Rapid Scan Electron Paramagnetic Resonance using an EPR-on-a-Chip Sensor

Reply from the authors

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Dear colleagues,

My co-authors and I would like to thank Daniella Goldfarb as editor and the reviewers for their efforts in evaluating our manuscript. We are pleased that the reviewers' comments are generally positive and provide valuable suggestions to improve the manuscript even further. In response, we revised the manuscript as detailed below (reviewers suggestions/remarks are indented, our replies not indented). Please note that the numbers of equations and line numbers changed with respect to the preprint.

RC1

General comment

> The manuscript presents a new method that combines the use of EPR on a chip technology with rapid scan (RS) approach in EPR. EPR on a chip uses a small microwave oscillator which is based on active microwave circuit coupled to LC circuit with inductive loop on which the sample is placed. EPR signal is recorded as changes in the oscillator frequency and/or amplitude at the resonance condition. RS with EPR on a chip can be very advantageous since instead of scanning the magnetic field, which has many limitations, one can scan the frequency without the need to have a low Q resonator. In general, the paper is well-written and presents nice experimental results. I have one major comment and few minor comments as follows:

We thank the reviewer for the kind words about our work and the manuscript.

Major comment

> The paper makes some claims about spin sensitivity, which are not convincing. It uses a test sample of BDPA with about 2x10^15 spins (this number is not written in the paper, but can be calculated using the data given), and shows measurements with SNR of 236 and then claims, based on data from another paper, that the absolute spin sensitivity of the setup is 6x10^7 spins. Same problem with the claims for concentration sensitivity. I am afraid this looks very unconvincing. The authors should either present clear experimental evidence for their claim spin and concentration sensitivities, or tone down their claims.

The calculation of the RS spin sensitivity was removed from the manuscript. The sensitivity for the AM signal of the CW measurement calculated from the SNR of the spectrum, the number of spins in the sample and the effective noise bandwidth of the detection system is now stated, which is of the order 10^13 spins/G/sqrt(Hz). In addition, the FM sensitivity is stated, which is of the order of 10^9 spins/G/sqrt(Hz). In the revised version of the manuscript, we now provide some reasoning why the AM sensitivity is worse than the FM sensitivity and also include more information about the AM detection using VCO-based EPRoC detector. Also, the number of spins in the sample (~10^15 spins) is now part of the sample description.

Minor comments:

> Line 33: Conventional EPR employs two types of experimental procedures. High Q is good mainly for CW.

We added the information that CW benefits from high Q.

> Line 43: kEuro and not TEuro.

The term was corrected.

> Line 55: Suggest to also cite related works, such as : "A Single-Chip Electron Paramagnetic Resonance Transceiver"" and "An Ultrasensitive 14-GHz 1.12-mW EPR Spectrometer in 28-nm CMOS"

We added the proposed citations and added some information on the different detection principles.

> Line 105: Less than 10 ppm is not that simple.. and also temperature stability is not simple..

We removed the statement of the homogeneity of the magnet to make the statement more general.

> Line 110: what is the max frequency of the AM demodulation?

The bandwidth of the implicit AM demodulator is a few hundred MHz (roughly 600 MHz). The information was added to the manuscript. Also, a more detailed description of the AM demodulation was added to the text in Sec. 2.1.

> Line 114 and other places: The claim for compactness of the system and the use of Rohde & Schwarz SMB100A and Anfatec eLockIn 203 and Zurich Instruments UHF-LIA as part of the setup seem to be conflicting.

We added the term "proof-of-principle" to the last sentence of the introduction to explain that we do not (yet) have a completely miniaturized spectrometer.

> Line 115: what is the minimal B1 that can be used to sustain working conditions for the VCO?

We added the minimal B1 of about 27 μT in the corresponding sentence.

> Line 121: What is the number of spins n the sample?

The number of spins (~10^15) is now stated in the text.

> Line 122: When referring to Appendices, please mention which Appendix.

All appendices are now specifically referenced in the text.

> Line 130: This discussion should come before mentioning AM modulation above.

The corresponding section was moved and extended to also include the remarks from RC2.

> Line 134: Possible cite this ref from Arxiv?

The article is now available as preprint of Magnetic resonance and is correctly cited.

> Line 140: Try to be more quantitative, what bandwidth you have, what is needed, etc..

The numbers are now given in the text with a reference to Appendix B, where the calculation is explained.

> Eqs 3 and 4: not clear why the authors talk about two types of conditions.

The two conditions are now mentioned in the discussion of Fig. 4.

> Line 165: Missing "of a"

The words "of a" were added to the corresponding sentence.

> Fig. 4: Is this plot for the same total acquisition time? bandwidth of detection? Is the amplitude and SNR are comparable?

The total acquisition time was different for the three saturation curves. The number of averages, however, was 50'000 for all curves. The sampling rate was 450 MHz for all time traces.

> Line 250: delete "is"

The word "is" was removed.

> Eq (9) : Please briefly explain why the driving function need to have "memory" to previous time periods and not simply reflect the frequency of excitation at a given time

We added an explanatory sentence to the Appendix A.

> Eq (12): This equation does not look intuitive. If T2 is very large the signal is changing slowly as you scan the frequency. Possibly it can be explained in 1-2 sentences.

This equation is now explained in the Appendix B.

> Line 338: re-arm?

We have removed the reference to the re-arm time in the main text and have given a description of the re-arm time of the lock-in amplifier in Appendix C.

RC2

General comments

> The manuscript present, for the first time, rapid scan measurements performed using a single-chip integrated oscillator. This approach was proposed and very briefly discussed in Ref. (Gualco et al., 2014), but not yet demonstrated experimentally. Contrary to the majority of previously reported works on the rapid scan, the rapid scan in this work is implemented as rapid frequency scan instead of rapid field scan. This is technically possible and very efficiently implemented because a microwave oscillator is used instead of a microwave resonator combined with a microwave source as in conventional EPR spectrometers. In the current implementation a scan range of 64 MHz at the maximum frequency of 1 MHz, which corresponds to a scan rate of 400 THz/s, has been demonstrated. This scan rate is slower that the best results reported to date for the rapid field scan. However, as claimed also by the authors, I believe that significant improvements are realistic. The single chip frequency rapid scan is, indeed, well suited to achieves scan widths, scan speeds, and scan rates well beyond the current limits of the magnetic field rapid scans. The EPR signal is detected as a variation of the oscillation amplitude as a function of the oscillation frequency. In principle, the measurement of the variation of the oscillation frequency would also be possible but, I guess, practically more complicated because the frequency variation due the EPR resonance would be much smaller than the frequency scan width, creating significant problem of "dynamic range" (which are difficult, although not conceptually impossible, to overcome). It is also important to underline that one of the major problems present in several of the previously reported single-chip integrated oscillator EPR detectors is the relatively large minimum B1, which creates saturation problems in conventional CW slow scan experiments. The use of the rapid scan overcome, at least partially, this issue since the optimum conditions are achieved with a larger B1. The rapid scan approach demonstrated here is certainly a very important milestone in the application of single-chip integrated oscillator as EPR detectors. For this reason, the manuscript certainly deserve to be published.

We thank the reviewer for their detailed comments, which greatly helped us to improve our manuscript.

Major specific comments

> Abstract, Figure 2, lines 190-195, conclusions: The way the spin sensitivity is computed is not clear to me. The authors use a BDPA sample of 0.67 nL. From the spin density of BDPA (about 1.5x10^27 spins/m3), the number of spins is about 10^15. Since the measured SNR is about 236 in a measuring time of 0.75 s (Figure 2), the spins sensitivity seems to me something like 4x10^12 spins/sqrt(Hz),

> whereas the one declared in the paper is 6x10^7 spins/sqrt(Hz). Since the difference is more than 4 orders of magnitude, I think there is something not correct or unclear in the author's reasoning. The reasoning of considering the previous results obtained with the frequency variation and extrapolate it to this case of amplitude detection based on the ratio in SNR between the CW and RS experiments performed here seems to me not "conceptually" correct (and not compatible with the results shown in Figure 2).
>
> Lines 203-210: Also this part of the "sensitivity discussion" is not clear to me. In particular the discussion of the the PSD and RMS noise values are not clear to me. PSD and RMS noise are two different quantities related by an integral once the integration bandwidth is properly defined. So the phrase "…the PSD noise is usually better than the RMS noise of an EPR spectrum…" does not make sense to me. I would suggest to the authors to define clearly how the experiment is performed (including the analog bandwidth and the digital processing) and the way they have computed the spin sensitivity from the processed data. This should be enough to compare it to other papers knowing the different way the experiments are carried out (CW, RS, pulsed), the experimental parameters (analog filtering, digital filtering, etc. etc.), and the given definition of the spin sensitivity. If the experimental conditions and parameters are properly described, each reader can easily "renormalize" them to his/her own sensitivity "definition".

The calculation of the RS spin sensitivity was removed from the manuscript. The sensitivity for the AM signal of the CW measurement calculated from the SNR of the spectrum, the number of spins in the sample and the effective noise bandwidth of the detection system are now stated, the former is of the order 10^13 spins/G/sqrt(Hz). Additionally, the FM sensitivity is now stated, which is about 10^9 spins/G/sqrt(Hz). We also explain why the AM sensitivity is worse than the FM sensitivity. Also, the number of spins in the sample (~10^15) is now part of the sample description.

> Lines 111: It is not clear if the voltage variation measured in this work is equal to the oscillation amplitude variation at the resonator ? This is a necessary information to evaluate if the amplitude detection implemented here can or not, in practice (and not in theory where effectively they should be similar in the respective optimized conditions) achieve the same spin sensitivity as the frequency detection reported previously using the same chip. To complete the comparison the frequency and amplitude noise spectral densities should also be also considered. This point is, of course, linked to the previous one. I wonder if the voltage amplitude measurement performed here is not "sub-optimal" (i.e., the voltage variation is significantly smaller than the voltage variation at the resonator, which in turn makes the spin sensitivity worse that in the case of the frequency variation detection if the voltage noise is not reduced by the same factor).

We agree that the given information about the AM detection was not detailed enough in the first version of the manuscript. Therefore, a more thorough description concerning the AM-sensitive detection has been added to the manuscript in Sec. 2.1 of the manuscript.

> Figure 2, Figure 3, lines 355-358: Why the two signals in Figures 2 and 3 are not identical ? I guess that it is because there is a mix of absorption and dispersion which gives non- identical signals when the frequency is scanned up or down (pure absorption signals would be have the same shape in the scan up and down, pure dispersion signals would have "mirror shapes" in the scan up and down). Please comment on this in the manuscript and write the details of the simulation in the Appendix E. It seems to me that the reported simulation results are not a result directly taken from EasySpin. Are the EasySpin absorption and dispersion signals combined with an appropriate phase shift maybe computed from an estimation of the Q-factor (as suggested by Equation 1) ? Or maybe a circuit simulator is used where the sample is modeled by a coupled resonator. This would be correct "quantitatively" for a CW slow passage at low B1 but I guess not for a RS.

The reviewer correctly explained the reason for the asymmetry, which was indeed missing in the manuscript. We now provide an explanation in the updated version of the manuscript. Additionally, the description of the simulation in Appendix E was extended to better explain the procedure.

> Figure 4 and Figure 5: In terms of precessing magnetization (i.e., Mxy), the maximum value for T1=T2 and the optimum level of B1 and scan speed is: (1/2)*Mo for the CW and Mo for the RS. So, in terms of precessing magnetization, the difference is 2 (and not 5). Of course, depending on the way the CW and RS signals are computed (field modulation amplitude, peak-to-peak or amplitude, etc. etc.) the ratio can be different. But, I would prefer to consider a more "fundamental" quantity which is the precessing magnetization. Of course, in practice the optimal condition for the CW with field modulation is obtained with a B1 and a field modulation amplitude which determines linewidth broadening, which might or not be "tolerable".

We agree with the reviewer that the "fundamental" quantity for the signal intensity is the precessing magnetisation. As already mentioned in the comment, the factor of 2 that we may gain with RS compared to CW is a theoretical concept since it only involves the precessing magnetisation. In this view, the spin system is completely saturated at (1/2)*Mo in CW. At this point, however, we do experience considerable line broadening in the spectrum, which complicates quantitative analyses.

Additionally, we added an explanation of the factor 5 (amplitude gain with higher B1 and faster scan rates), which was misleading in the preprint. The factor 5 may be gained considering the rapid scan measurements only as shown in the manuscript.

Minor comments

> Line 43: Typo: "50 kEuros" instead of "50 TEuros".

We corrected this mistake.

> Line 84: I agree that the approach proposed here could allow in the future to perform rapid scans larger than 20 mT (600 MHz). However in this manuscript it

> is demonstrated up to about 64 MHz. I think that this should be mentioned also here.

It is now mentioned in the text that we use a much smaller sweep width in the experiment. For that, we added the term “proof-of-concept” to the manuscript.

> Line 99: I think that it should be mentioned that “The rapid scan with single-chip integrated oscillators was proposed and briefly discussed in Ref. (Gualco et al., 2014), but not yet demonstrated experimentally. Here we report …..”

We added a similar statement to the manuscript.

> Line 105: “< 10 ppm”. Please specify on which volume you are considering <10 ppm homogeneity.

The statement about the homogeneity was removed and replaced by a more general statement.

> Lines 159 and 281: The reason why the “..in these experiments was limited by the RF generator to ….” is not very clear. I would suggest to add a couple of sentences to clarify this point. I guess this is related to the chip architecture and, in particular, to the way the frequency scan is implemented (more complex, clever, and efficient that a simple voltage externally applied to the integrated varactor).

We added a better explanation to the manuscript to describe the limitation of the RF generator. Additionally, we added more information about the chip architecture in Sec. 2.1.

> Line 250: Typo: “…about 5 is may be..” instead of “…about 5 may be..”

We removed the word “is”.

> Line 120: The minimum value of B1 produced by the chip is 27 uT or so. BDPA has significant saturation from B1 in the order of 100 uT or so. So the choice to use only BDPA as sample for this work does not allow to show one of the advantages of the RS when applied to the single-chip approach. The minimum B1 is often relatively large and might cause significant saturation in the conventional CW slow scan. I would suggest the authors to, at least, comment on this point (even if obvious for an expert). Although definitely not “necessary” and “important” for this manuscript, an RS experiment on a sample which is “deeply saturated” in the conventional CW slow scan mode would be a nice addition to the manuscript. A less elegant but maybe still valid example could be the use a very small sample of BDPA placed in close proximity to the coil wire where B1 is significantly larger to show that the RS scan can solve this saturation issue.

We agree that BDPA is not the ideal signal to demonstrate the benefits of RS due to its fast relaxation times. However, to facilitate an accurate and fair comparison between CW and RS, a sample that does not saturate at the fairly large B1 values is needed. Therefore, we added an explanation in the discussion of Fig. 4 explaining that BDPA is not the optimal sample to show the benefits of RS-EPR due to its fast relaxation rates.