

Behavior of fine-particle elemental data near the detection limit

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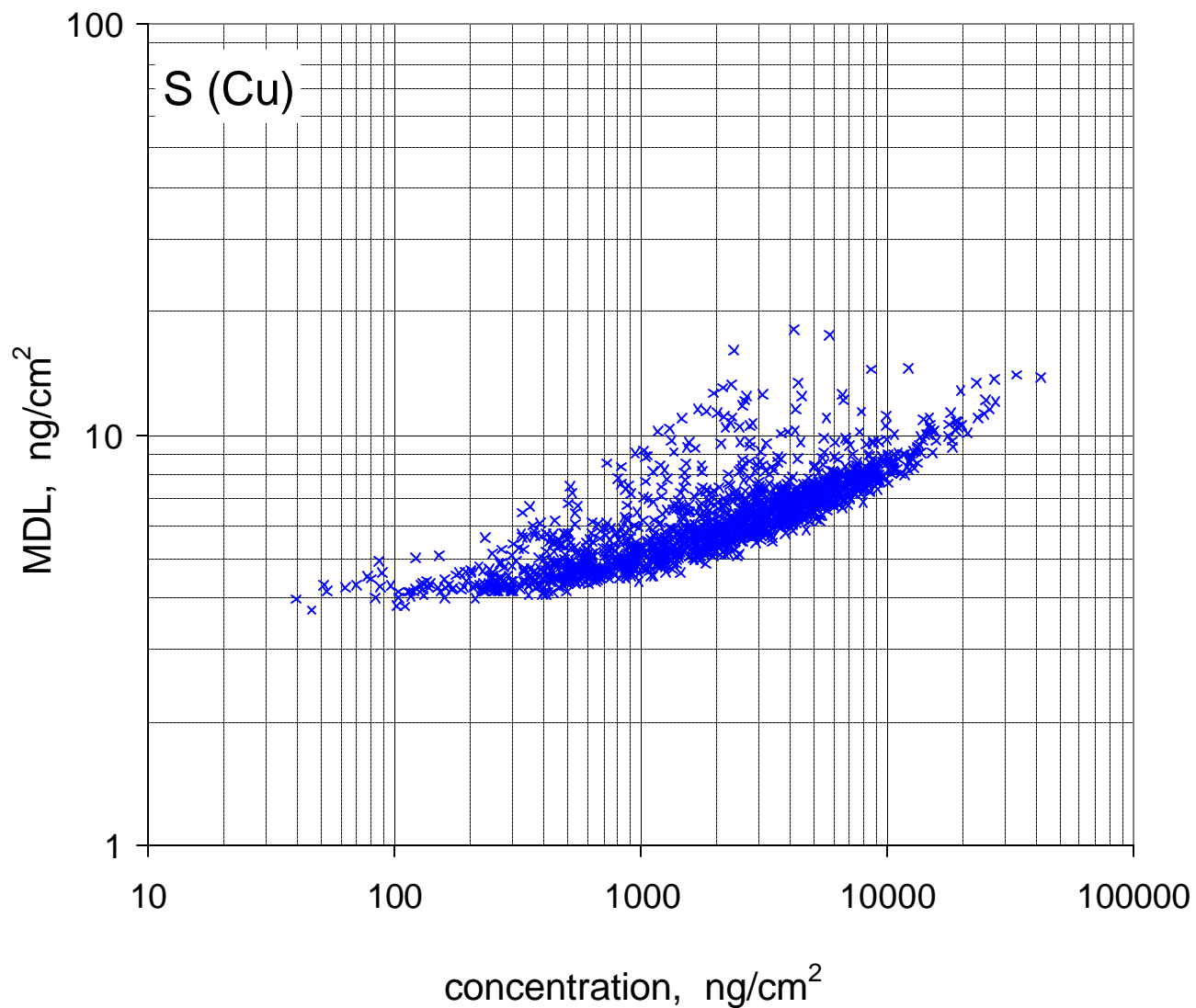
Work in Progress



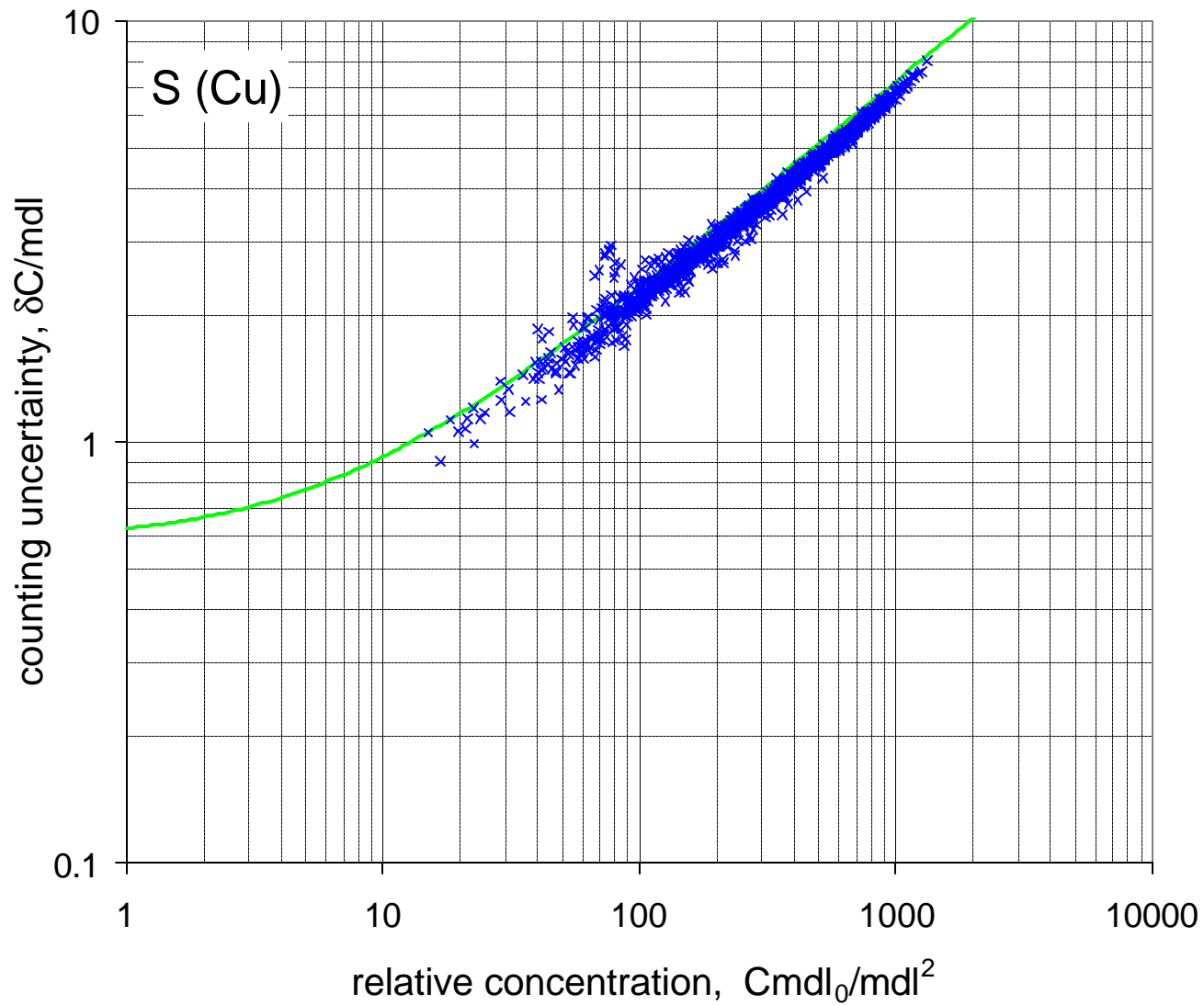
IMPROVE elemental concentrations are determined by X-Ray Fluorescence (XRF) analyses at CNL, using equipment and software developed in-house. Three values are reported for each detected element in each sample: its concentration, the estimated uncertainty in the determination of that concentration, and the estimated minimum concentration at which the element should be detectable in the absence of interference by other elements.

The concentration, uncertainty, and minimum detection limit are calculated internally by the data-reduction software*, from various details of the observed spectrum. No one of the three values is fixed by the other two:

* [Rapid Analysis of Composition by Elements \(RACE\)](#)

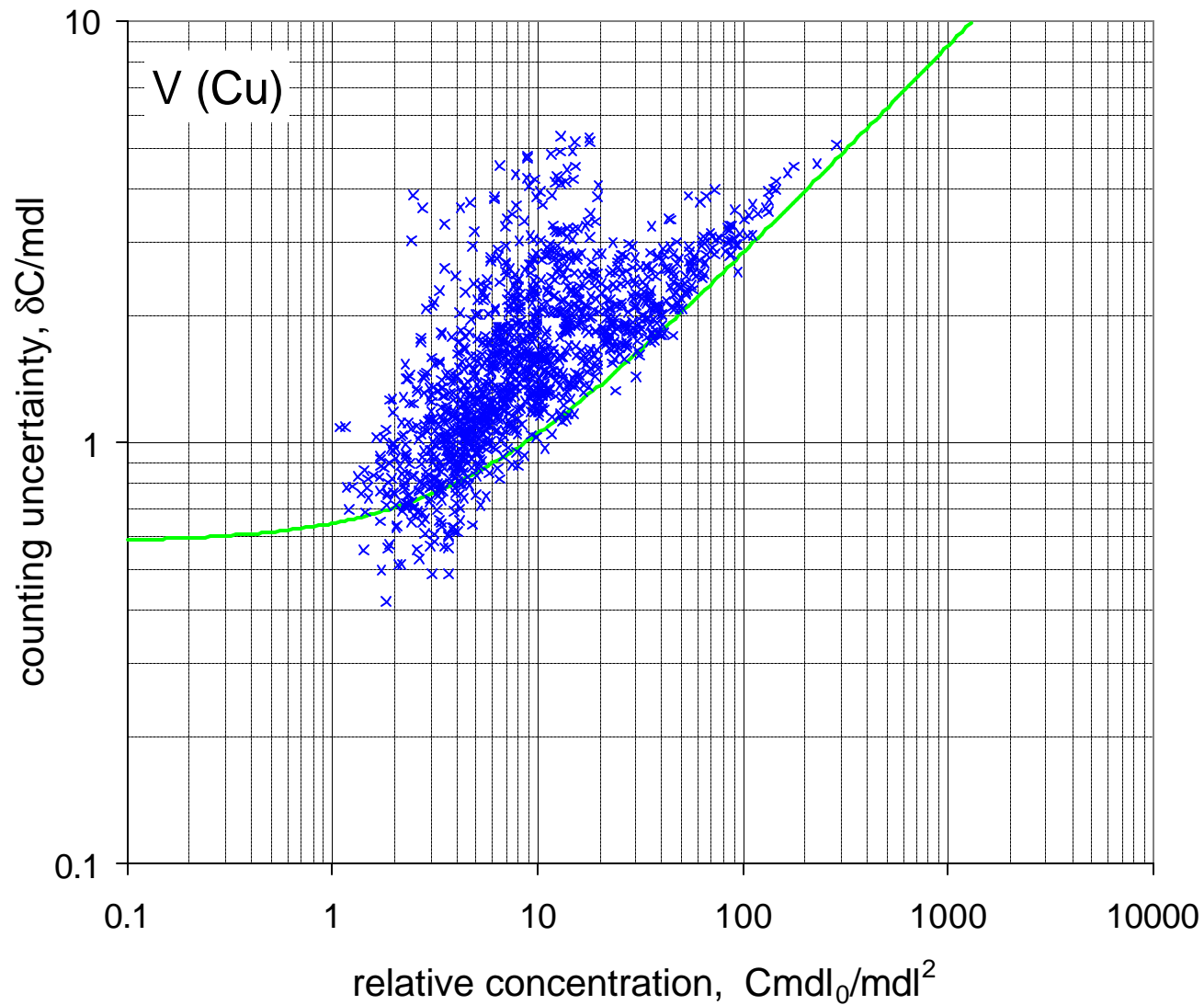


Empirical relationship between detection limit and concentration, in January 2003 sulfur measurements from the full IMPROVE network. Sulfur was detected in all 1531 samples analyzed.



Approximation of RACE counting uncertainty estimates (symbols) by equation (*) with fixed coefficients (curve), for January 2003 sulfur measurements from the full IMPROVE network.

$$* \quad \frac{dC}{mdl} \cong \sqrt{b \cdot K \left(\frac{C}{mdl^2} \right) + a}$$



The same plot for V, whose primary peak overlaps a secondary Ti peak. The subtraction of titanium's contribution (based on its primary peak) shifts vanadium concentrations to the left without lowering uncertainty.

A multiple analysis experiment:

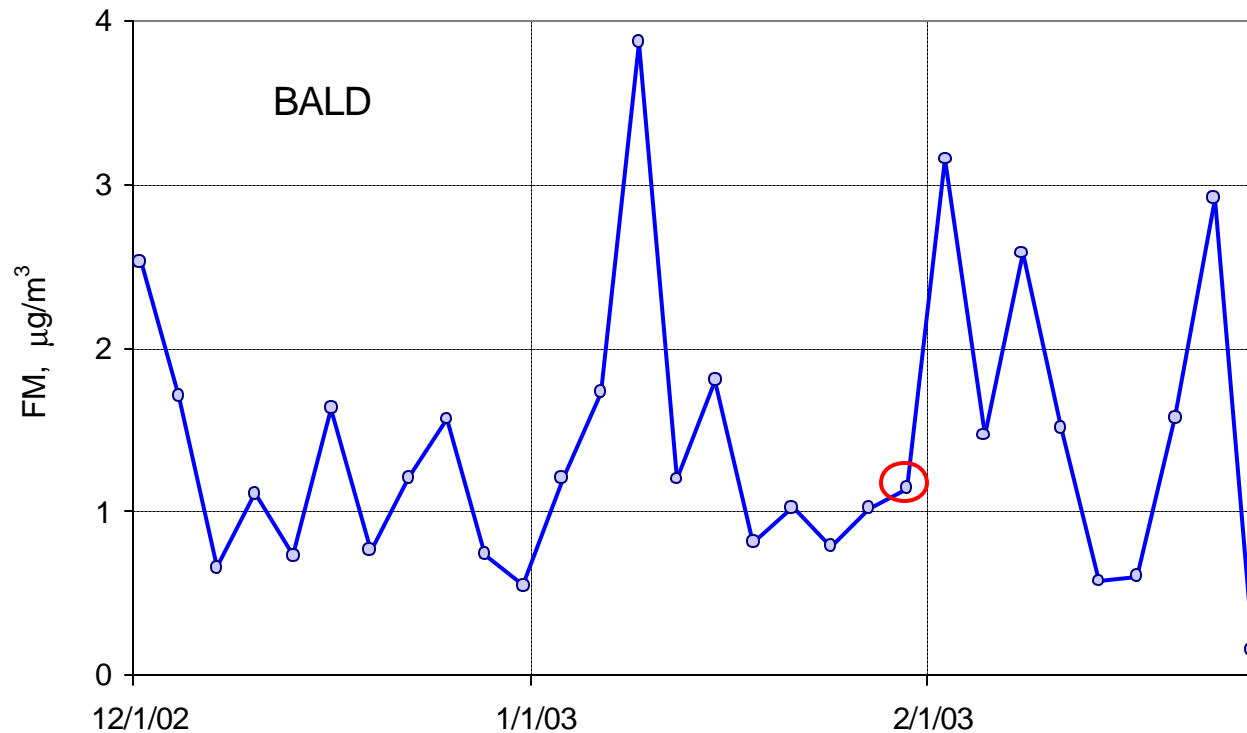
200 Cu XRF runs of the same sample,

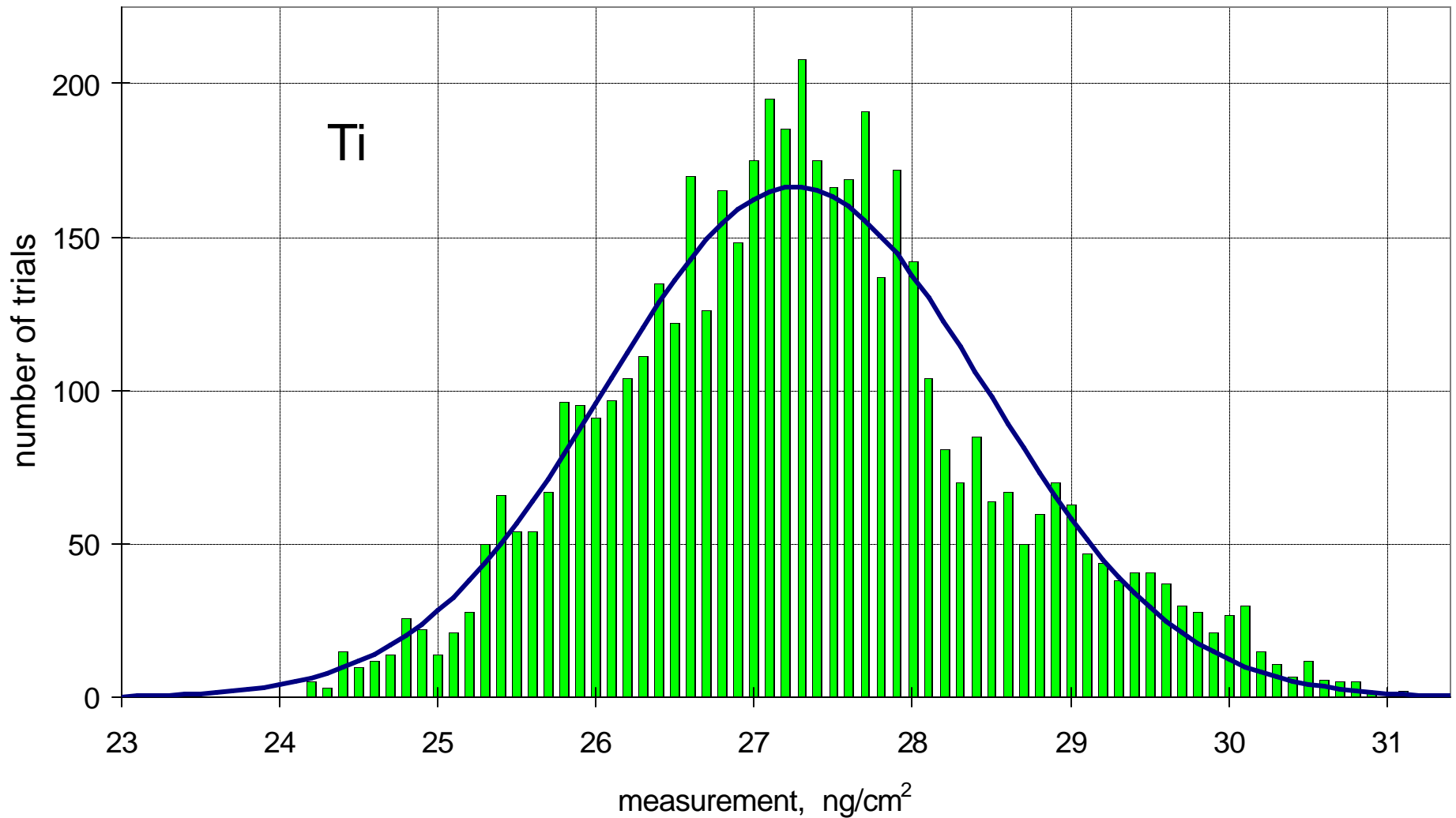
5 Cu XRF runs on each of

5 different blank Teflon filters,

$200 \times 5 \times 5 = 5000$ spectrum readings by RACE

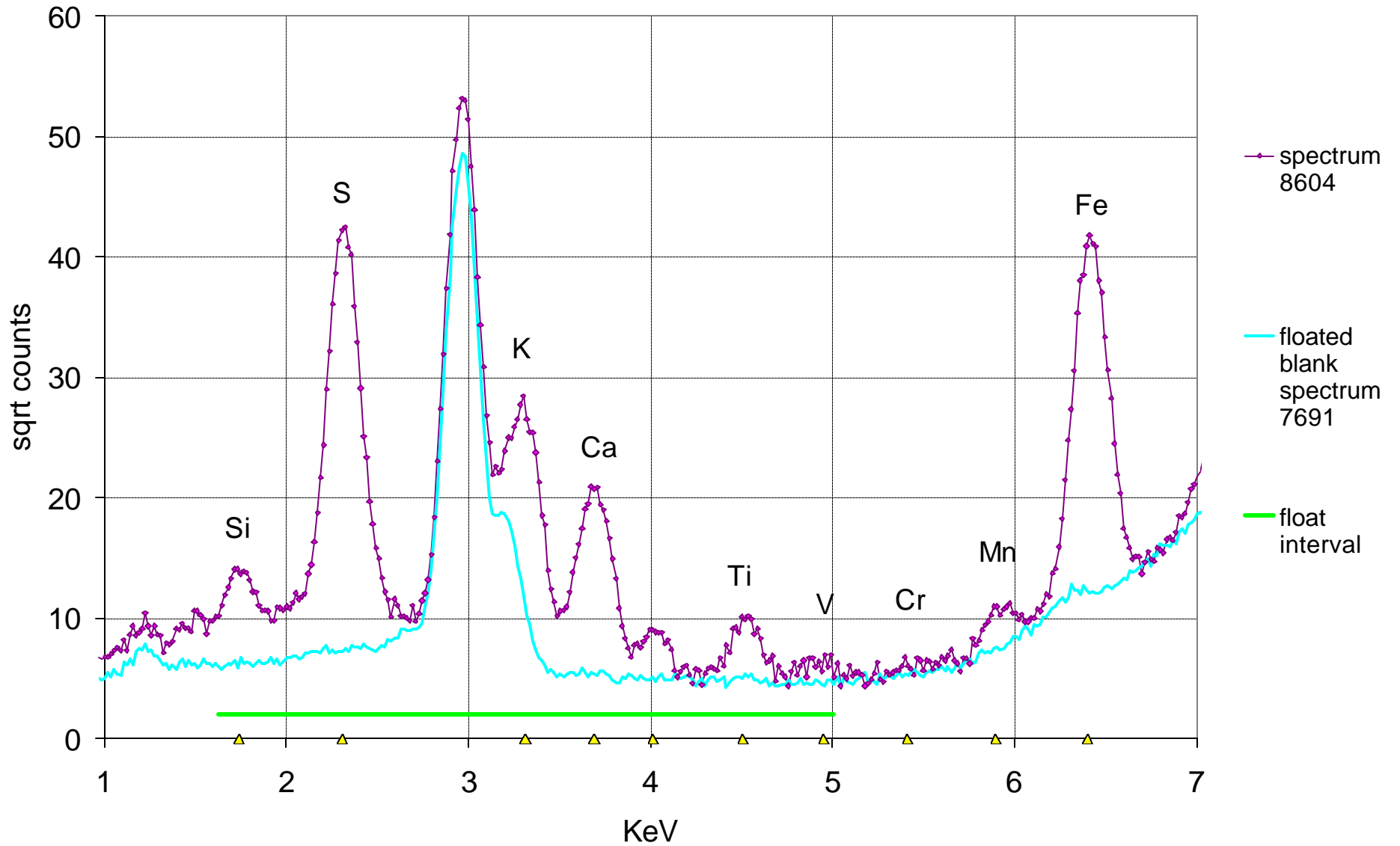
The sample: Mount Baldy AZ, 1/30/2003.





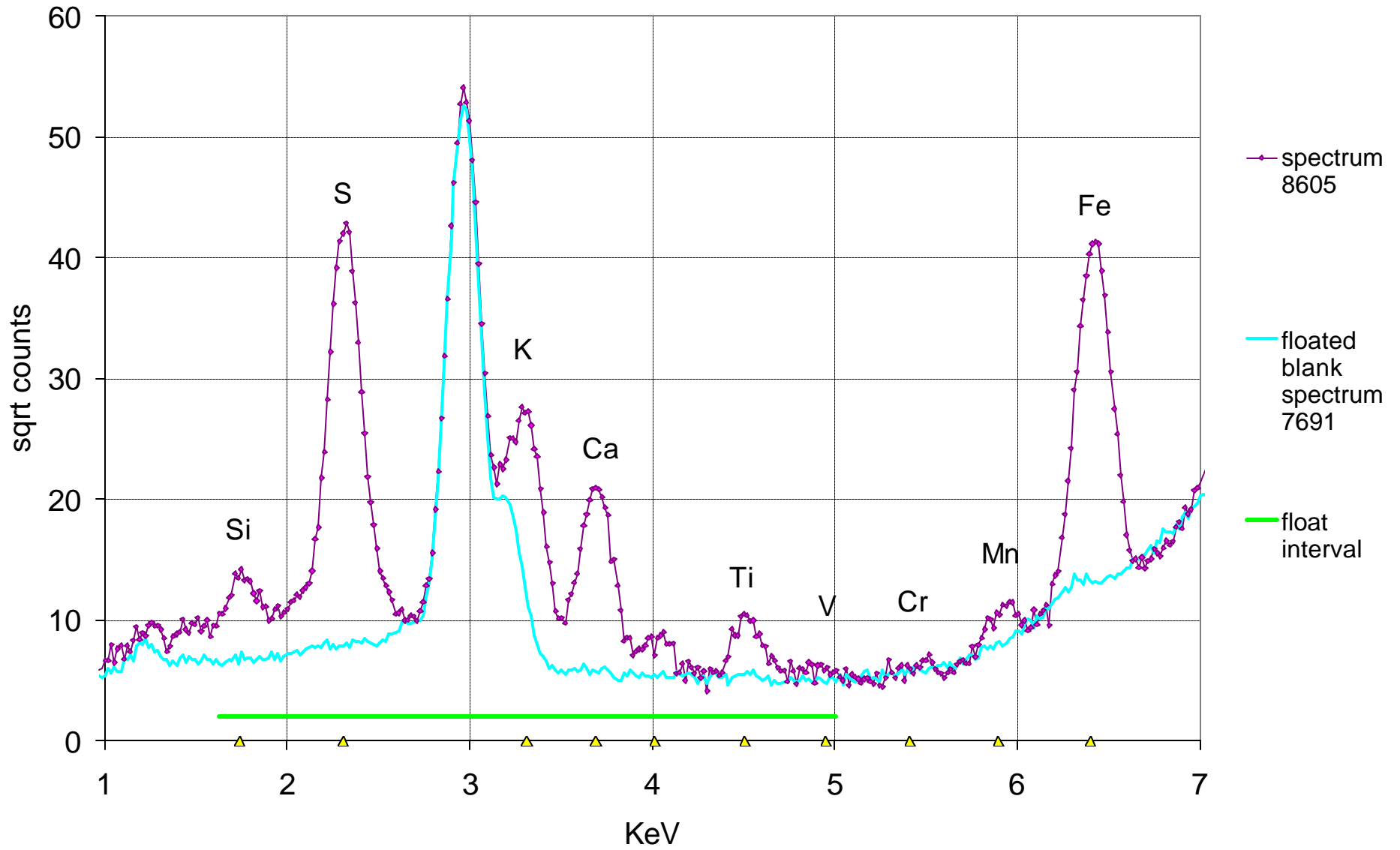
Replicate analyses of the same sample allow direct observation of the uncertainty inherent in spectroscopy. The above histogram shows the distribution of concentrations (ng/cm²) reported for Ti, which was detected in all 5000 trials. The normal distribution plotted for comparison has a standard deviation equal to the rms of RACE's theoretical uncertainty estimates for the individual trials.

SQRT of spectrum 8604



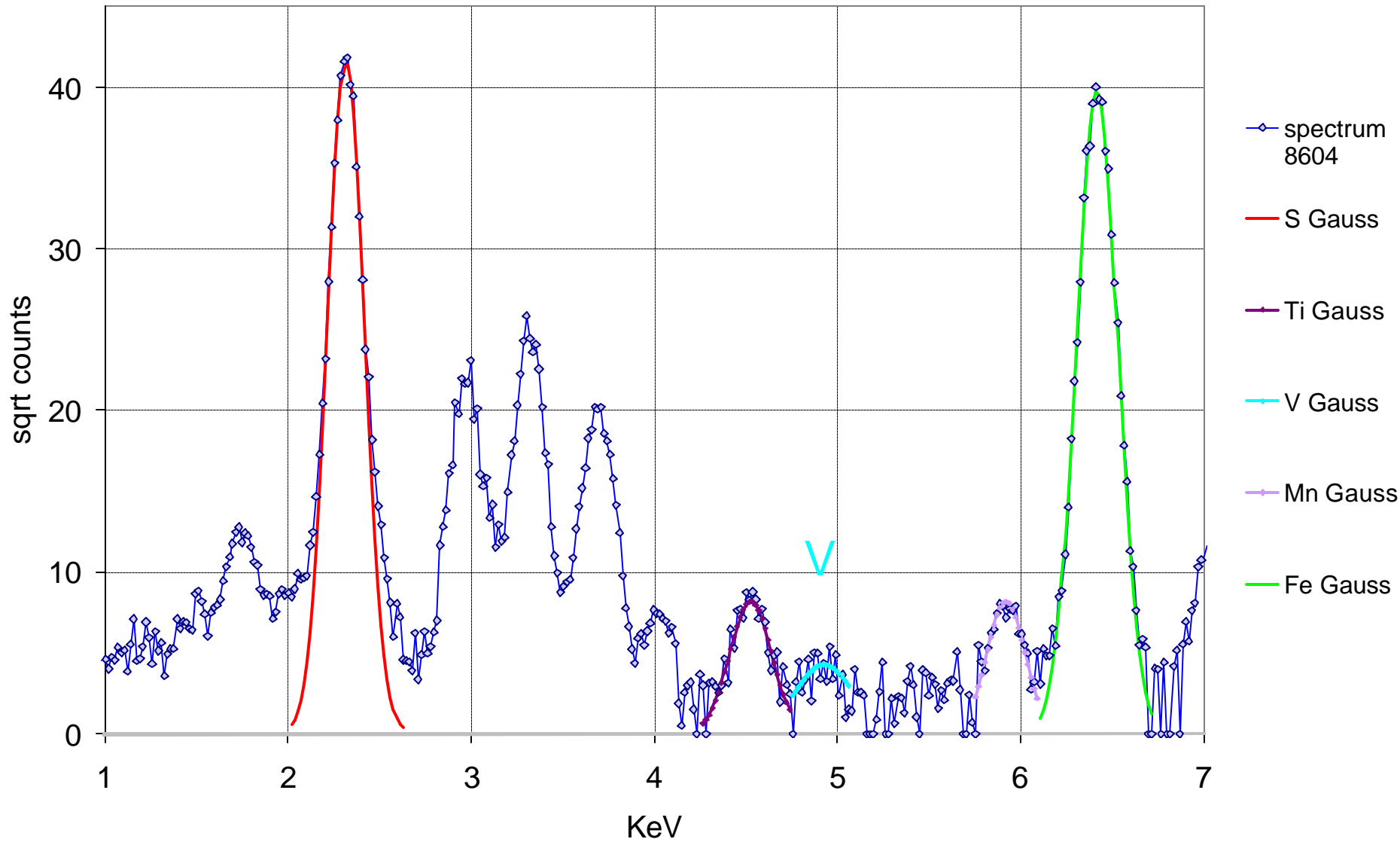
The irreducible uncertainty in the analysis...

SQRT of spectrum 8605



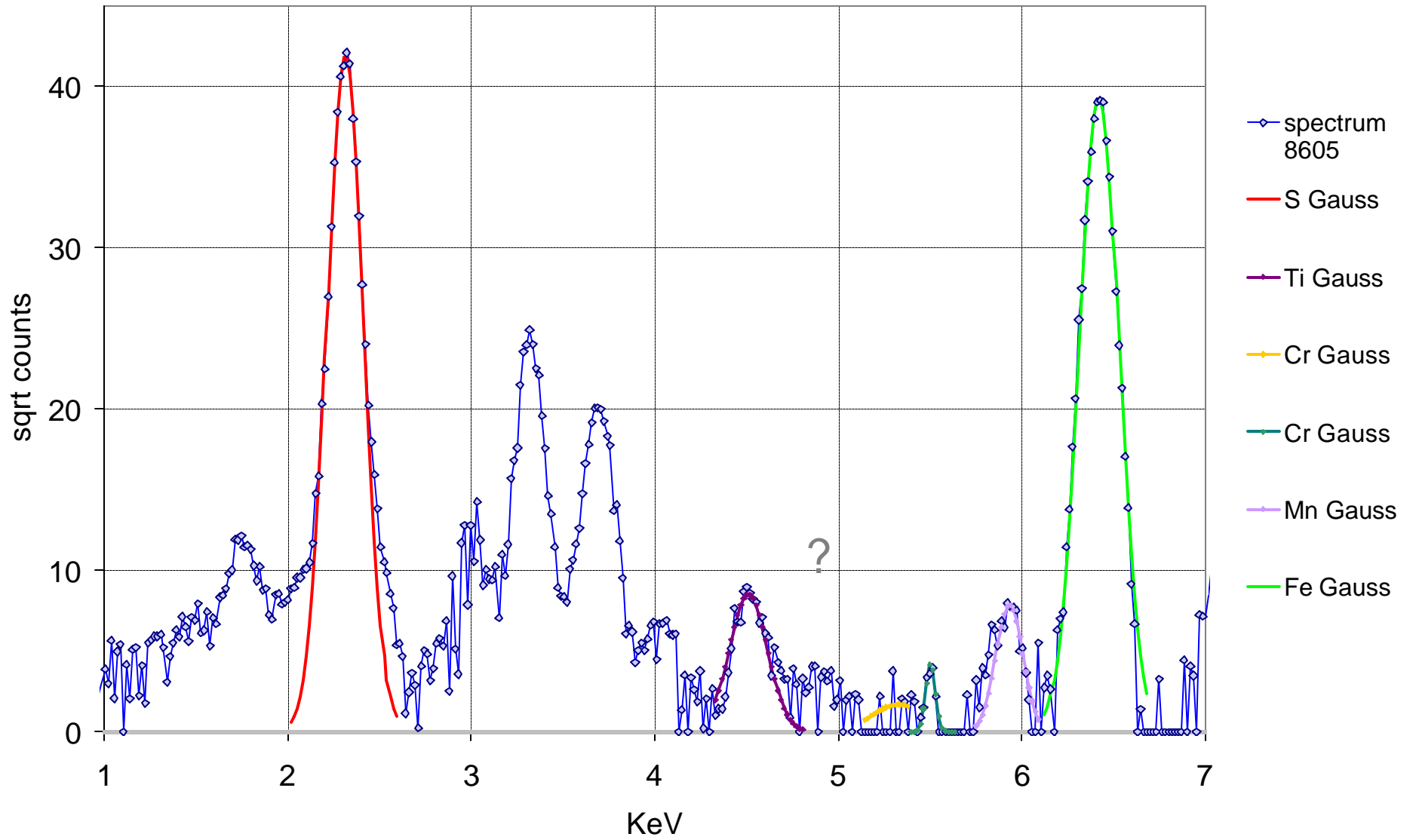
is counting statistics.

SQRT of (spectrum - blank) difference

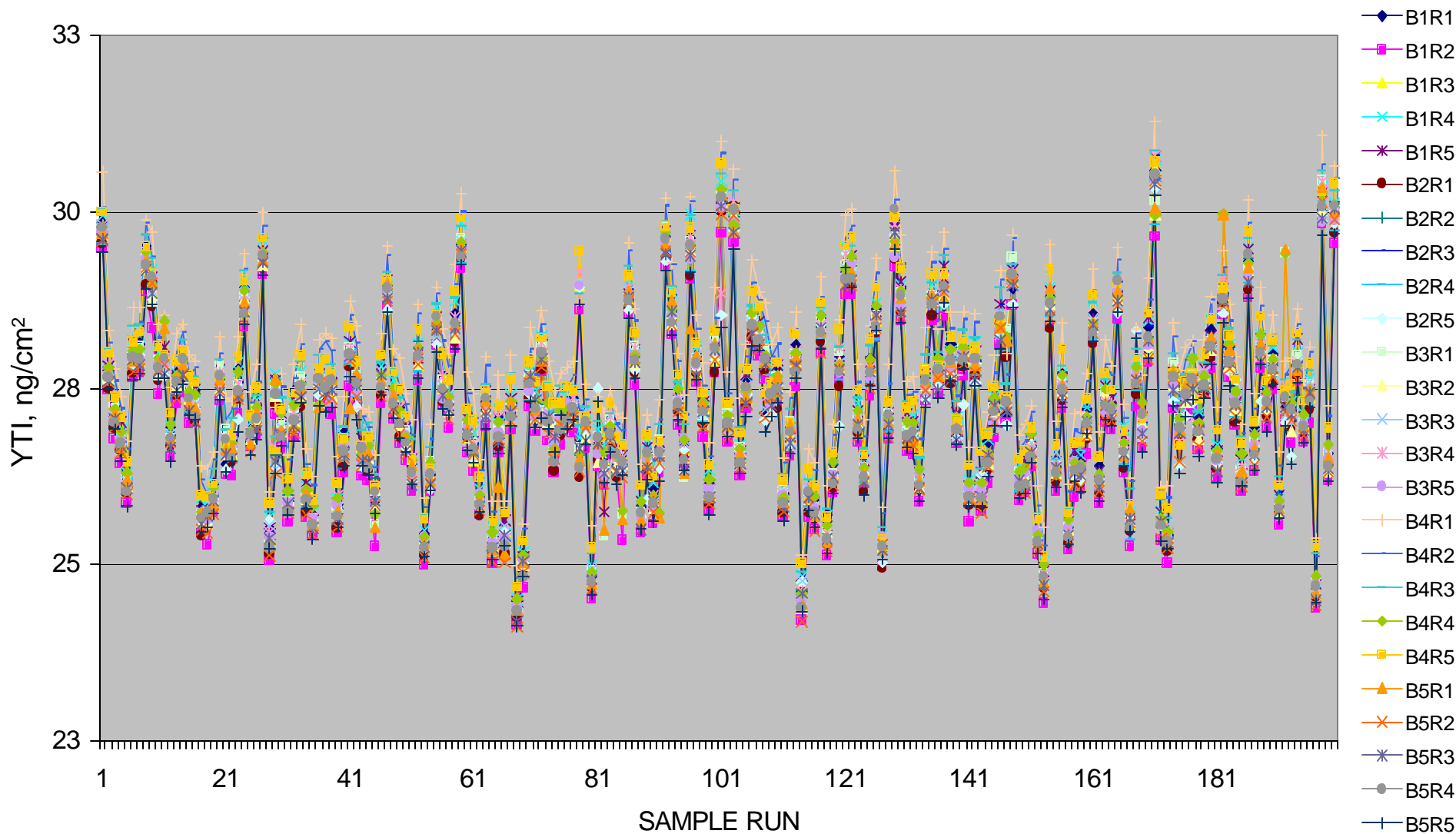


Now you see it,

SQRT of (spectrum - blank) difference

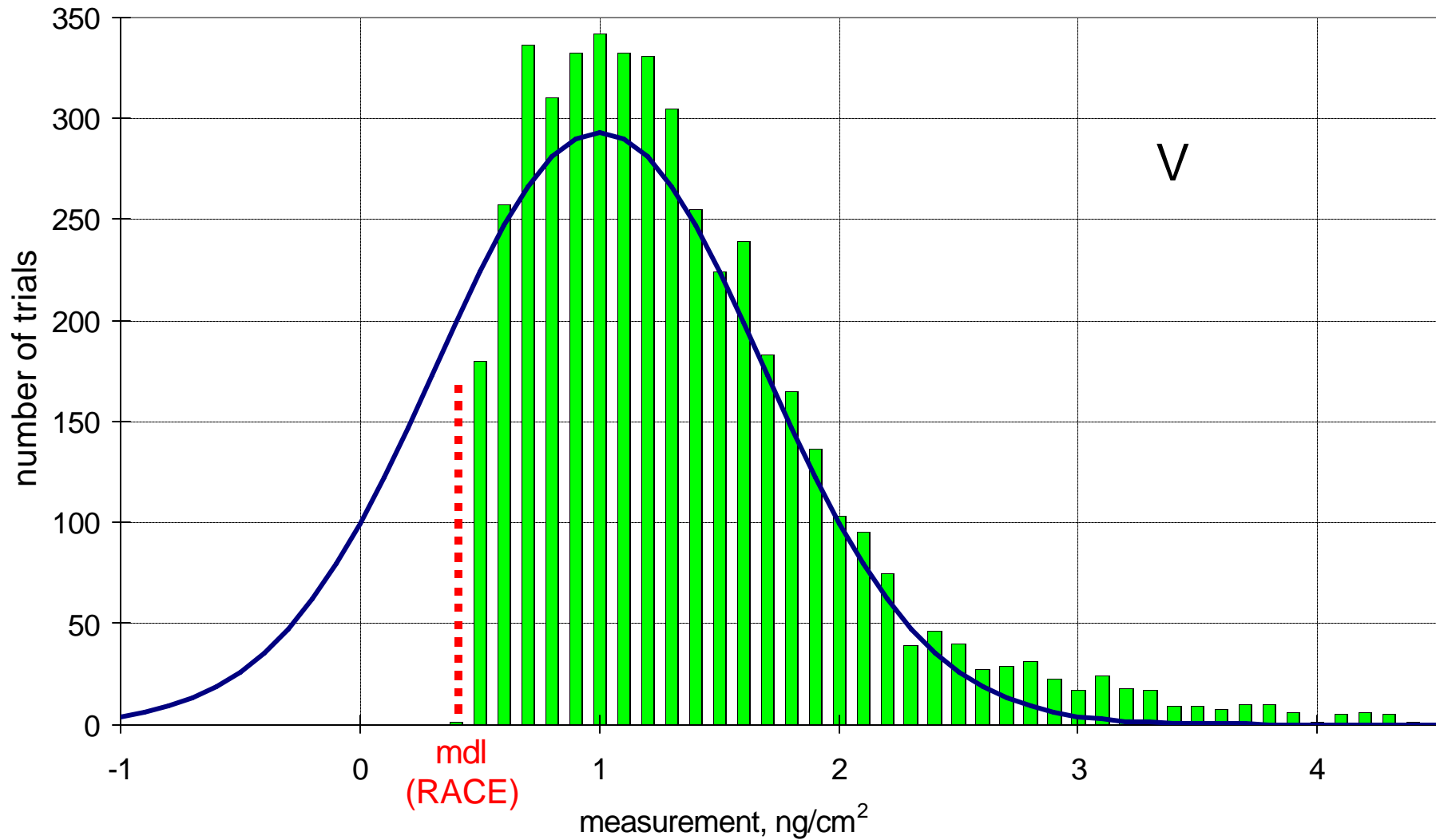


Now you don't!

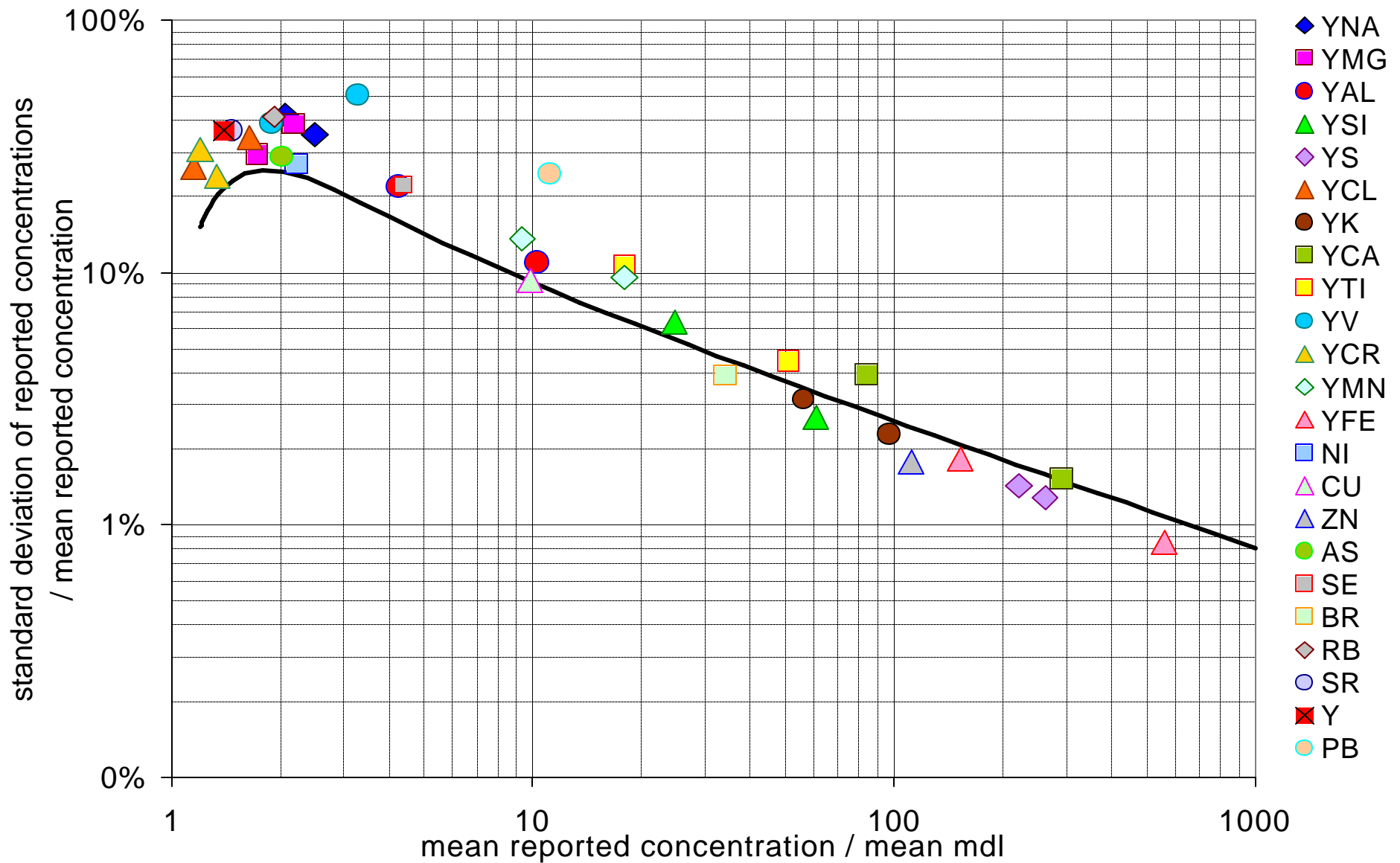


An important finding from the multiple analyses is that most of the imprecision in reported concentrations arises from noise in the sample spectrum, not from variability in the blank measurement or from RACE's estimation of the background. This supports the theoretical model underlying estimation of mdl and uncertainty.

BLANK
RUN



V was detected in 4583 (92%) of the 5000 trials, and the lower bound for reported values coincides with the RACE estimate of the mdl. Distortion of the presumptively normal error distribution is evident.

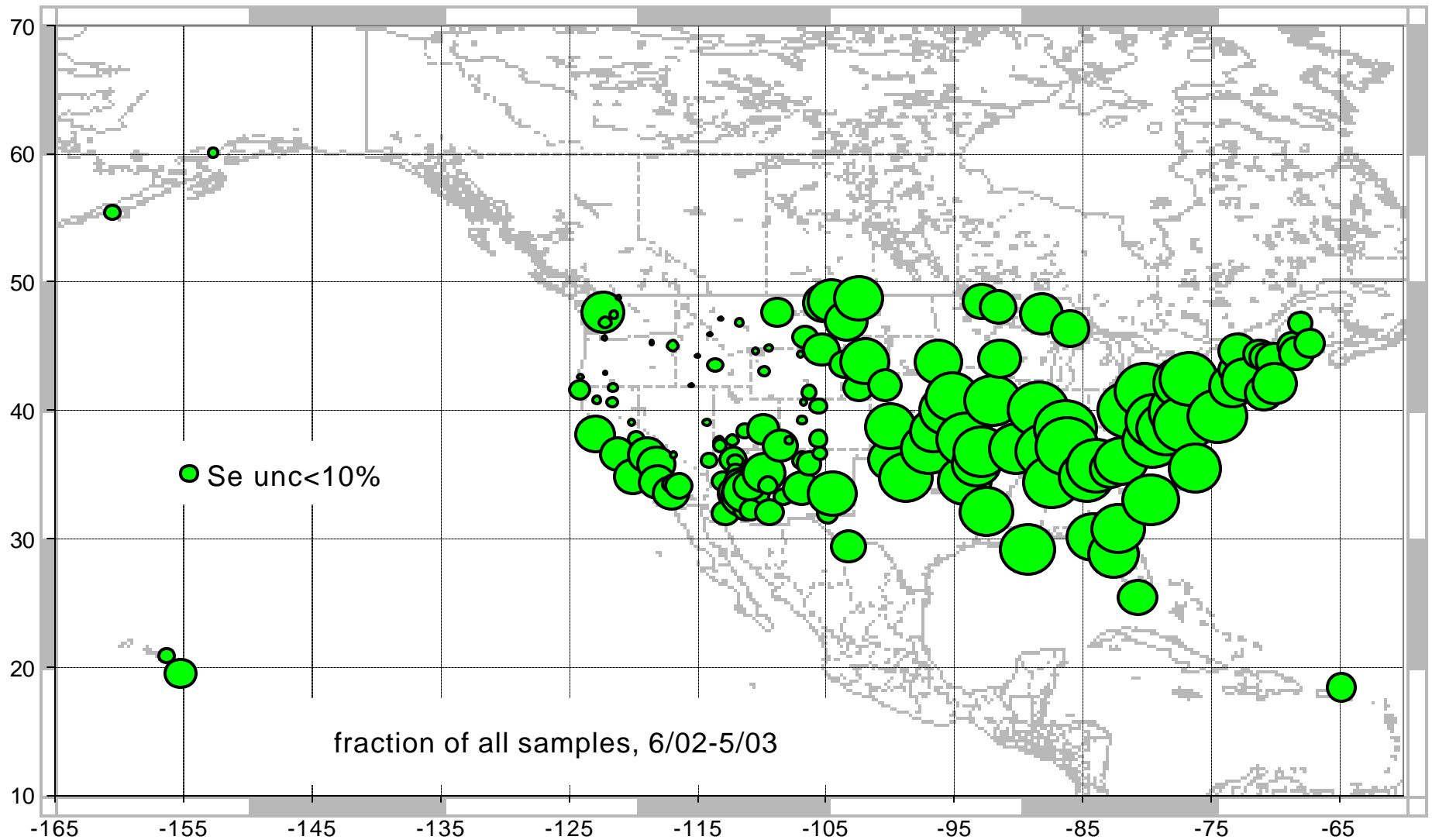


‘Observed’ precision as a function of mdL-normalized concentration. A “minimum quantifiable value” L_Q is often defined as the concentration at which analytic uncertainty is 10% or less (IUPAC, 1995). Our L_Q appears to be about $10 \times \text{mdL}$, in both theory and practice.

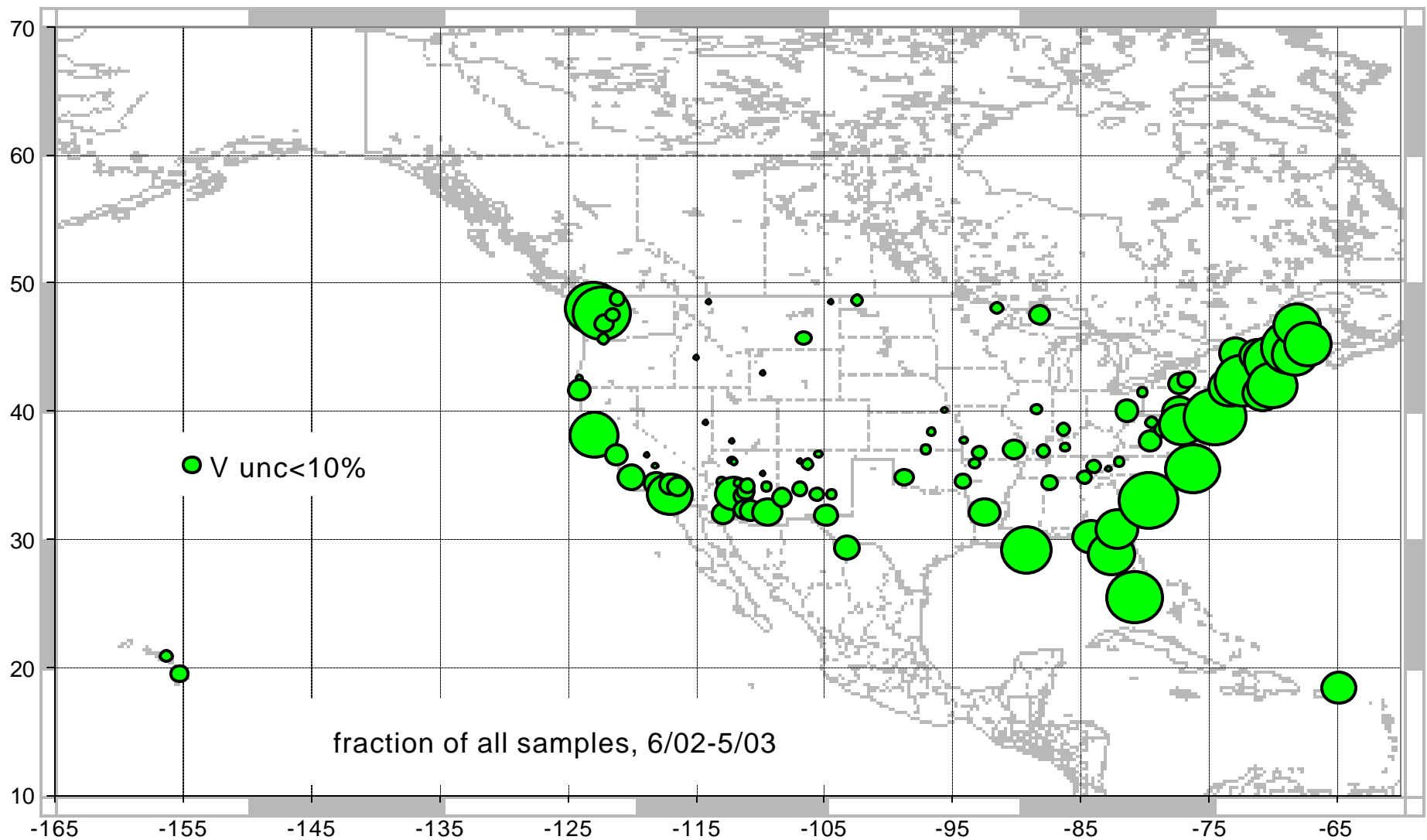
Many of the IMPROVE elemental data do not meet the “quantitative” criterion of $< 10\%$ uncertainty. For the last year of data now on CIRA (6/02-5/03), the fraction of all network samples for which $UNC/VAL < 10\%$ is:

S	Fe	K	Ca	H	Zn	Br	Si	Ti
100%	100%	99%	98%	98%	97%	96%	79%	74%
Mn	Pb	Se	Cu	Sr	Al	Ni	V	Cl
57%	41%	35%	35%	26%	22%	11%	11%	8%
As	Rb	Cr	P	Zr	Na	Mg	Mo	
2%	2%	1%	0%	0%	0%	0%	0%	

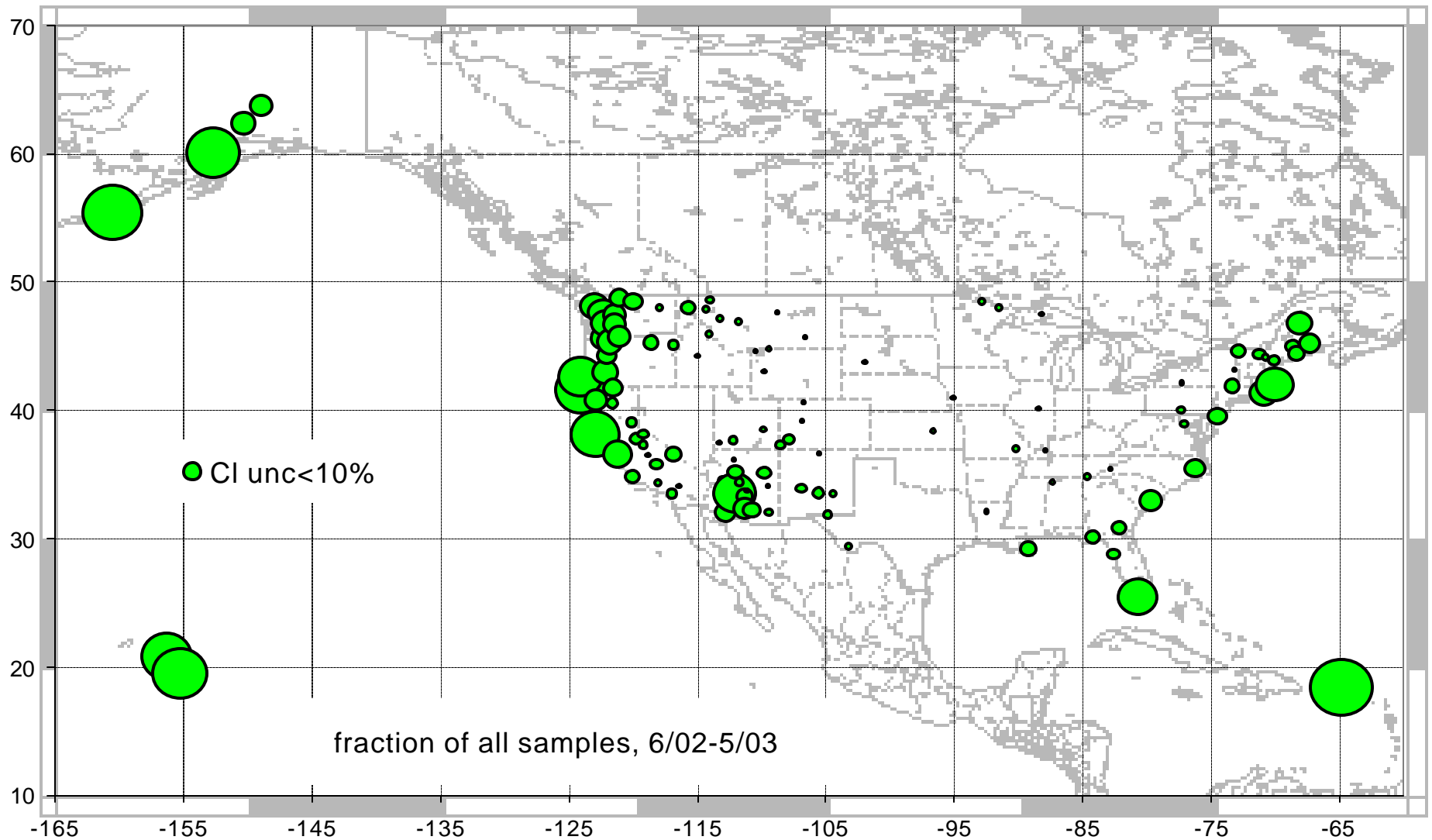
One might worry that an element quantified in only a small subset of all samples supplies little useful information, but elements that are scarce in terms of the overall network may nonetheless be routinely quantified at particular sites. The following maps show the geography of Se, V, and Cl as examples: marginal in the network as a whole, they are routinely quantified in their respective source regions.



Annual Se quantification. Max = 99%, at QUCI, consistent with its standard interpretation as a marker of coal combustion.



Annual V quantification. Max = 75%, at BRIG (90% in winter). V is a good marker of residual oil combustion.



“ocean-view properties” Bubble areas are proportional to the fraction of samples in which CI was quantified. Max = 96%, at VIIS.