Sub-ppb/K temperature drift of NMR field probes using intrinsic magnetostatic compensation

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Motivation: Magnetic field monitoring with NMR field probes[1] is a powerful tool for sequence development and quality assurance in MRI. Especially in protocols where long term stability is required (e.g. BOLD or phase fMRI, MR-thermometry, etc.), a correction for drifts and other slow disturbances may enhance the quality of the MR measurements substantially[2]. However, since these effects are often driven by thermal processes, e.g. through gradient heating, they potentially affect also the NMR field probes used for their characterization. Their temperature dependence is caused by a series of physical effects. By carefully identifying, quantifying and eventually manipulating them, it is possible to play them off against each other and to come up with an NMR field probe, whose temperature dependent frequency shift is reduced by more than an order of magnitude (from 11 ppb/K to below 0.1 ppb/K for H_2O-based probes), increasing the stability of the field monitoring substantially.

Theory: In a simple model the precession frequency of a spin in the detector liquid can be described as follows (up to 1st order in χ_i and σ):

$$\omega = \gamma B_0 \left(1 + \sum_i \eta_i \chi_i + D\chi_{sample} - \sigma\right) \quad \textbf{(eq 1)}$$

Where γ is the gyromagnetic ratio, η_i a geometry factor describing the field at the center of the volume of interest produced by the remote magnetized structure of volume susceptibility χ_i (e.g., the field produced by the magnetized probe cast), D the geometry factor of detector liquid volume[3], χ_{sample} the total magnetic susceptibility of the detector liquid and σ its chemical shift. Thermally induced drifts of the field probe frequency are caused by two processes: (i) The temperature dependence of the chemical shift σ is caused by a temperature dependent change in the electronic environment of the nucleus. Especially when strong intermolecular interactions are present (e.g. hydrogen bridge bonding in water), the temperature dependence can be very pronounced (10.3 ppb/K [4]) and is used to conduct NMR-thermometry[5]. The presence of paramagnetic substances can lead to an additional, temperature-dependent chemical shift (NMR-shift reagents). However, these mechanisms have been found to be of less importance for the systems used in this work. (ii) Temperature dependent susceptibility changes originate from various physical effects. For diamagnetic substances (Langevin and Landau diamagnetism), the molar susceptibility χ_m is independent of temperature and only material density changes $n_0(T)$ affect the relevant volume susceptibility $\chi = \chi_m n_0$. Paramagnetic species can have both, temperature independent (Pauli and Van-Vleck paramagnetism) and temperature dependent (Langevin paramagnetism) contributions. The temperature dependence of the latter (which is relevant in this work), originate from the Boltzmann statistics of the net polarization of the magnetic moments in an external field. It leads to a $1/T$-dependence of the molar susceptibility (Curie-Law). For small temperature changes ΔT, it can be linearized as

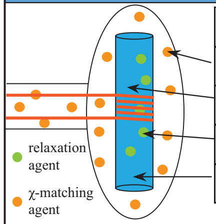
$$\chi_m(T_0 + \Delta T) = \chi_m(T_0) - \chi_m(T_0)\frac{\Delta T}{T_0} \quad \textbf{(eq. 2).}$$

Density changes will also change the volume susceptibility but are in general negligible compared to the Curie-dependence. Looking at eq. 1, it can be seen that the temperature-dependent, relative frequency variation can be modeled as:

$$\Delta\omega(\Delta T) = \sum_i n_i \Delta\chi_i(\Delta T) + D\Delta\chi_{sample}(\Delta T) + (-\Delta\sigma(\Delta T)) \quad \textbf{(eq. 3).}$$

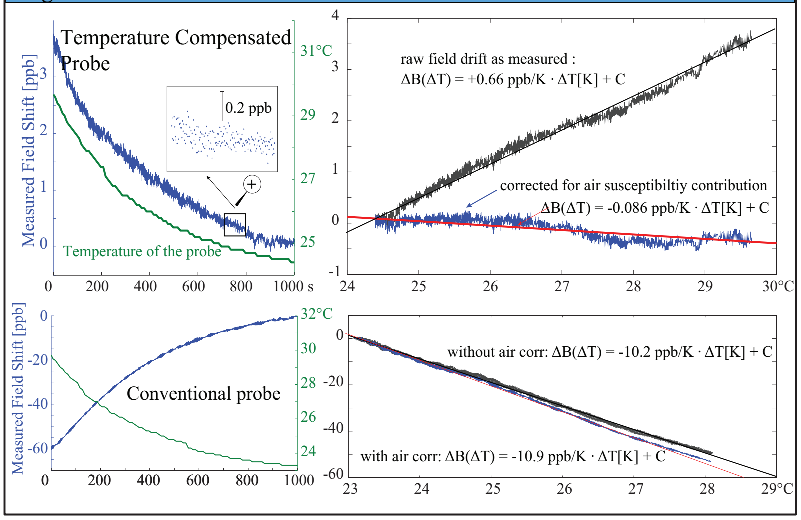
Hence, the temperature dependence of the probe's precession frequency can be zeroed by balancing all the involved terms through an adjustment of their geometry factors and susceptibilities.

Figure 1



Structure	Geometry n_i, D	$\Delta\chi(\Delta T)$ /$-\Delta\sigma(\Delta T)$ [ppb/K], T_0 = 295 K	Physics
χ-matched epoxy of probe head	0.0475	-34.4	Curie behavior of χ-matching agent
χ of detector liquid (H_2O) excl. relaxation agent	-1/6	-1.253 [7]	H-bridge bonding and density changes[7]
relaxation agent in detector liquid	-1/6	$-\frac{\chi_V(T_0)}{295\,K}$	Curie behavior
chemical shift of detector liquid (H_2O)	1	-10.3 [4]	H-bridge bonding[4]

Figure 2



Methods: All the relevant contributions have been identified by means of numerical simulations or experiments, and the corresponding geometry factors (n_i and D) were calculated.[6] The respective susceptibility changes were estimated from eq. 2, 3. As can be seen in figure 1, for the given geometry, all the temperature dependences come with a negative sign and even a partial compensation of the effects can only happen due to the negative sign of the geometry factor of the capillary filling. This is a direct consequence of the sphere of Lorentz. Accordingly, the amount of bulk susceptibility shift induced by the paramagnetic relaxation agent dissolved in the detector liquid is the only parameter where leverage can be applied. Solving for $\chi_V(T_0)$, a required susceptibility shift of +21 ppm induced by the relaxation agent is needed to cancel all the competing effects. For commonly used relaxation agents (e.g. Cu^{2+} or Gd^{3+} salts) this would lead to relaxation times far below useful levels for conventional monitoring applications (< 1 ms). Instead Dy^{3+} was used; compared to its magnetic moment, Dy^{3+} is a rather ineffective relaxation agent. The optimal concentration is 37.7 mM of $Dy(NO_3)_3.5H_2O$ in H_2O.

Results: Five temperature stabilized NMR field probes were constructed as described above. Their behavior under thermal changes was measured in a 3 T whole human MR scanner (Philip Healthcare, the Netherlands). The test-probes were mounted in an insulation box (styro-foam) and heated by adding a block of heated aluminum. After removal of the Al-block, the field probe was left for about one minute to settle in a thermal equilibrium. During the following slow cool down (it took about 20 min to reach ambient temperature) the resonance frequency of the field probe was measured repeatedly. B_0 and clock drifts were monitored using an additional set of four thermally isolated field probes located around the insulation box (watchdog). The temperature of the test-field probe, as well as of the watchdog probes were logged with four fluoroptic temperature sensors. It is to be noticed, that the air contained within the insulation box is equally cooling down during the experiment. The effect of the associated susceptibility change (-2.59 ppb/K[8]) will corrupt the field measurement. However, knowing the probe's geometry factor (= 0.3 for an oblate ellipsoid of 20x13x16 mm), the contribution due to the changing air-magnetization can be quantified. Figure 2 shows the measured temperature dependence of a temperature-compensated and a conventional field probe (25 mM $CuSO_4$ doping) and a linear regression of their drift for the corrected and the uncorrected data.

Discussion: A method to compensate for temperature-induced drifts of NMR-field probes was introduced and tested successfully. Compared to a conventional field probe, the T-dependence was reduced by more than two orders of magnitude. Although the T_1 was slightly shorter than for conventional probes (45 vs 55 ms), the probe's $\xi = SNR\cdot\sqrt{BW}$ remained unaffected ($9\cdot10^4\ \sqrt{Hz}$), and a thermal field measurement precision of 20 pT (0.006 ppb @ 3 T) was calculated. The presented solution does not require calibration or additional hardware and the field probe can be used without further constraints or limitations. So far, the suggested method was validated on the example of a H_2O-based proton probe field. However, the method is generally applicable and could be used to compensate probes with different detector substances as well, increasing the range of potential probe liquids. The availability of field probes that are immune to temperature variations enables field monitoring applications of yet higher accuracy and flexibility. Furthermore, the presented method could also be used to build temperature-stabilized reference phantoms for other MR-applications.

References: **[1]** De Zanche et al., *MRM,* 60:176 (2008). **[2]** Kasper et al., *MRM, n/a (2014)* **[3]** Chu et al., *MRM,* 13:239 (1990) **[4]** Hindman, *J. Chem. Phys.*, 44:4582 (1966) **[5]** Ishihara et al., *MRM* 34:814 (1995) **[6]** Marques & Bowtell, *Concept. Magn. Reson. B,* 25B:65 (2005) **[7]** Philo & Fairbank, *J. Chem. Phys.,* 72:4429 (1980) **[8]** Davis, R. S. *Metrologia, 35:*49 (1998)