency drift to the intrinsic properties of the vapor cell nor quantify the clock frequency aging in terms of the buffer gas pressure evolution inside the vapor cell.

Only few authors have addressed explicitly the aging or drift of the intrinsic frequency of the vapor cell alone, i.e., when other sources of drift arising from the clock system operation are excluded, that could be caused by a change of buffer-gas pressure. For instance, Kazantsev et al. employed measuring the clock frequency shifts for precision measurement of buffer gas pressure. Recently, Hasegawa et al. studied aging in micro-fabricated Cs-Ne vapor cells using CPT spectroscopy of the Cs clock transition $(6S_{1/2}, F = 3, m_F = 0 \leftrightarrow 6S_{1/2}, F = 4, m_F = 0)$, by extrapolating the clock frequency to zero light intensity. However, no drift of the clock resonance frequency could be shown. Straessle et al. discussed permeation of Nitrogen buffer gas into their Rb micro-cells to assess the hermeticity of micro-cells.

The motivation of our present study is to identify and quantitatively analyze the possible sources of clock frequency drift in miniature atomic clocks, induced by potential aging of the miniature vapor cells, such as, e.g., a slow change of buffer gas pressure. We identify the sources of clock frequency variations which in standard clock operation conditions mask the frequency drifts due to aging of the cell. Extrapolation of the clock frequency to zero light level is used to record the intrinsic cell frequency that is unaffected by light-shift effects. Repeating the measurements over time permits to observe the aging of this intrinsic cell frequency, which is crucial for the long-term stability of the atomic clock.

Permeation of noble gases, e.g., Ne, through the intact solid cell walls is a known process that can cause a change...
of buffer-gas pressure in a vapor cell. The evolution of the buffer gas pressure \( P_{in}(t) \) inside the cell can be described in terms of a permeation rate \( L \) (units of mbar-l/s, in analogy to a leak rate) for the buffer gas volumetric flow into or out of the cell by\(^{18} \)

\[
P_{in}(t) = P_{ext} - (P_{ext} - P_{in})e^{-t/\tau} = P_{ext} - (P_{ext} - P_{in})e^{-t/\tau}.
\]

(1)

Here \( P_{ext} = 0.018 \text{ mbar} \) is the partial pressure of Ne in the atmosphere, \( P_{in} = P_{in}(t = 0) \), \( V \) is the volume of the vapor cell (10 \( \mu l \) in our case), and \( P_{ref} = 1013 \text{ mbar} \) is the atmospheric reference pressure. The process of Eq. (1) has the time constant of\(^{18} \)

\[
\tau = \frac{V P_{ref}}{L}.
\]

(2)

The permeation rate \( L \) through a membrane of area \( A \) and thickness \( d \) is expressed in terms of the permeation constant \( K \) (m\(^2\)s\(^{-1}\)Pa\(^{-1}\)) as

\[
L = \frac{K A}{d} P_{ref}^2.
\]

(3)

Permeation of gases such as He, Ne, Ar, and N\(_2\) through different materials has been studied by several authors,\(^{19-23}\) with He as the smallest molecule showing the strongest permeation. Permeation of He through silica and borosilicate glasses was reported by Norton\(^{19}\) and Harding\(^{20}\) for the temperature range of \(-80 ^\circ\text{C} \) to \(700 ^\circ\text{C} \) and by Altemose\(^{21}\) for 100 \( ^\circ\text{C} \) to 600 \( ^\circ\text{C} \). Ne permeation was studied by Wortmann and Shackelford\(^{22}\) for vitreous silica glasses at 0 \( ^\circ\text{C} \) to 50 \( ^\circ\text{C} \), by Kanezashi \textit{et al.}\(^{23}\) for silica glass at 300 \( ^\circ\text{C} \) to 600 \( ^\circ\text{C} \), and by Shelby\(^{24}\) for borosilicate glasses at 200 \( ^\circ\text{C} \) to 560 \( ^\circ\text{C} \). Recently, Zameroski \textit{et al.}\(^{25}\) have discussed the impact of He permeation into an alkali vapor cell on their measurement of collisional shift rates of Cs optical transitions, using data from Altemose\(^{21}\). To summarize, most of these works reported on the permeation of He through different glasses at elevated temperature ranges where permeation is enhanced,\(^{19}\) while no study has been reported so far on the impact of Ne permeation through borosilicate glass in atomic clock applications. Table I lists permeation constants for He or Ne from literature. Expected permeation rates, time constants, and initial linear drift of intrinsic cell frequency due to permeation are given, calculated for the microfabricated Cs-Ne cell under study (see below), using \( P_{in} = 60 \text{ mbar} \) and the Ne pressure shift coefficient of 530 Hz/mbar.\(^{26}\) Because \( K \) for permeation of both He and Ne through Si\(^{27}\) is several orders of magnitude smaller than through borosilicate glass,\(^{18,24}\) one can neglect the Si parts of the cell here and treat \( \tau \) of Eq. (2) applying to the cell’s borosilicate windows only. Note that because for our Ne buffer gas cells \( P_{in} \gg P_{ext} \), a negative drift of the intrinsic cell frequency is expected.

The Cs micro-cells studied (see Fig. 1(b)) are similar to those described by Hasegawa \textit{et al.}\(^{16,17}\). The cells are composed of a 1.4 mm thick Si wafer, closed on both sides by a 0.5 mm thick borosilicate33 glass\(^{28}\) plate using anodic bonding.\(^{29}\) The cells have a two chamber design, with one chamber housing a Cs dispenser and a separate chamber of 2 mm diameter for atom interrogation. After cell sealing, atomic Cs is released from the dispenser by local heating with a laser beam, using the post-activation process reported by Nieradko \textit{et al.}\(^{30}\). The cells also contain pure Ne buffer gas that shows a nonlinear temperature dependence of the Cs clock transition frequency, resulting in suppressed tempera-ture sensitivity close to the inversion temperature of 81 \( ^\circ\text{C} \).\(^{26,31}\)

We measure the intrinsic frequency of the Cs-Ne vapor cells using an experimental atomic clock,\(^{31,32}\) see Fig. 1(a). A distributed feedback (DFB) diode laser emits light at 894 which is frequency modulated by a fiber coupled Electro Optic Modulator (EOM) driven by a frequency synthesizer at \( \approx 4.6 \) GHz (half the Cs ground-state splitting), resulting in a phase modulation index of \( M = 1.53 \) for the optical spectrum. CPT resonances are excited with the two first-order modulation sidebands, of right-handed circular polarization, coupling the \( |F_g = 3, m_F = 0 > \) and \( |F_g = 4, m_F = 0 > \) states to

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**TABLE I.** Comparison of permeation constants \( K \) for He and Ne from the literature, and predicted resulting valued for \( \tau \), \( L \), and intrinsic cell frequency drift for the microfabricated cell under study, at 81 °C.

<table>
<thead>
<tr>
<th>Permeation system</th>
<th>( K ) (m(^2)s(^{-1})Pa(^{-1}))</th>
<th>( L ) (mbar-l/s)</th>
<th>( \tau ) (days)</th>
<th>Initial frequency drift (day(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>He through Pyrex 7740 (Ref. 20)</td>
<td>( 6.5 \times 10^{-19} )</td>
<td>( 2.0 \times 10^{-9a} )</td>
<td>( 62^a )</td>
<td>( -9.6 \times 10^{-12a} )</td>
</tr>
<tr>
<td>Ne through silica (Ref. 22)</td>
<td>( 1.9 \times 10^{-21} )</td>
<td>( 5.6 \times 10^{-12a} )</td>
<td>( 2.1 \times 10^{4a} )</td>
<td>( -1.7 \times 10^{-10a} )</td>
</tr>
<tr>
<td>Ne through Pyrex 7740 (Ref. 24)</td>
<td>( 1.06 \times 10^{-22} )</td>
<td>( 3.1 \times 10^{-13a} )</td>
<td>( 3.8 \times 10^3a )</td>
<td>( -9.6 \times 10^{-12a} )</td>
</tr>
</tbody>
</table>

*Values calculated from reference data for \( K \).
\[ F_e = 4 \text{ m} \, F = 1 > \] on the Cs D1 line, with a total optical intensity of 0.5 mW/cm². We test two similar vapor cells, samples 1 and 2, with Ne buffer gas pressures of 62 and 77 mbar, respectively. The vapor cell under test is housed in the clock physics package, where it is held at a temperature of 81 °C (inversion temperature of Cs clock transition for Ne buffer gas?), and a DC magnetic field of 5.8 μT is applied to lift the Zeeman degeneracy of the Cs ground states. We refer to these experimental conditions as the clock operation conditions.

Fig. 2 shows a typical CPT resonance, with a line width of 6.7 kHz and a contrast of 0.62%. For measuring the clock frequency, we close the clock loop and use a phase comparator to measure the local oscillator (LO) frequency against a 5 MHz H-maser reference (frequency stability of \( \approx 10^{-15} \) at 1000 s, long-term drift of \( 5 \times 10^{-15} \) day).

We now identify different sources of instability in clock operating conditions, evaluated as Allan deviation at one day of integration time here to obtain upper limits on the deterministic long-term changes. The intensity light shift coefficient \( \chi^{c2} \) is given by the slope of the clock frequency as a function of the light intensity. With \( x = 300 \text{ Hz cm}^2/\text{mW} \) and a fractional intensity instability of the DFB laser, \( \sigma_{\Delta I/\Delta L} = 4.5 \times 10^{-3} \) at one day, the clock fractional frequency instability at one day induced by the intensity light shift is obtained as

\[
\sigma_x(\tau) = \frac{I \sigma_{\Delta I/\Delta L} \chi}{\nu_{c2}} = (9.7 \pm 1.4) \times 10^{-11}. \tag{4}
\]

Similarly, we use a frequency light shift coefficient \( \beta \) of \(-644 \text{ mHz/MHz} \) (Ref. 32) and estimate the fractional frequency instability of the DFB laser, \( \sigma_{\Delta I/\Delta \nu} \approx 7 \times 10^{-9} \) at one day, for laser frequency locking to the buffer-gas broad-ened Cs D1 absorption lines. The fractional clock frequency instability at one day induced by the frequency light shift is then

\[
\sigma_\beta(\tau) = \frac{\nu \sigma_{\Delta I/\Delta \nu} \beta}{\nu_{c2}} = (1.2 \pm 0.1) \times 10^{-10}. \tag{5}
\]

The second-order Zeeman effect induces a clock frequency offset of \( +1.4 \) Hz, calculated from the second-order Zeeman coefficient \( K_0 = 427 \times 10^8 \text{ Hz/m}^2 \), and the total magnetic field at cell location (including applied C-field, geomagnetic field, effect of magnetic shields, etc.) measured on magnetically sensitive Zeeman transitions. Repeated measurement of the magnetic field over the study duration (see Fig. 3) yields the clock fractional frequency variations due to the second order Zeeman effect of \((8.7 \pm 2.1) \times 10^{-14} \) at one day, which includes the deterministic variations of external magnetic fields here. Using the first-order temperature coefficient of \((4.8 \pm 0.5) \times 10^{-10}/\text{K} \) measured for the vapor cell and an estimated 10 mK of cell temperature variation at one day, we calculate a temperature-induced fractional clock frequency instability of \((5.1 \pm 0.2) \times 10^{-12} \) at one day (long-term deterministic drifts from potential aging of key electronic components are estimated to be ten times smaller). The impact of the cell barometric effect on the clock frequency instability depends on the environmental pressure variation, measured at one day as \( 5 \times 10^{-3} \) mbar. By scaling Riley’s data to our cell, we find a barometric sensitivity of our cell of \( 5 \times 10^{-6} \text{ Hz/mbar} \) and a corresponding clock frequency instability of \((2.4 \pm 1.0) \times 10^{-15} \) at one day.

Table II summarizes the upper limits on the deterministic variations in the clock frequency shifts, in terms of \( \sigma(\tau) \) at \( \tau = 1 \) day. The total frequency variation is calculated as \((2.2 \pm 0.5) \times 10^{-10} \) day, with the light-shift as dominating contribution. The measured clock frequency stability reaches \( 3 \times 10^{-11} \) at 100 s and \( 2.7 \times 10^{-10} \) at one day, in close agreement with the total clock frequency variation from Table II. Clock frequency drifts recorded over several days are around \( 1 \times 10^{-10} \) day, also consistent with the upper limits of Table II.

In order to avoid the dominant instability contribution due to the light shift, we periodically determine the intrinsic cell frequency by recording the clock frequency for different light intensities and extrapolating to zero light intensity. The temporal variation in the statistical uncertainty from this extrapolation is computed to be \((4.2 \pm 1.1) \times 10^{-13} \) day. We

<p>| TABLE II. Upper limits on the long-term deterministic variations in sources of clock frequency shifts. |</p>
<table>
<thead>
<tr>
<th>Source of frequency shift</th>
<th>( \sigma(\tau) ) in clock operation conditions (at 1 day)</th>
<th>( \sigma(\tau) ) in zero-light extrapolation (at 1 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency light shift</td>
<td>((1.2 \pm 0.1) \times 10^{-10})</td>
<td>((4.2 \pm 1.1) \times 10^{-13})</td>
</tr>
<tr>
<td>Intensity light shift</td>
<td>((9.7 \pm 1.4) \times 10^{-11})</td>
<td>((9.7 \pm 1.4) \times 10^{-11})</td>
</tr>
<tr>
<td>Cell temperature shift</td>
<td>((5.1 \pm 0.2) \times 10^{-12})</td>
<td>((5.1 \pm 0.2) \times 10^{-12})</td>
</tr>
<tr>
<td>Cell barometric shift</td>
<td>((2.4 \pm 1.0) \times 10^{-15})</td>
<td>((2.4 \pm 1.0) \times 10^{-15})</td>
</tr>
<tr>
<td>Second order Zeeman shift</td>
<td>((8.7 \pm 2.1) \times 10^{-14})</td>
<td>((8.7 \pm 2.1) \times 10^{-14})</td>
</tr>
<tr>
<td>Total variation</td>
<td>((2.2 \pm 0.24) \times 10^{-10})</td>
<td>((5.6 \pm 0.2) \times 10^{-12})</td>
</tr>
</tbody>
</table>
TABLE III. Time constant and linear drift of intrinsic cell frequency from Fig. 3, and resulting permeation rates L and permeation constants K, for the micro-fabricated cell under study at 81 °C.

<table>
<thead>
<tr>
<th>Permeation system</th>
<th>K (m² s⁻¹ Pa⁻¹)</th>
<th>L (mbar l/s)</th>
<th>τ (days)</th>
<th>Frequency drift (day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne through borofloat33</td>
<td>(5.7 ± 0.7) × 10⁻²²a</td>
<td>(1.7 ± 0.2) × 10⁻¹²a</td>
<td>69700 ± 8500</td>
<td>(−5.2 ± 0.6) × 10⁻¹¹</td>
</tr>
</tbody>
</table>

*aValues calculated from τ from Fig. 3.

Table: Frequency drift (day⁻¹)

<table>
<thead>
<tr>
<th>Cell sample</th>
<th>PSel (mbar)</th>
<th>Tcell (°C)</th>
<th>Intrinsic cell frequency drift (day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>62</td>
<td>81</td>
<td>(−5.2 ± 0.6) × 10⁻¹¹</td>
</tr>
<tr>
<td>2</td>
<td>77</td>
<td>150</td>
<td>(−4.5 ± 0.2) × 10⁻¹⁰</td>
</tr>
</tbody>
</table>

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Schott borofloat33 datasheet, Schott technical glass solutions GmbH, Jena, Germany, see http://www.schott.com/borofloat.


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