High precision isotope ratio measurements of Sr and Nd at the nanogram level using the Phoenix TIMS with next generation Faraday detectors

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34th IGC presentation 2958

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What are the parameters required for high precision measurements of small samples? (on Faraday collectors)

- High Sensitivity
  - Instrument sensitivity
  - Use of activators
- Low noise
  - Close to theoretical Johnson noise
  - Baseline stability
- Gain stability between detectors
  - Required for static analyses
- Multidynamic measurements
  - Eliminates gain and efficiencies
  - But can it be used on small samples?

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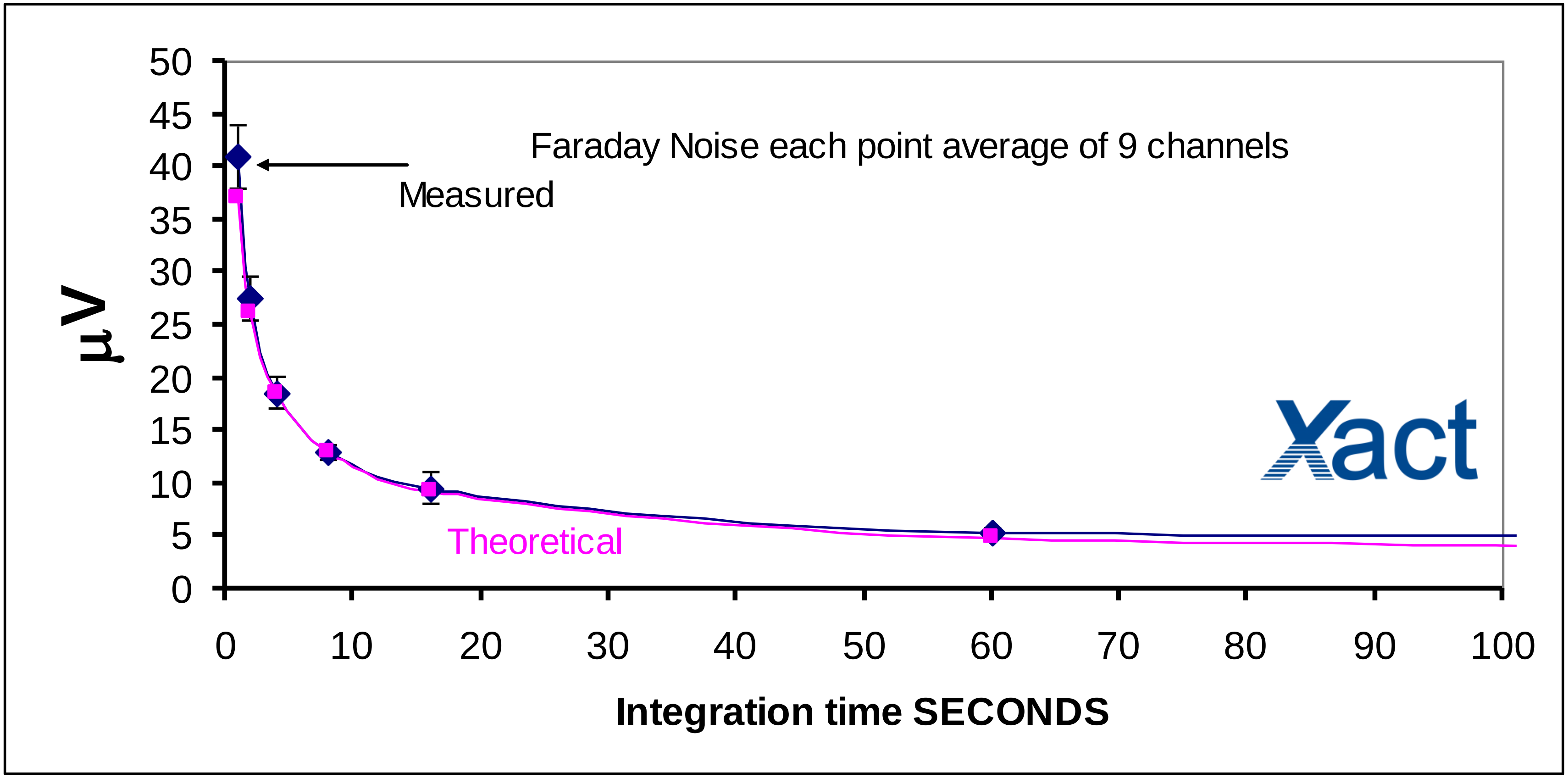
How quiet are *X*act amplifier/resistor boards



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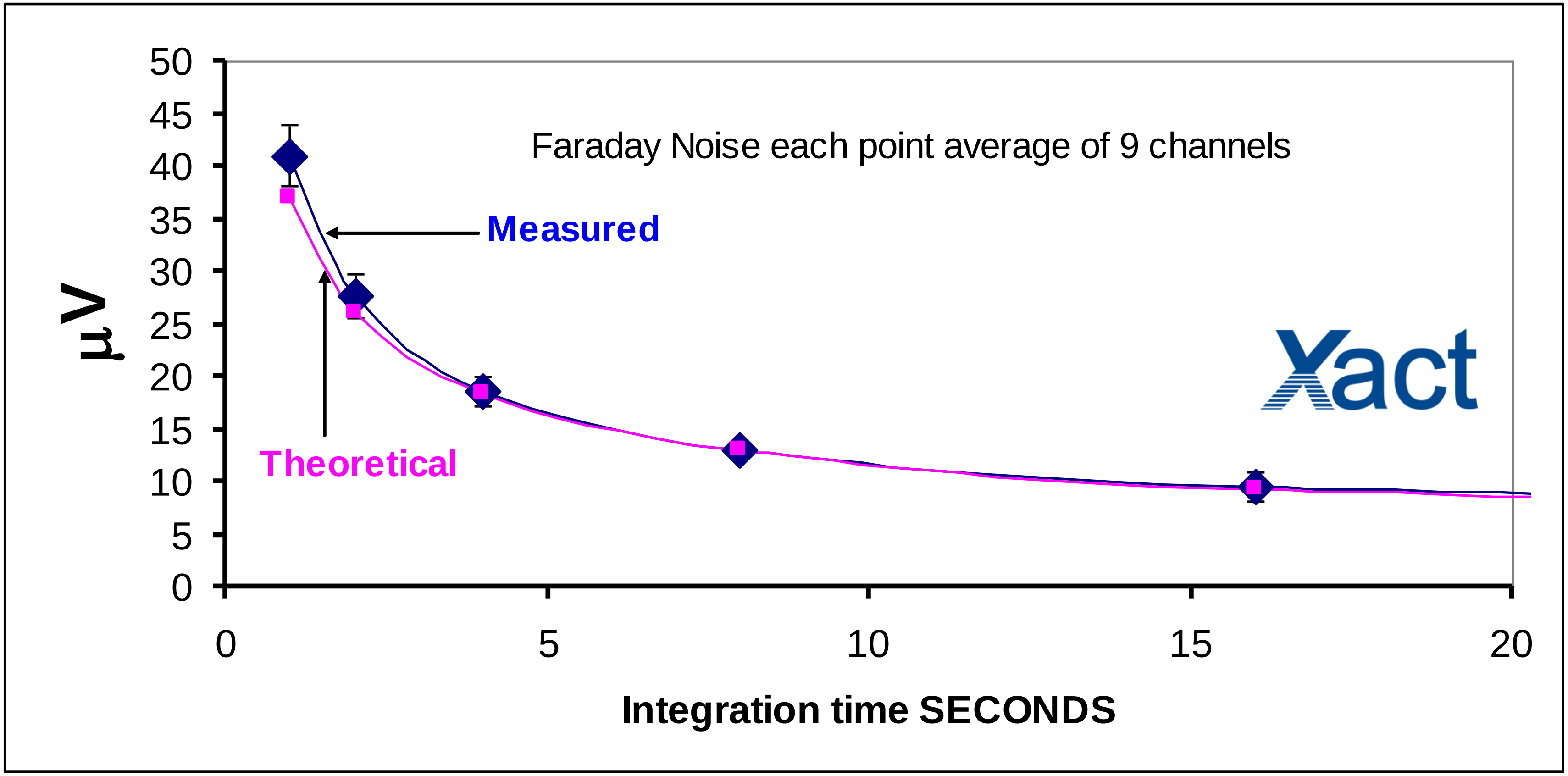
How quiet are *X*act amplifier/resistor boards



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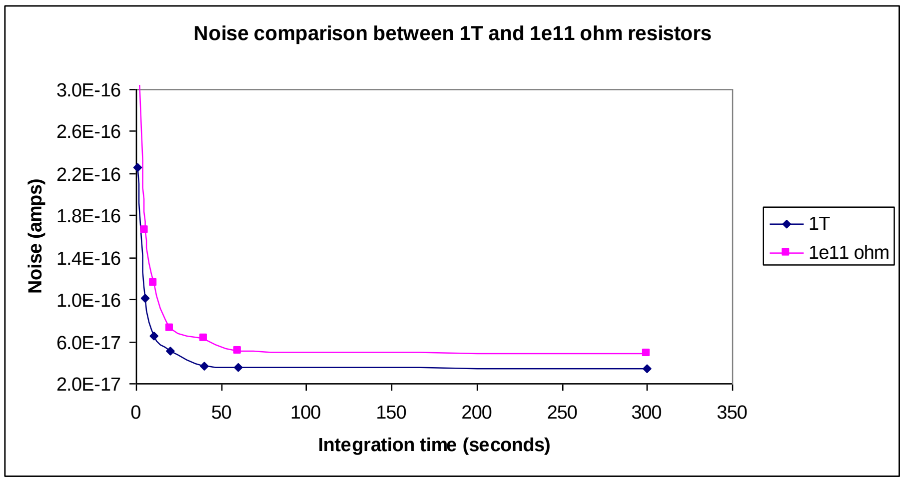
Noise comparison between $1e^{11}$ and 1T resistors



Noise (Amps)			
Integration time (seconds)	$1e^{12}$ ohm n=5	$1e^{11}$ ohm n=4	$1e^{11}/1e^{12}$
1	2.3E-16	3.8E-16	1.7
5	1.0E-16	1.7E-16	1.6
10	6.5E-17	1.2E-16	1.8
20	5.1E-17	7.3E-17	1.4
40	3.6E-17	6.3E-17	1.7
60	3.6E-17	5.1E-17	1.4
300	3.5E-17	4.9E-17	1.4

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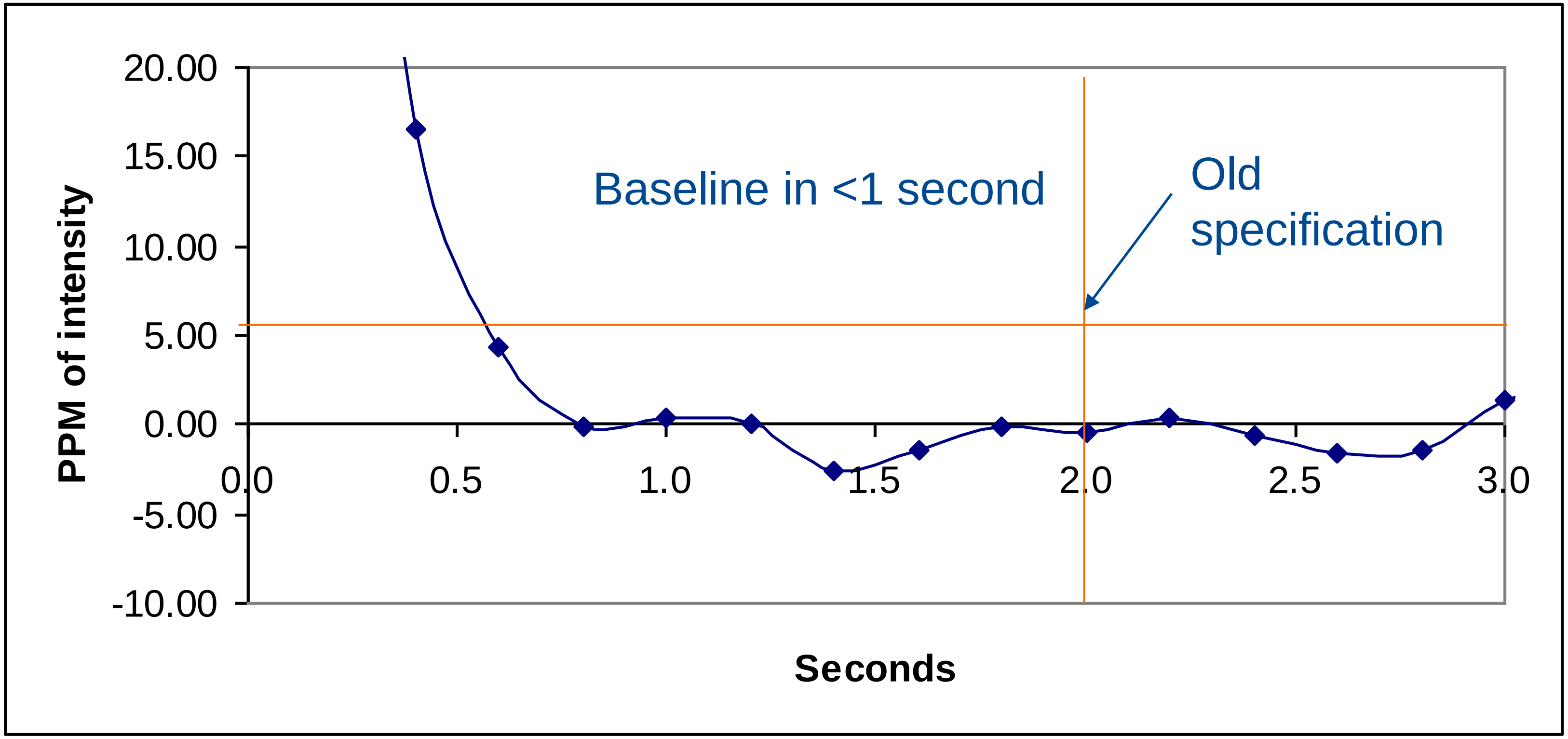
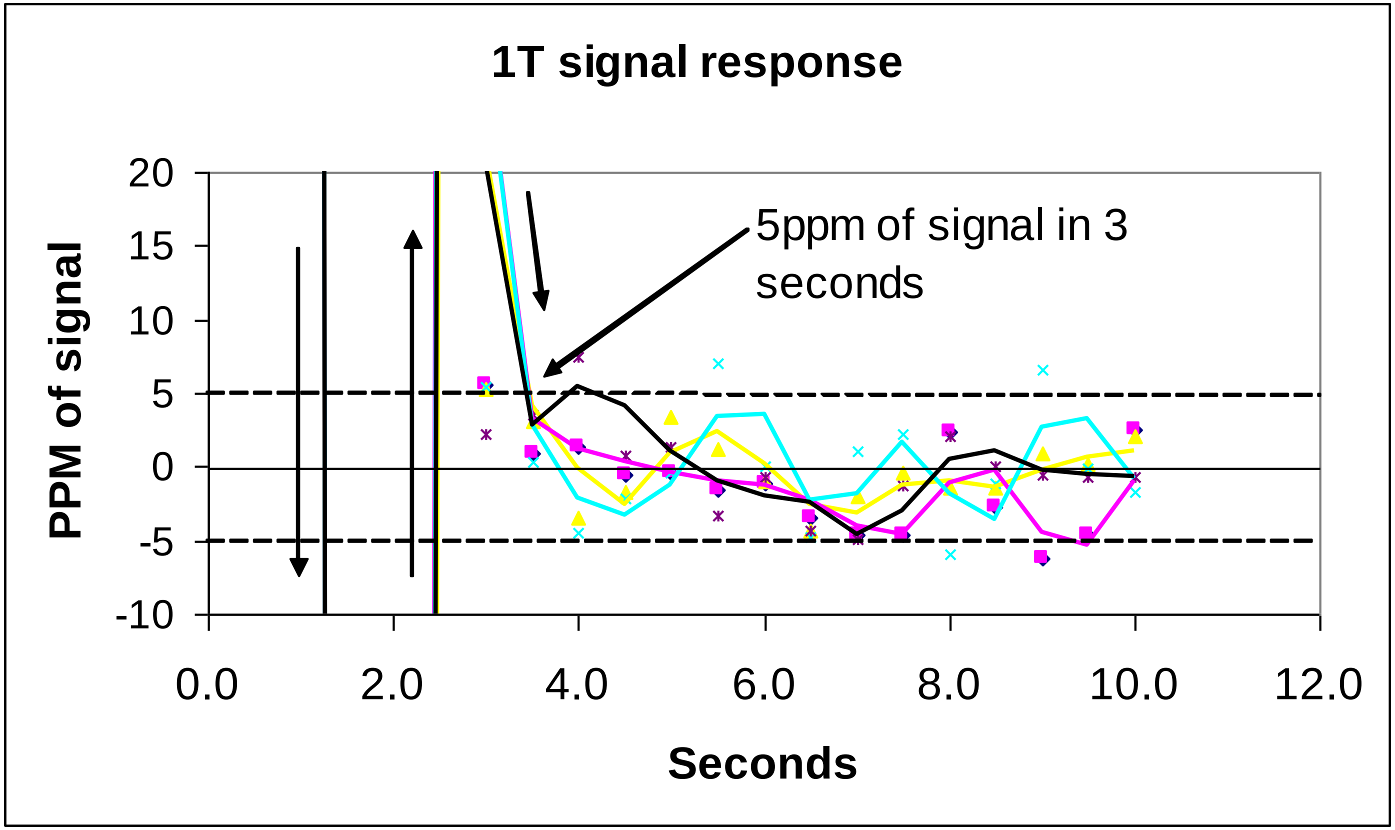
How fast are *X*act resistors (1e[11] ohm)?

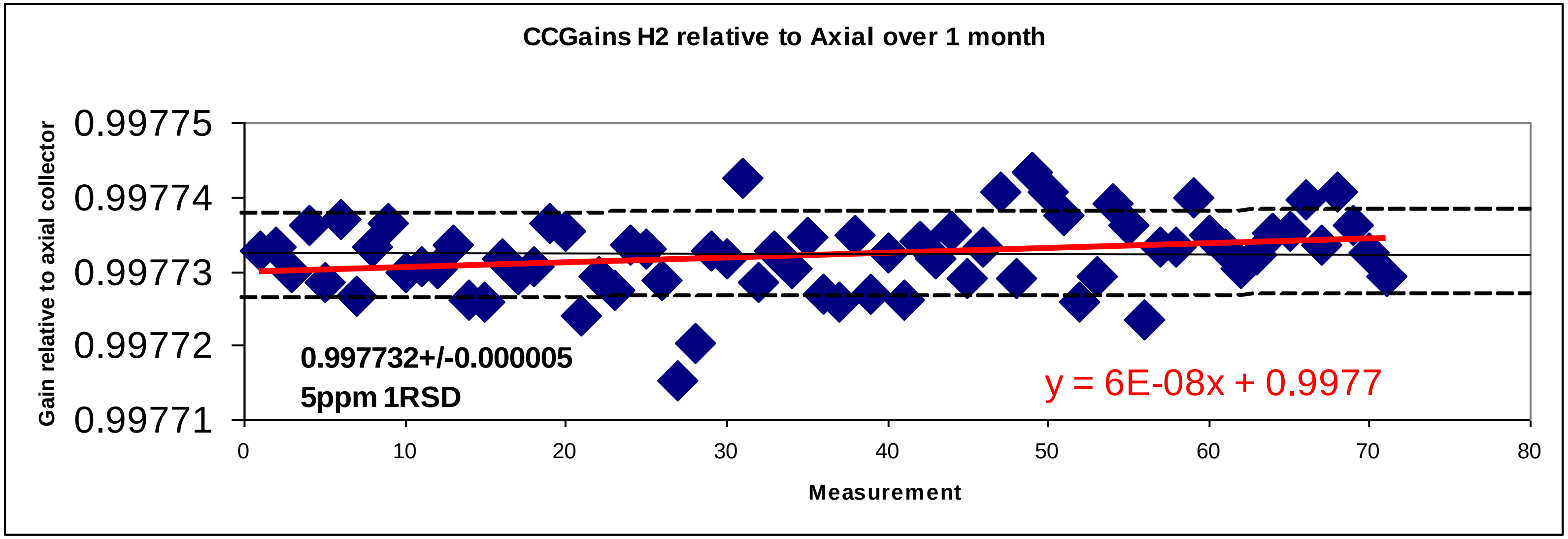


1T baseline in 4 seconds



Gain stability 5ppm over 1 month

No drift.



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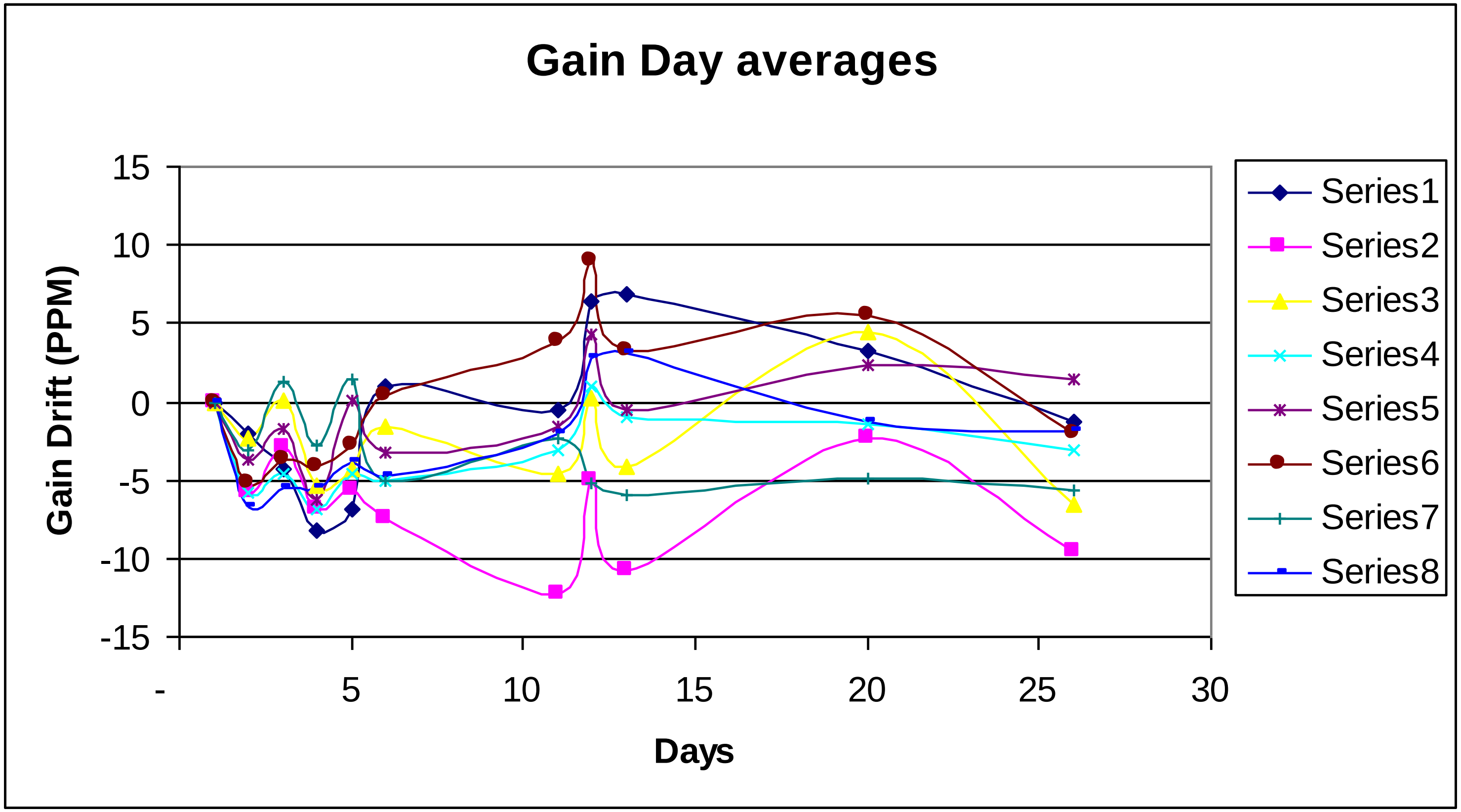
Day averages

Reduced scatter shows subtle coherent trends.

Measured on factory floor with no environmental temperature control



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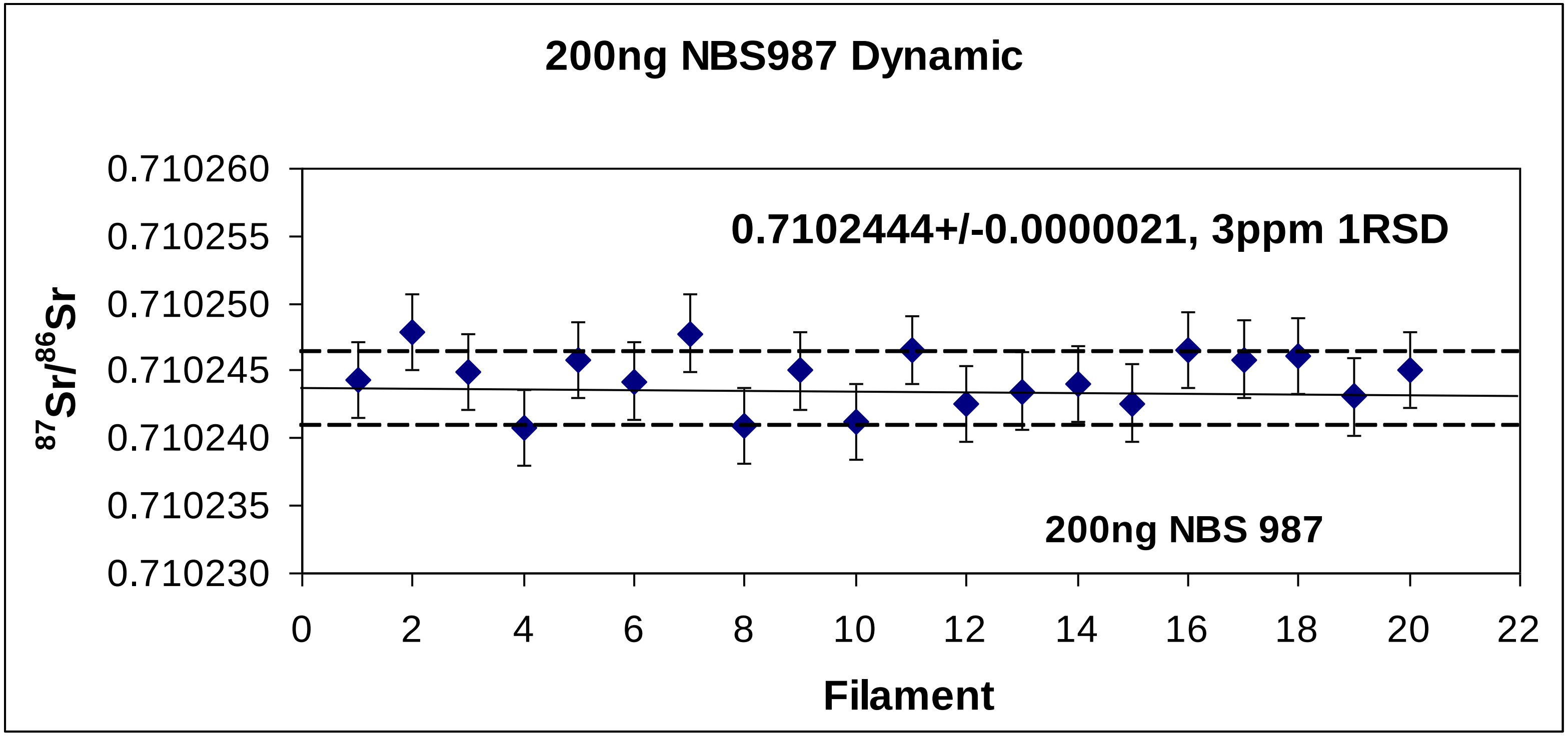
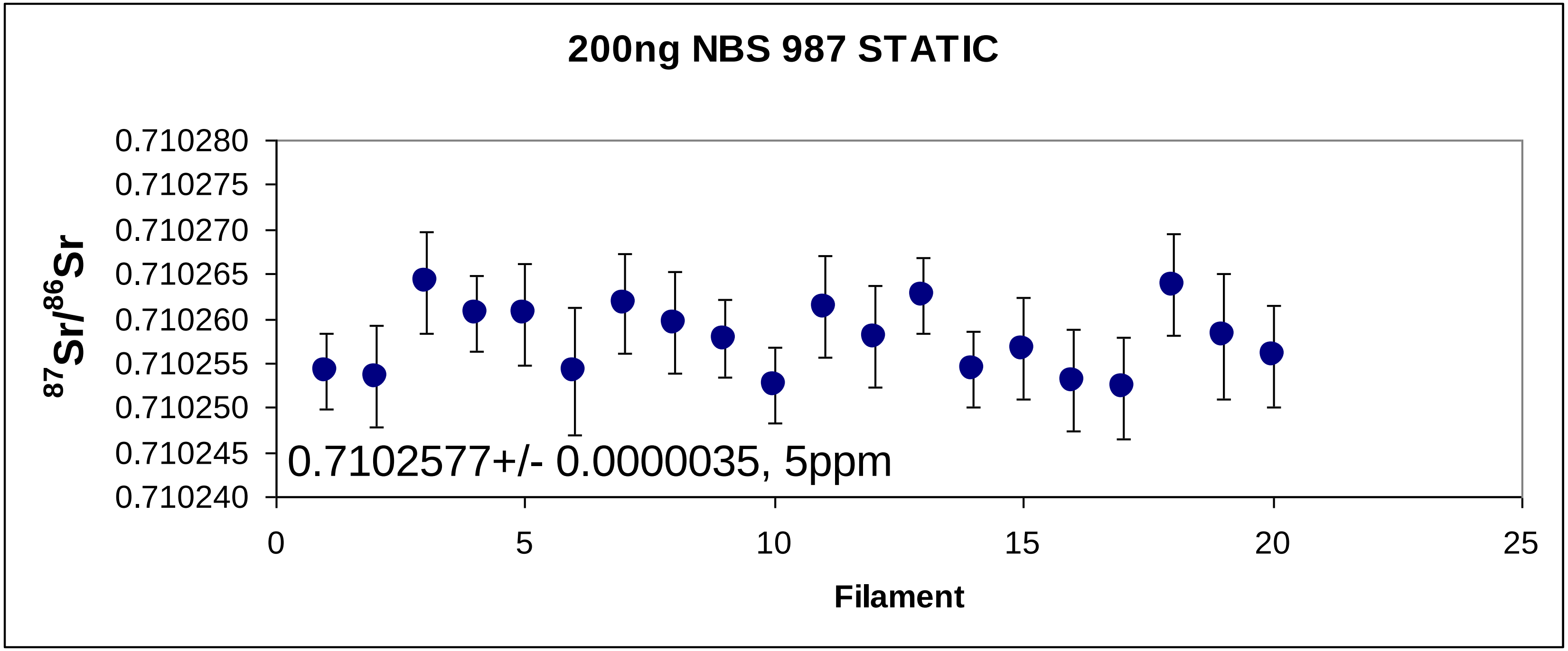
Sr dynamic precision 3ppm reproducibility (5volt ion beam)



Static precision 5ppm no gain corrections between analyses (5 volt ion beam)



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How small a sample of Nd can be measured on Faradays

- Nd+ ion atom efficiency is about 2.5% (triple filament)
- NdO+ is higher than this.

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How small an ion beam can we measure with good precision and accuracy? 50mv on 1e^{11}, 10mv on 1T

	^{142}Nd (amps)	^{142}Nd (mv)	^{143}Nd/^{144}Nd	%1se	^{145}Nd/^{144}Nd	%1se	^{142}Nd/^{144}Nd	%1se
1E+11	7.1E-12	706	**0.512095**	**0.0003**	**0.348402**	**0.0003**	**1.141827**	**0.0005**
	4.9E-12	485	**0.512096**	**0.0004**	**0.348395**	**0.0004**	**1.141819**	**0.0006**
	3.0E-12	296	**0.512082**	**0.0008**	**0.348399**	**0.0008**	**1.141837**	**0.0012**
	1.1E-12	105	**0.512113**	**0.0016**	**0.348371**	**0.0020**	**1.141793**	**0.0019**
	4.9E-13	**49**	**0.512057**	**0.0028**	**0.348383**	**0.0030**	**1.141822**	**0.0042**
	1.1E-13	11	**0.512261**	**0.0106**	**0.348341**	**0.0135**	**1.143178**	**0.0139**
	4.9E-14	5	**0.511754**	**0.0191**	**0.348499**	**0.0340**	**1.142667**	**0.0265**
	3.6E-14	4	**0.512215**	**0.0257**	**0.348698**	**0.0274**	**1.142779**	**0.0221**
	^{142}Nd (amps)	^{142}Nd (mv)	^{143}Nd/^{144}Nd	%1se	^{145}Nd/^{144}Nd	%1se	^{142}Nd/^{144}Nd	%1se
1T	6.88E-12	688	**0.512121**	**0.0003**	**0.348419**	**0.0003**	**1.141855**	**0.0005**
	4.98E-12	498	**0.512127**	**0.0003**	**0.348421**	**0.0003**	**1.141861**	**0.0005**
	2.94E-12	294	**0.512117**	**0.0006**	**0.348415**	**0.0006**	**1.141837**	**0.0007**
	9.67E-13	97	**0.512169**	**0.0010**	**0.348432**	**0.0017**	**1.141870**	**0.0013**
	5.16E-13	52	**0.512116**	**0.0023**	**0.348425**	**0.0022**	**1.141833**	**0.0018**
	1.26E-13	**13**	**0.512106**	**0.0042**	**0.348400**	**0.0050**	**1.141863**	**0.0045**
	4.83E-14	5	**0.512418**	**0.0083**	**0.348734**	**0.0123**	**1.141554**	**0.0105**

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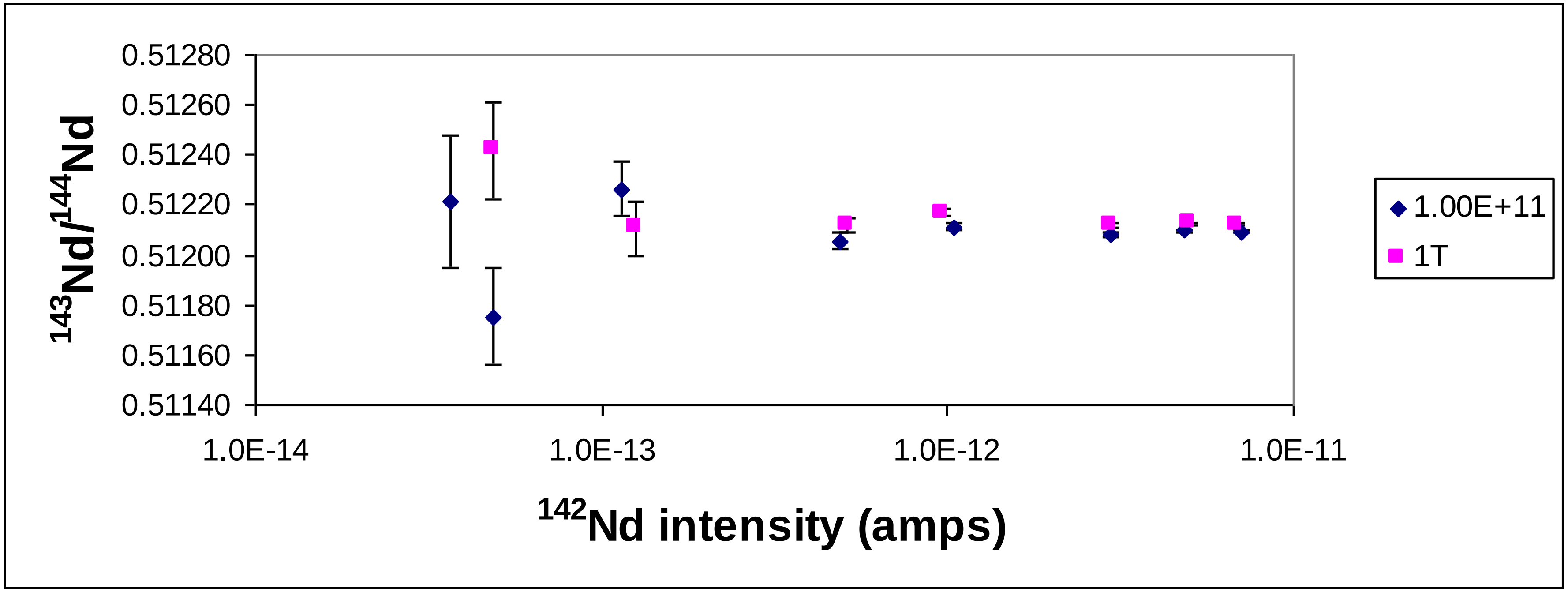
Errors expand below 1e^{-13}A



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10.5% ion/atom efficiency

<20ppm reproducibility 300mv $^{142}Nd^{16}O$

2ng NdO 1T resistor data											
	$^{142}Nd/^{144}Nd$	%1se	$^{143}Nd/^{144}Nd$	%1se	$^{145}Nd/^{144}Nd$	%1se	$^{148}Nd/^{144}Nd$	%1se	$^{142}Nd^{16}O$ amps	Minutes	ion/atom efficiency
1	1.141818	0.0008	0.512085	0.0006	0.348413	0.0006	0.241589	0.0012	3.3E-12	152	9.0%
2	1.141821	0.0008	0.512099	0.0008	0.348420	0.0009	0.241589	0.0015	2.9E-12	187	9.5%
3	1.141816	0.0007	0.512103	0.0007	0.348419	0.0007	0.241594	0.0010	3.1E-12	206	11.4%
4	1.141764	0.0010	0.512085	0.0007	0.348409	0.0006	0.241603	0.0013	3.1E-12	207	11.5%
5	1.141838	0.0010	0.512080	0.0007	0.348406	0.0006	0.241590	0.0015	3.1E-12	229	12.6%
6	1.141776	0.0010	0.512093	0.0007	0.348428	0.0006	0.241598	0.0015	3.1E-12	206	11.5%
7	1.141789	0.0009	0.512091	0.0007	0.348423	0.0006	0.241597	0.0014	3.2E-12	206	11.5%
8	1.141773	0.0011	0.512078	0.0007	0.348412	0.0007	0.241607	0.0016	3.1E-12	187	10.1%
9	1.141818	0.0009	0.512097	0.0007	0.348419	0.0006	0.241593	0.0013	3.2E-12	206	11.6%
10	1.141762	0.0014	0.512084	0.0009	0.348417	0.0008	0.241587	0.0014	3.2E-12	103	5.8%
11	1.141838	0.0007	0.512109	0.0006	0.348410	0.0006	0.241598	0.0011	3.0E-12	204	11.0%
Mean	**1.141801**	**0.0009**	**0.512091**	**0.0007**	**0.348416**	**0.0007**	**0.241595**	**0.0013**	**3.1E-12**	**190**	**10.5%**
1SD	**0.000029**	**0.0002**	**0.000010**	**0.0001**	**0.000006**	**0.0001**	**0.000006**	**0.0002**	**1.1E-13**	**35**	**2%**
1RSD	**0.0025%**		**0.0019%**		**0.0018%**		**0.0026%**				

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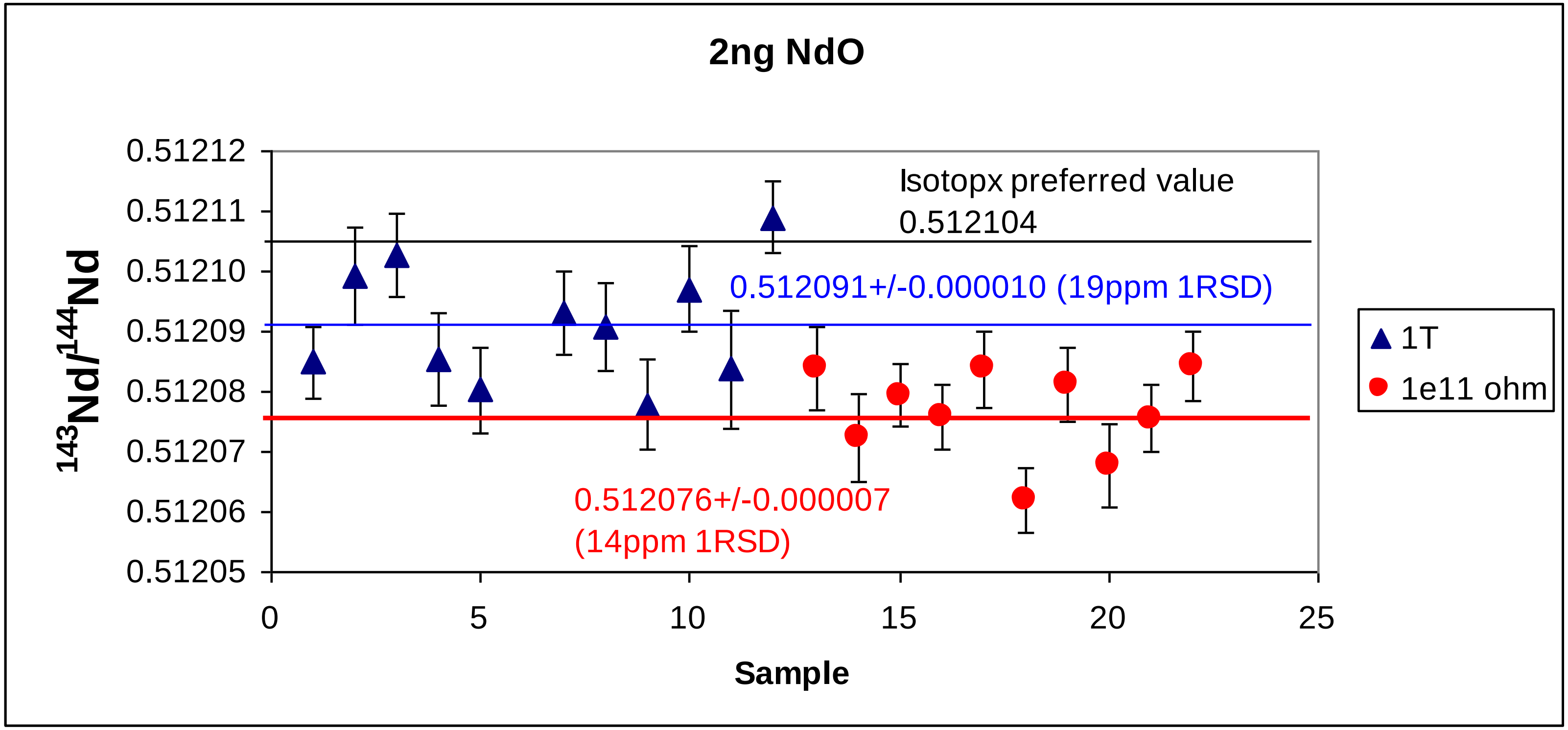
2ng Nd measured as oxide at 300mv $^{142}Nd^{16}O$



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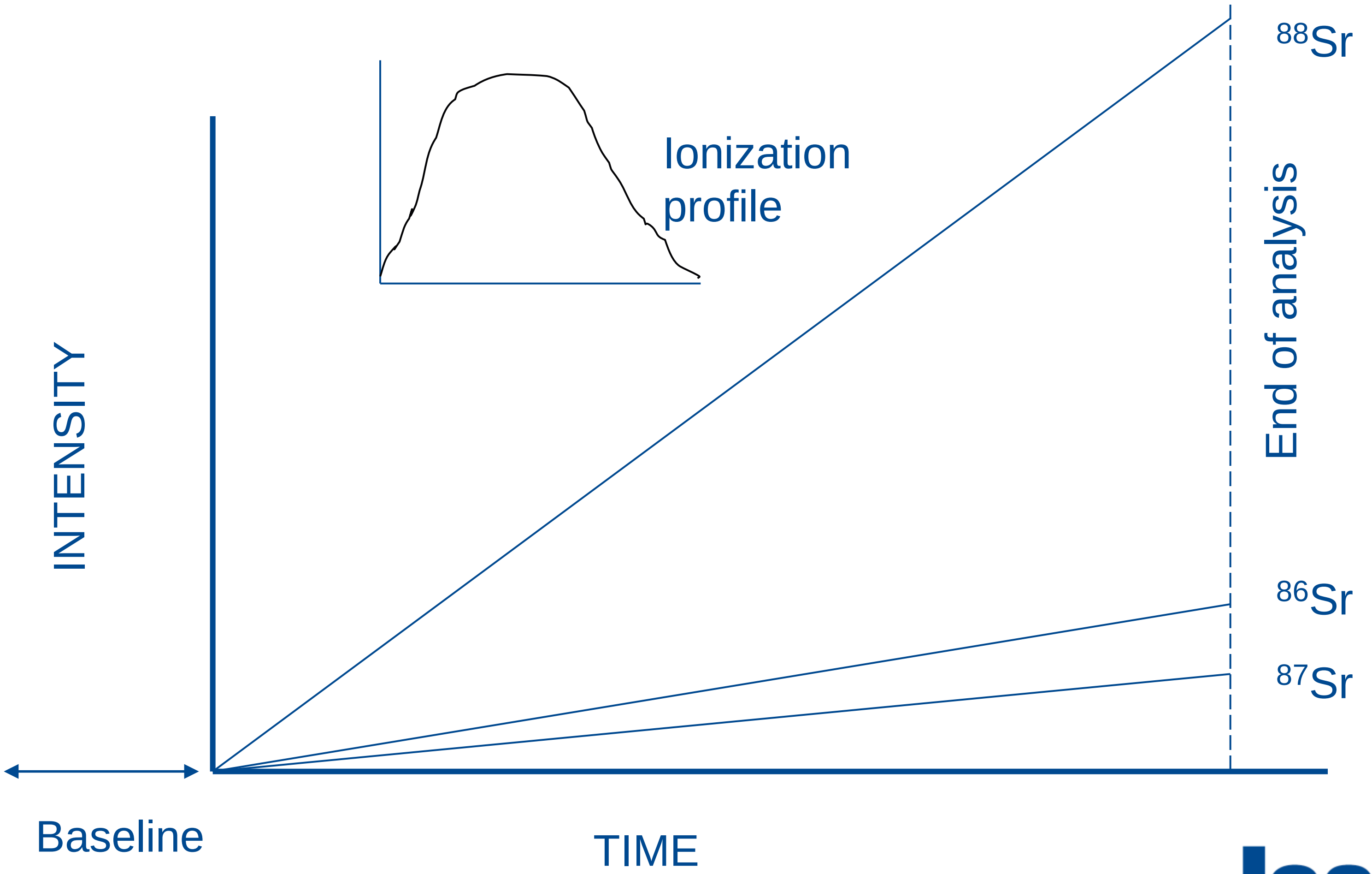
Total evaporation measurements

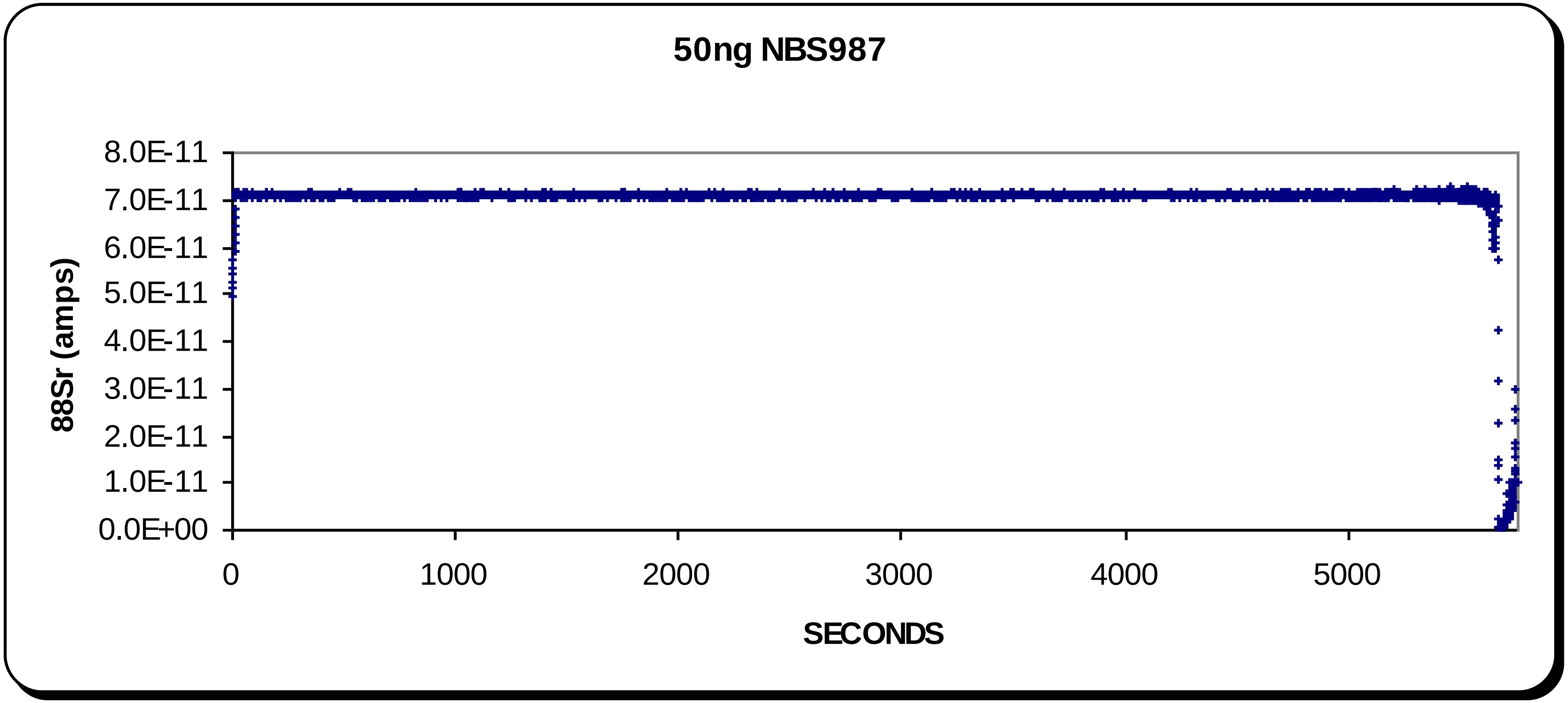
- Widely used in nuclear applications to overcome mass fractionation by taking the average isotopic composition of the whole evaporation process.
- Baselines , peak centring and focussing at the start of the measurement prior to filament current ramping
- All above must remain stable during the evaporation.
- Used for small Sr in this application
- Potential benefit for micro-drilled samples, ice cores?

Total Evaporation
(summed isotope ratios)



Baselines <u>must</u> remain constant throughout analysis

50ng Sr ion beam profile
7v for nearly 2 hours Efficiency 3.5%
(No focussing or peak centring)



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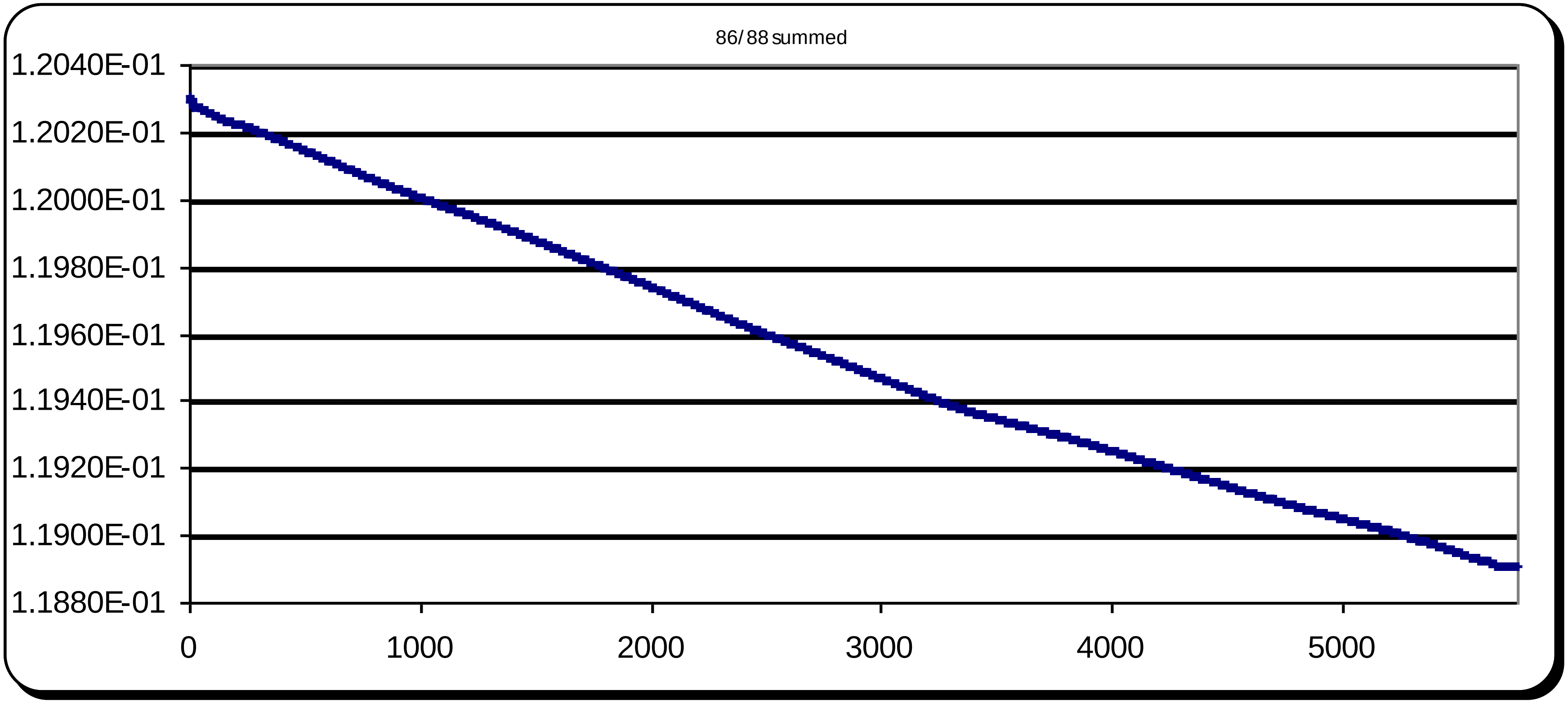
$^{86}Sr/^{88}Sr$ (summed) 50ng NBS 987



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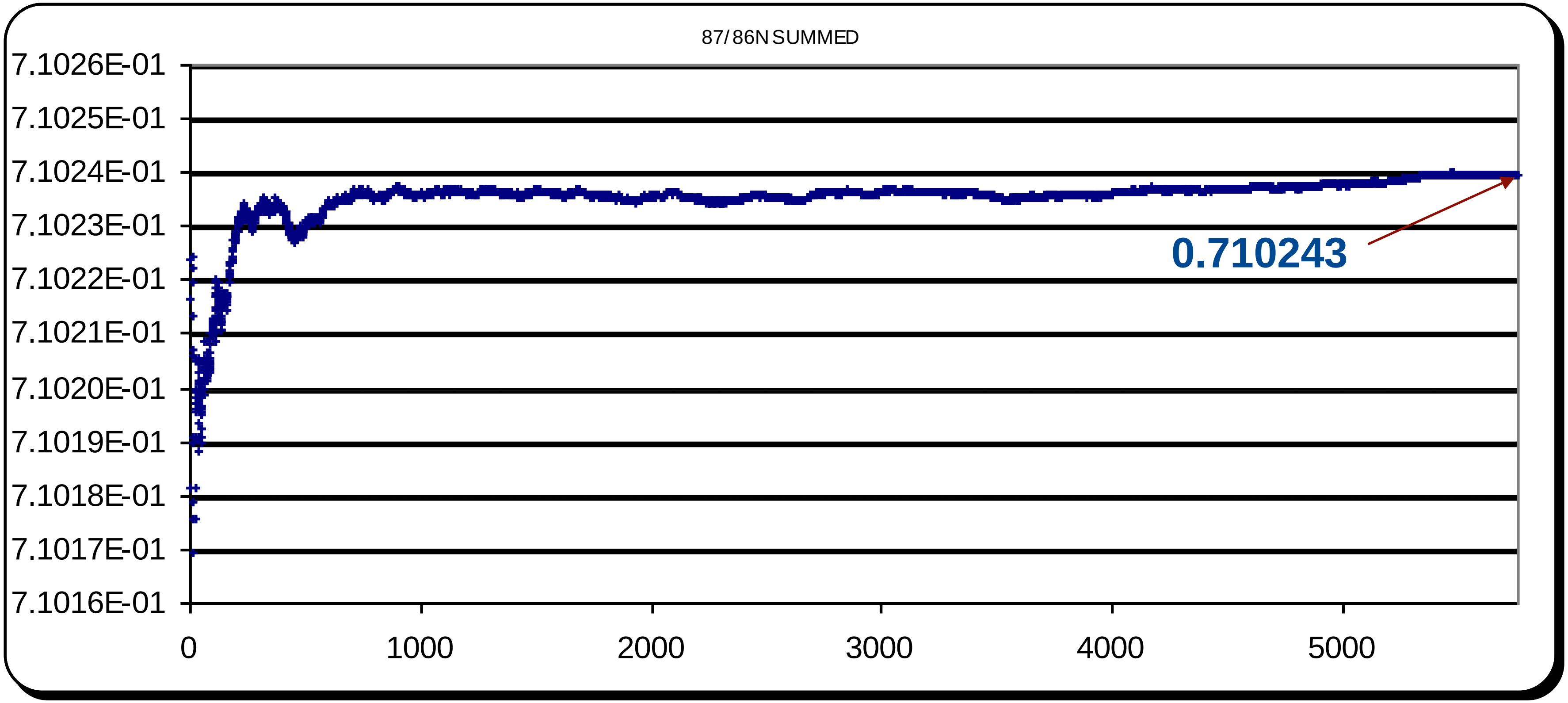
$^{87}Sr/^{86}Sr$ (summed)



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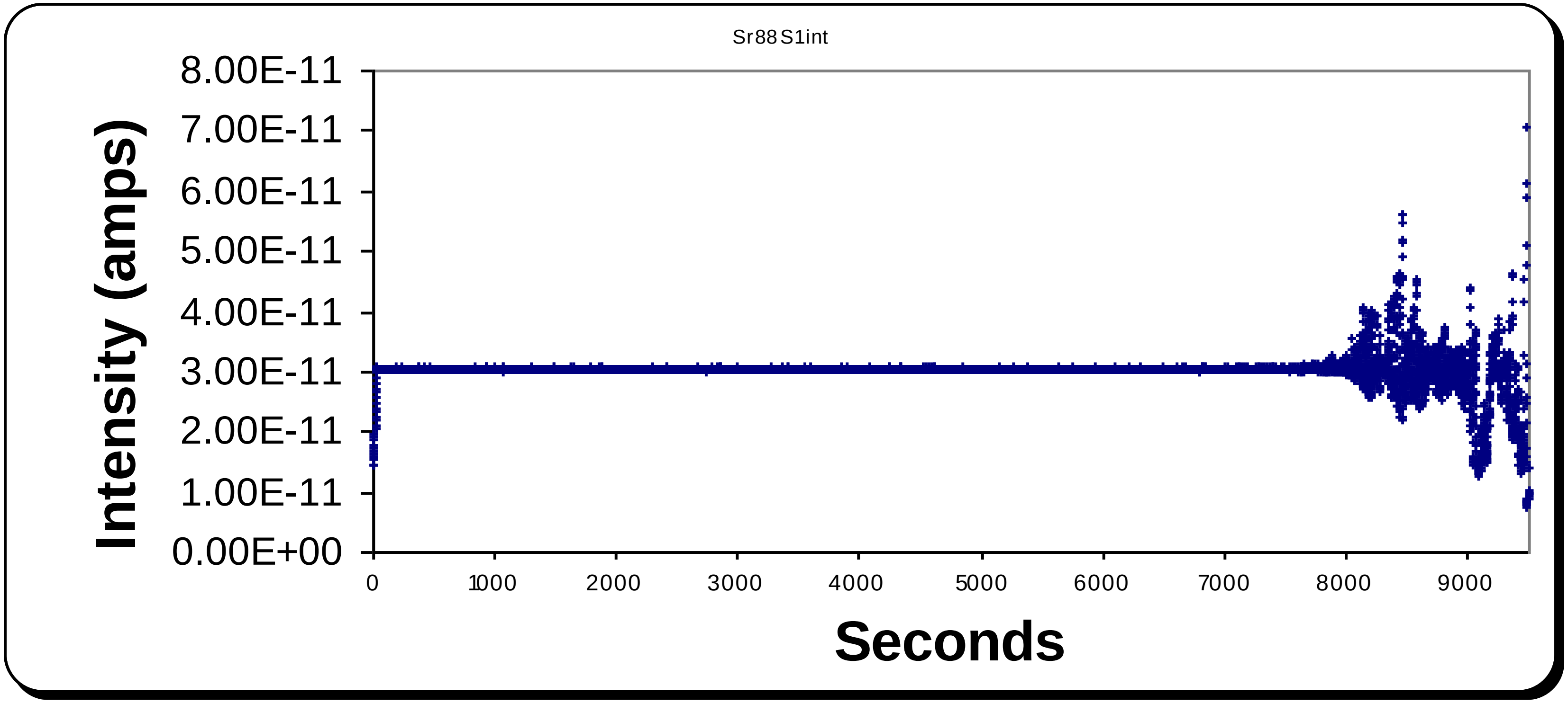
1ng Sr 3volts ^{88}Sr for 150 minutes Efficiency= 13%



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Total evaporation measurements of NBS 987 <1ng

	Total Evaporation NBS 987			
	100pg	**200pg**	**500pg**	**1ng**
	0.710244	0.710320	0.710249	0.710266
	0.710255	0.710279	0.710263	0.710262
	0.710285	0.710269	0.710265	0.710274
	0.710242	0.710222	0.710264	0.710278
	0.710256	0.710298	0.710273	0.710253
	0.710320	0.710229	0.710253	0.710265
	0.710299	0.710250	0.710249	0.710257
	0.710229		0.710249	0.710273
	0.710285		0.710272	0.710254
	0.710303		0.710268	0.710258
mean	**0.710272**	**0.710267**	**0.710261**	**0.710264**
1SD	**0.000031**	**0.000036**	**0.000010**	**0.000009**
1RSD (PPM)	**43**	**50**	**14**	**12**

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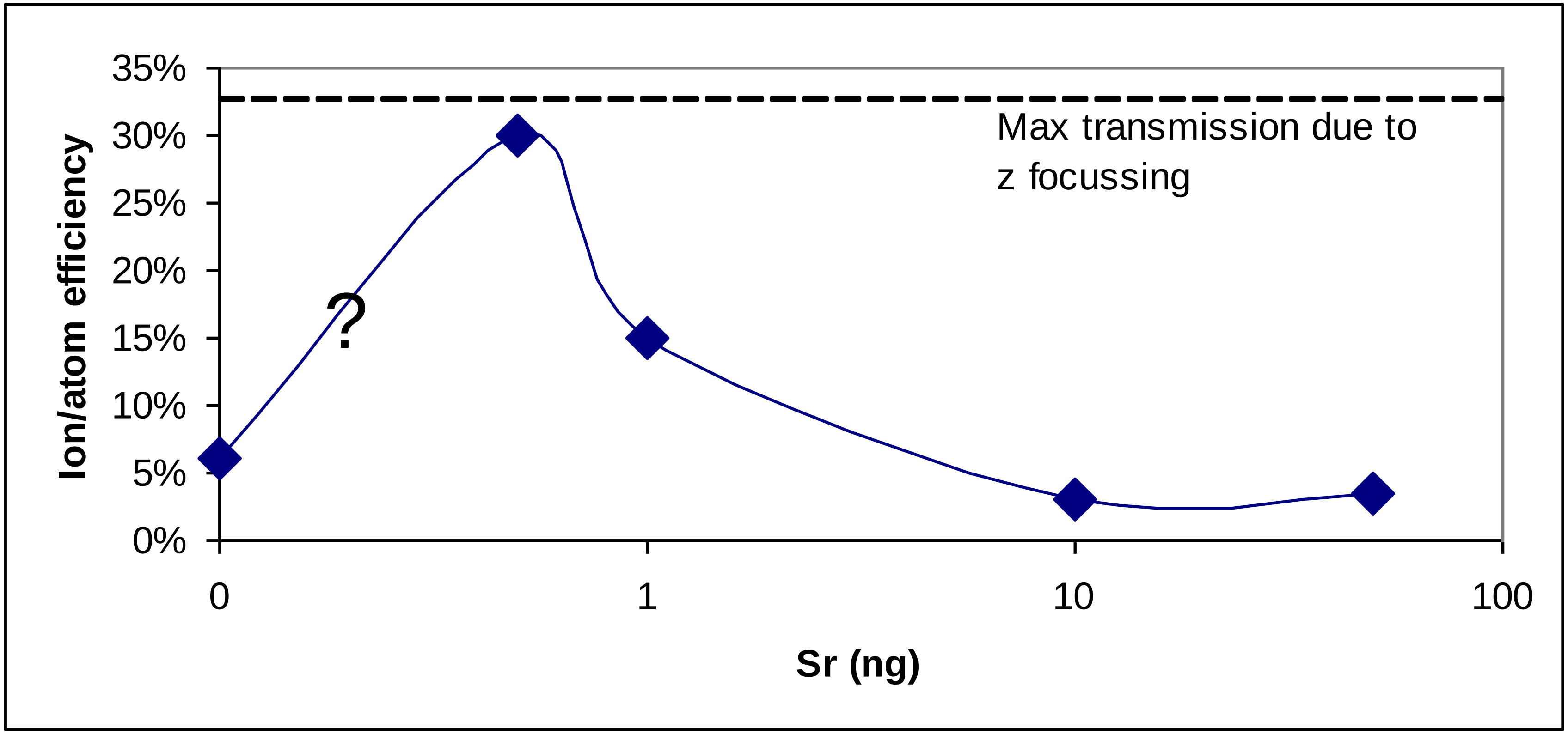
Ion/Atom detection efficiency for Sr with TaCl activator on rhenium filament



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Conclusions

- Sub nanogram isotope ratio measurements of Sr can be easily made using total evaporation analyses.
- NdO measurements at the nanogram level produce 20ppm reproducible $^{143}Nd/^{144}Nd$
- 1T resistors are 1.5 to 2 times less noisy than 1e11 depending on integration time.
- 1e11 ohm and 1T ohm resistors produce analytically similar data with ion beams >50mv.
- 1T resistors show analytical advantage below 10mv. No benefit to Sr and Nd, Probable benefit for small sample Os, Pb and U isotopes.
- Static Isotope ratio reproducibilities of 5ppm are now possible with new amplifier boards in a temperature controlled environment. (no need for dynamic amplifiers)
- Boards are upgradeable on Sector 54, IsoProbe-T and IsoProbe-P instruments.

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Thank you for your attention!

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