

# Comparing relative double integral values in EasySpin vs. Xenon

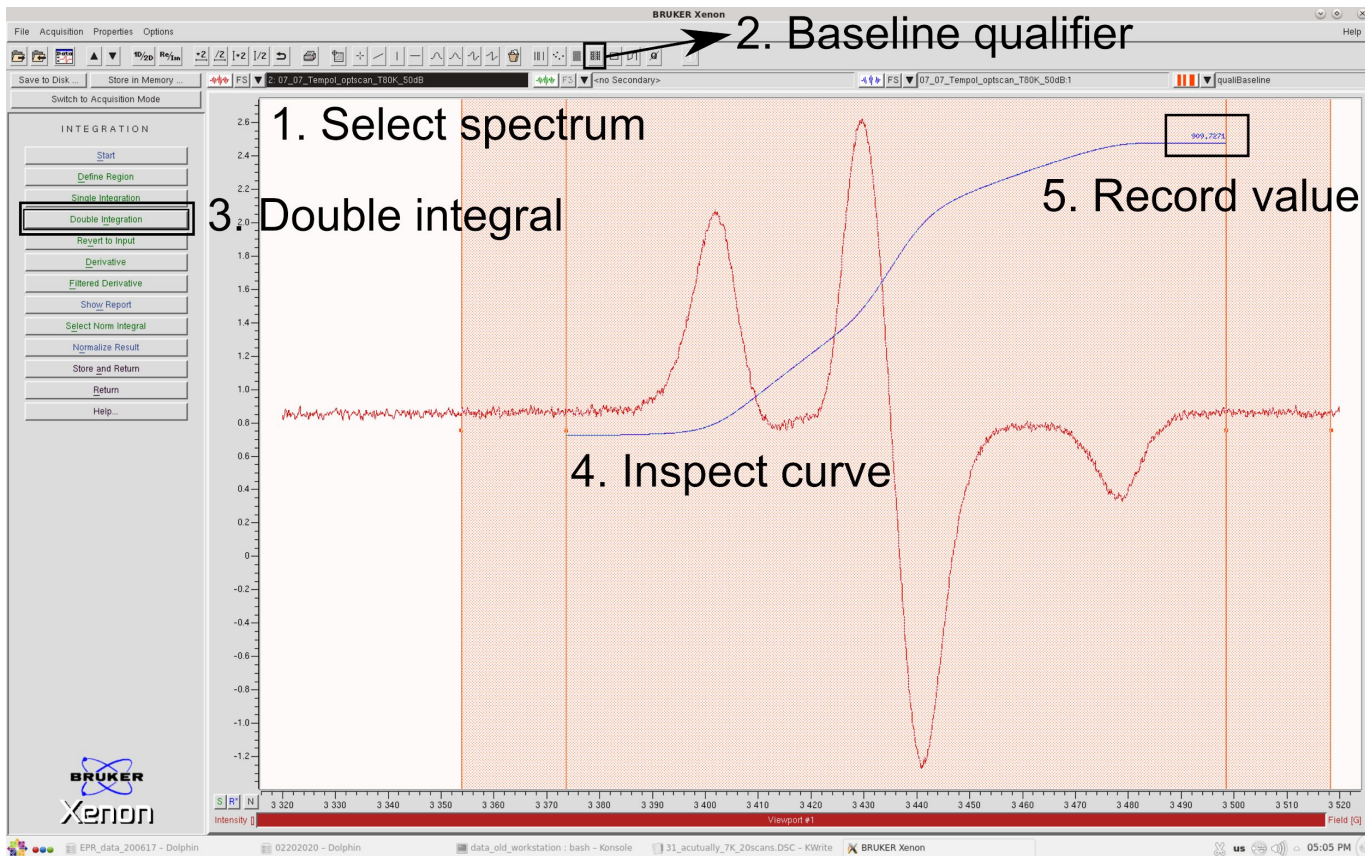
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9/9/20

# Outline

- I have recorded CW X-band EPR spectra of validated TEMPOL solutions, as well as, Cu ICP and Mn standards.
  - Sample temperatures = 25 - 80 K
  - 30% glycerol + MilliQ water solvent
  - Care was taken to avoid saturation.
- Measure the double integral (e.g. integral of the absorption spectrum) using Xenon, EasySpin and OriginLabs.
- Relative ratio of double integral when measured by EasySpin is different the value from Xenon or OriginLabs.
- Unclear if our issue is incompetence with EasySpin or a larger issue.

# Straightforward to measure DI in Xenon.



# Relative DI values from Xenon and OriginLabs

500  $\mu\text{M}$  CuICP standard Xenon double integral value = 15816.26 (arb.)

635.5  $\mu\text{M}$   $\text{MnCl}_2$  Xenon double integral value = 50915.19 (arb.)

Ratio = 3.219 (This step was also completed using OriginLabs and the ratio is 3.063.)

We used a modified version of the equation shown in Fig 11. 1 of *Quantitative EPR* by Eaton *et al.* to correct for differences in acquisition parameters and total electron spin. Then the ratio DI equals ratio of spins.

Calculated concentration of Mn sample based on Xenon ratio = 661.2  $\mu\text{M}$  (4% error)

# Double Integral from EasySpin

500  $\mu\text{M}$  CuICP standard EasySpin double integral value = 277410 (arb.)

635.5  $\mu\text{M}$   $\text{MnCl}_2$  EasySpin double integral value = 189430 (arb.)

Ratio = 0.683

After apply the correction factor the calculated concentration of Mn sample based on EasySpin ratio = 140.25  $\mu\text{M}$  (-78% error!)

# EasySpin Double Integration Script Template

```
% Template script for determination of Double Integral
% CuICP standard
% JTD 9/9/20
%=====

clear, clf

%
% update with filename
%

[b,s,param]=eprload('07_07_Tempol_optscan_T80K_50dB.DTA');

%plot(b/10,s,'k');

%
% Zero-order baseline correct using basecorr
%

s_bc=basecorr(s,1,0);

%plot(b/10,s_bc,'k');

%
% Integral
%
s_bcI=cumsum(s_bc);

%plot(b/10,s_bcI,'k');
```

```
%
% Polynomial baseline correction
% from EasySpin forum Matt Krzyaniak
%

tail = b/10 < 337 | b/10 > 350 & b/10 < 352;
[p,Es,mu]=polyfit(b(tail)/10,s_bcI(tail),4);
baseline=polyval(p,b/10,Es,mu);

s_bcIbc=s_bcI-baseline;

%plot(b/10,s_bcIbc,'k',b/10,s_bcI,'b',b/10,baseline,'r');

%
% Integral of absorptive spectrum (aka double integral)
%

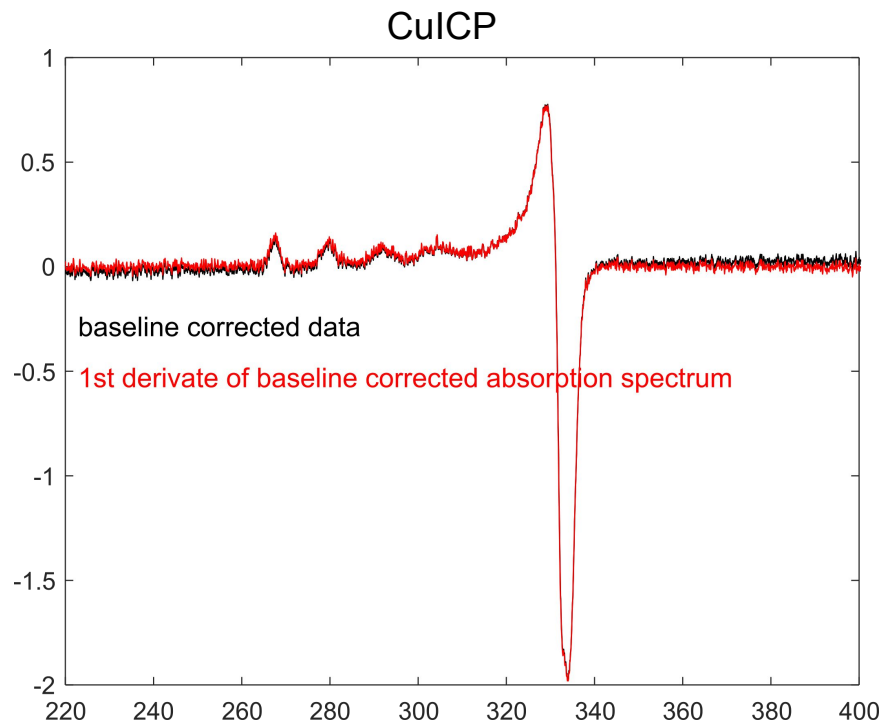
DI=sum(s_bcIbc);

%
% check by taking numerical derivative of baseline corrected
% absorptive spectrum
%

s_bcIbc_deriv=diff(s_bcIbc);
b_deriv=b(1:length(s_bcIbc_deriv));

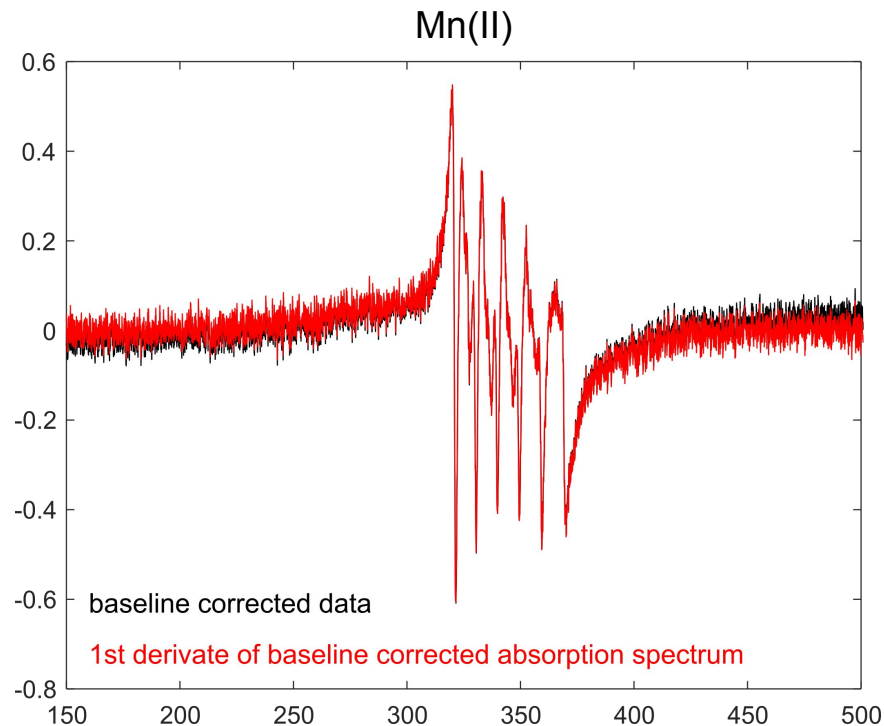
plot(b/10,s_bc,'k',b_deriv/10,s_bcIbc_deriv,'r');
```

# Control of EasySpin manipulations by scripts is OK.



DI = 2.7741e+05

Ratio = .683!



DI = 1.8943e+05

Why is my ratio so different when using  
EasySpin vis-a-vis Xenon?