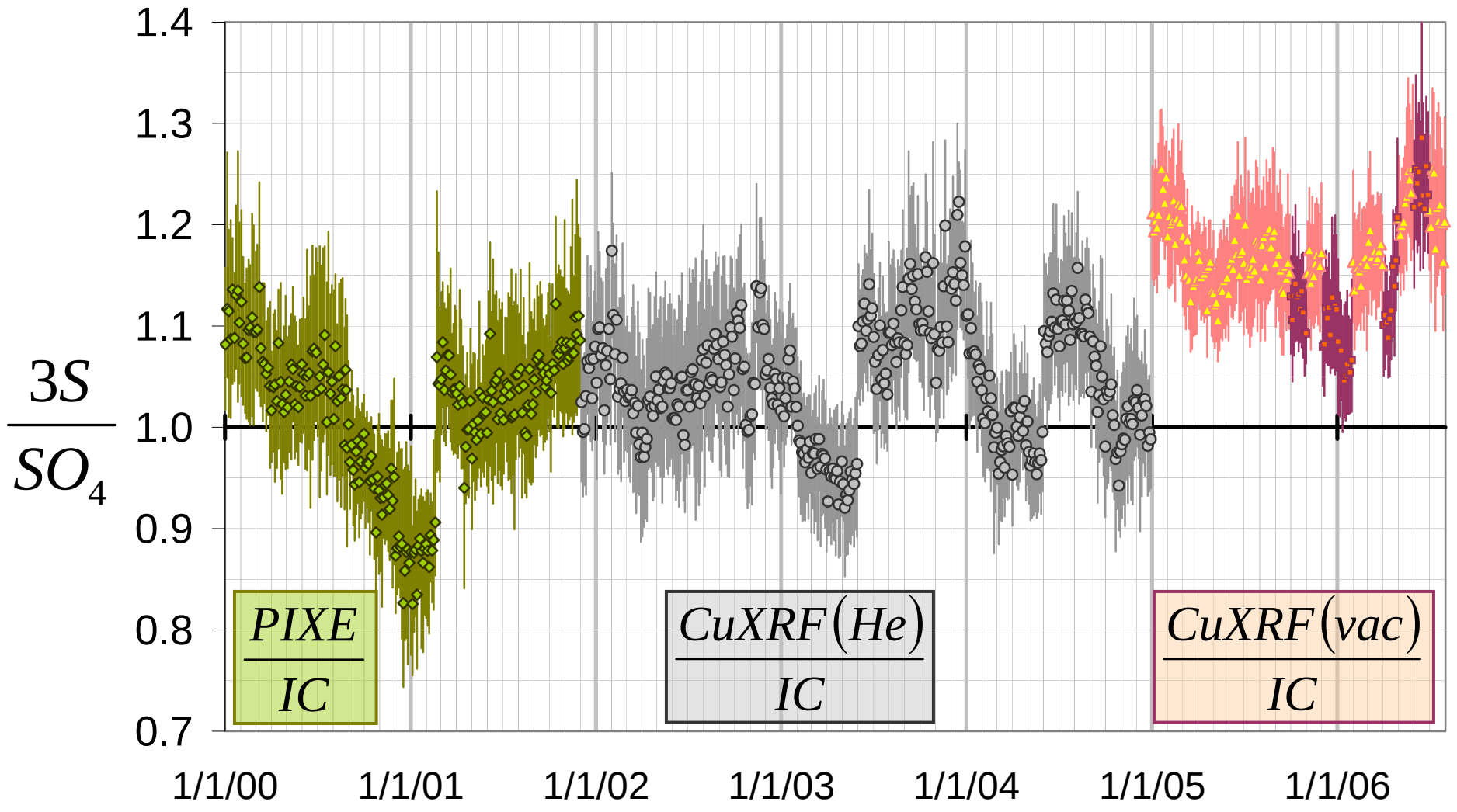
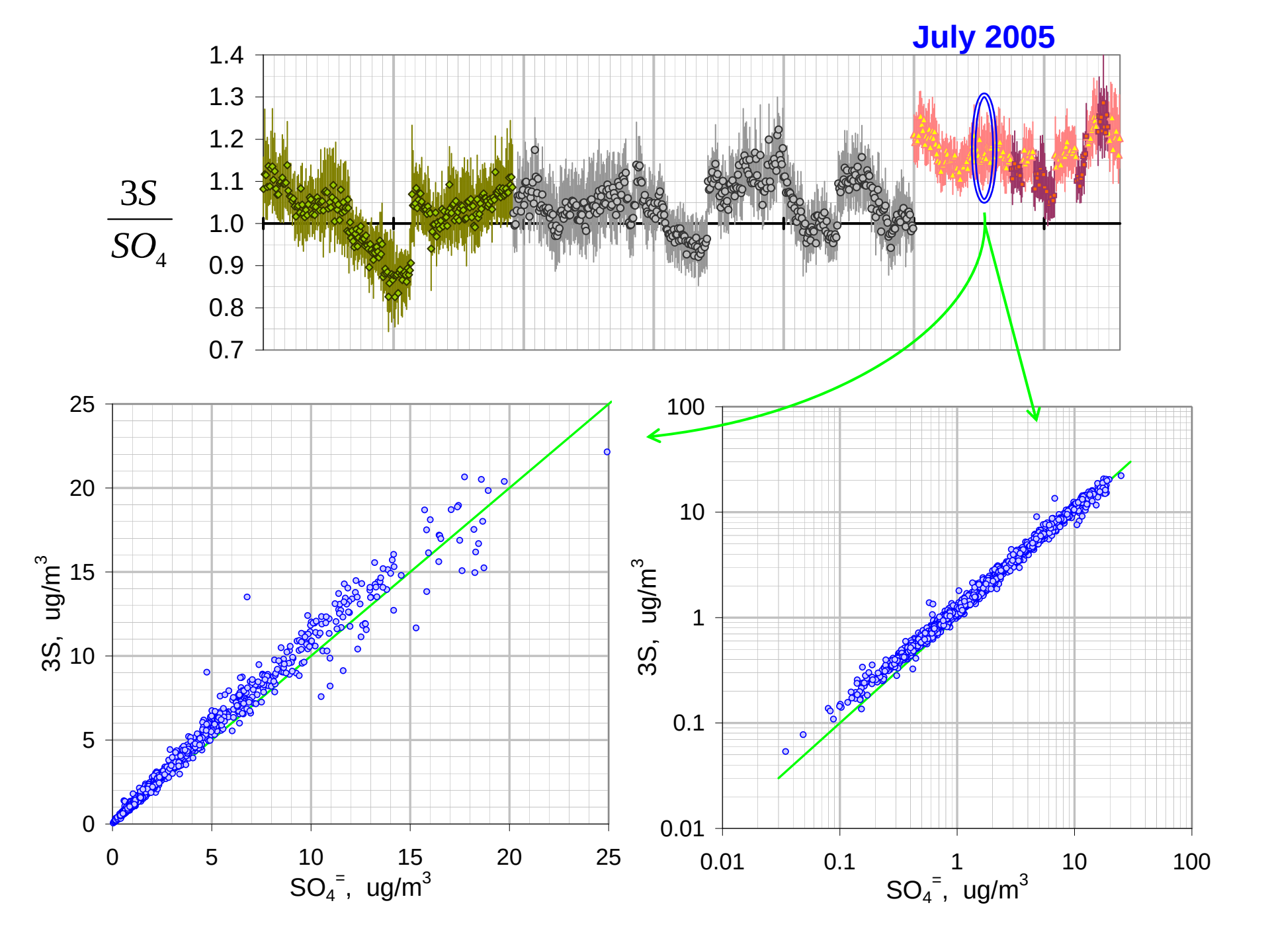
A year’s progress in XRF

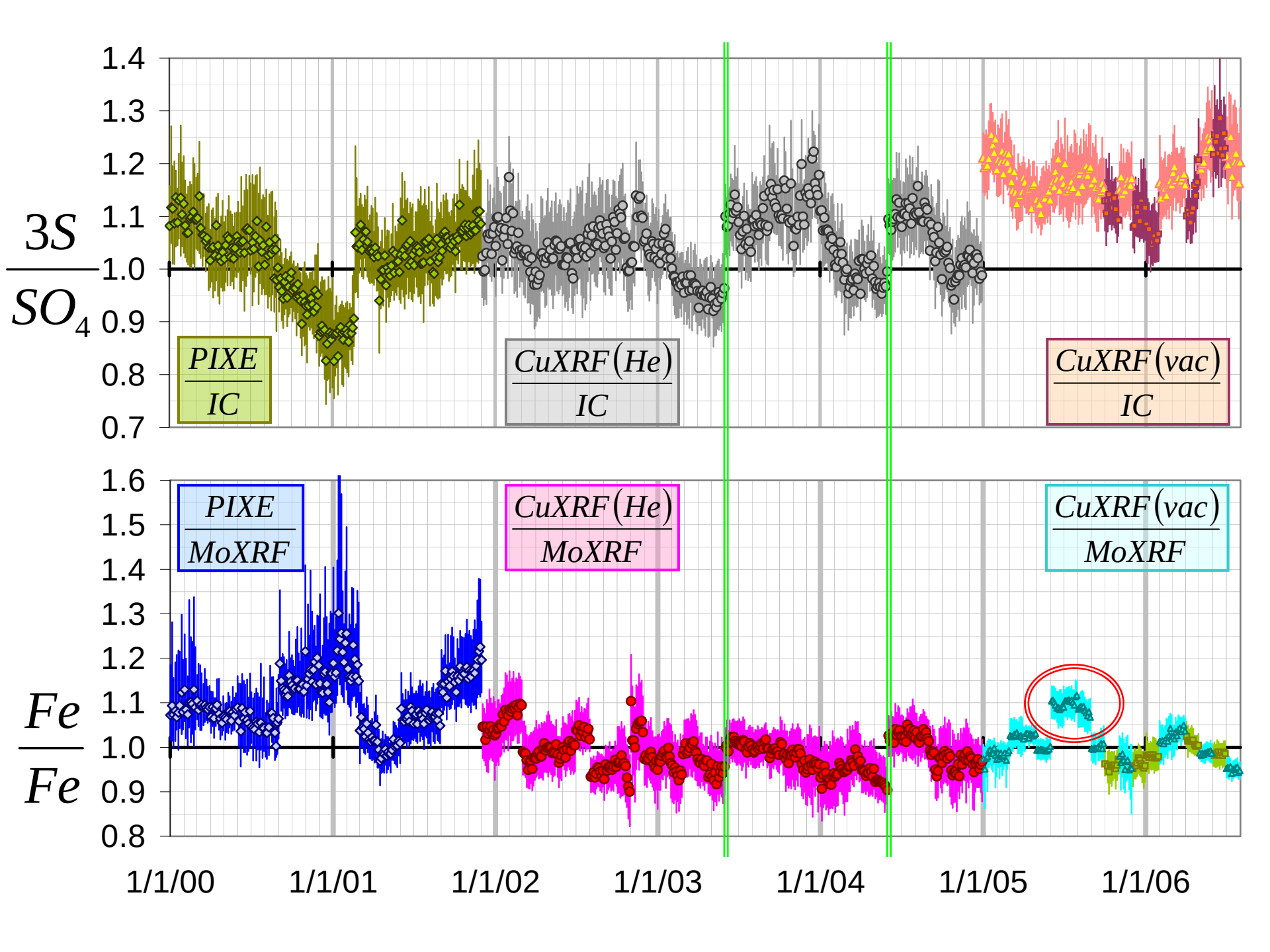
- Performance
- Documentation
- Understanding

Warren H. White, Durango 9/2007

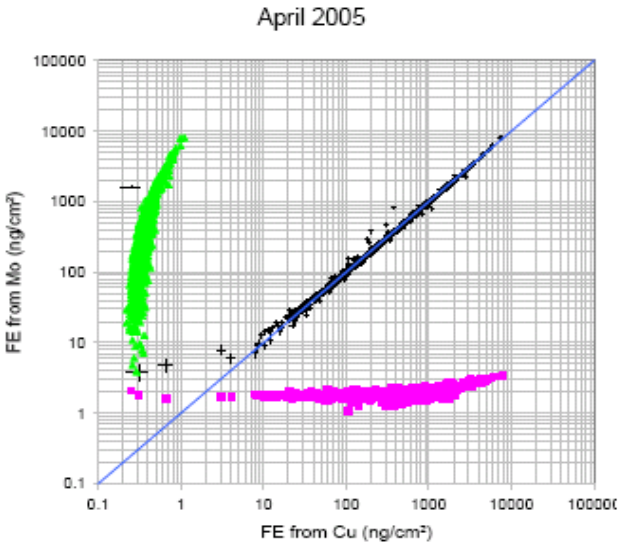
MEDIAN AND INTERQUARTILE RANGE
ENTIRE NETWORK, ALL DETECTED CONCENTRATIONS

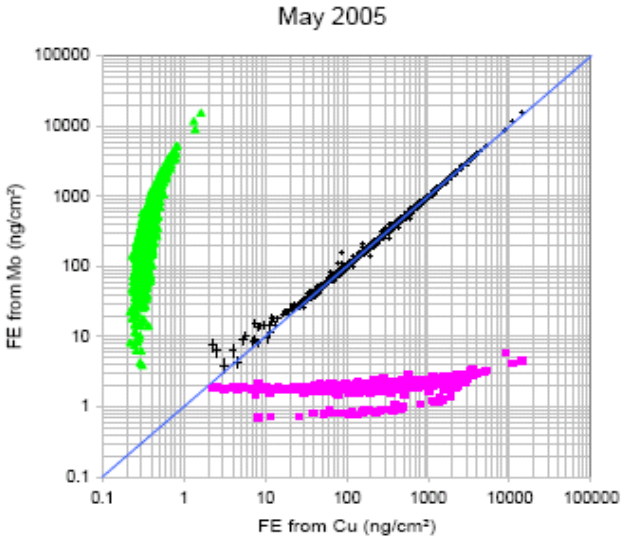



July 2005
$\frac{3S}{SO_4}$
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
25
20
15
10
5
0
3S, ug/m3
0
5
10
15
20
25
SO4=, ug/m3
100
10
1
0.1
0.01
3S, ug/m3
0.01
0.1
1
10
100
SO4=, ug/m3


3S / SO4
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
PIXE / IC
CuXRF(He) / IC
CuXRF(vac) / IC
Fe / Fe
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
PIXE / MoXRF
CuXRF(He) / MoXRF
CuXRF(vac) / MoXRF
1/1/00
1/1/01
1/1/02
1/1/03
1/1/04
1/1/05
1/1/06

http://vista.cira.colostate.edu/improve/Data/QA_QC/QAQC_UCD.htm





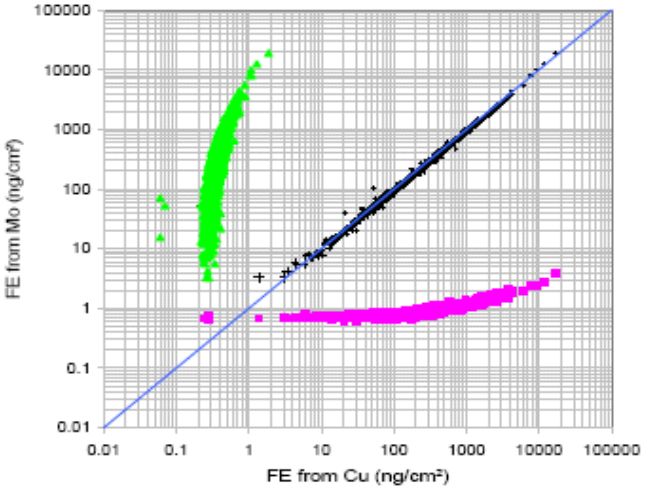
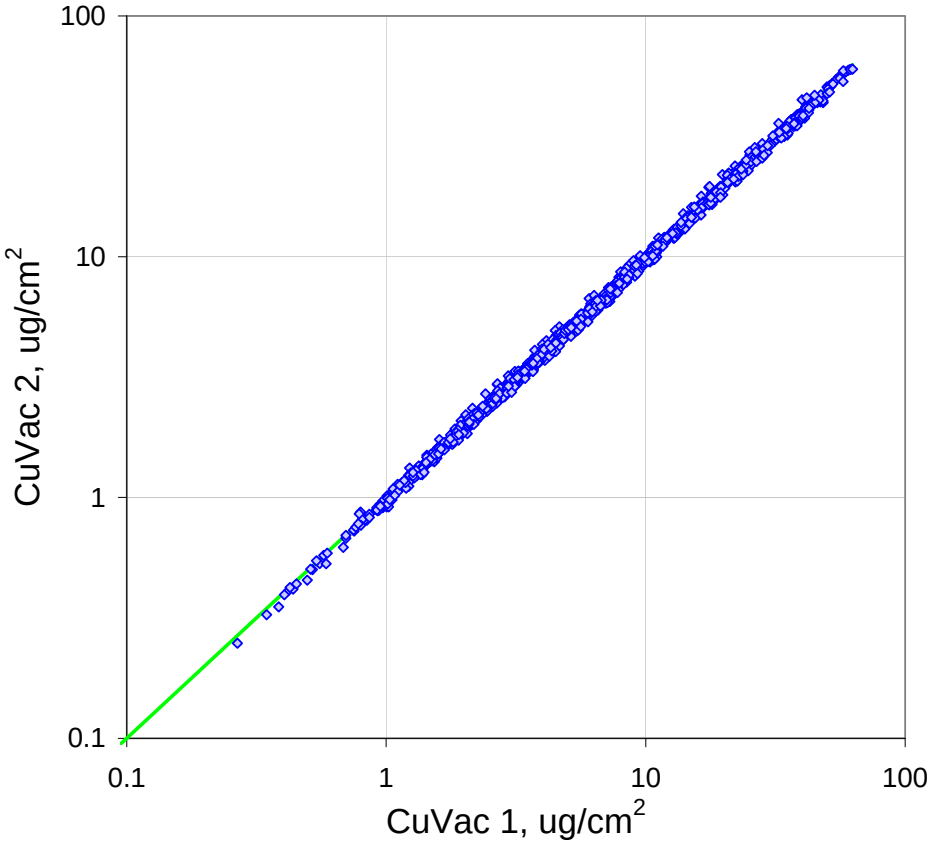
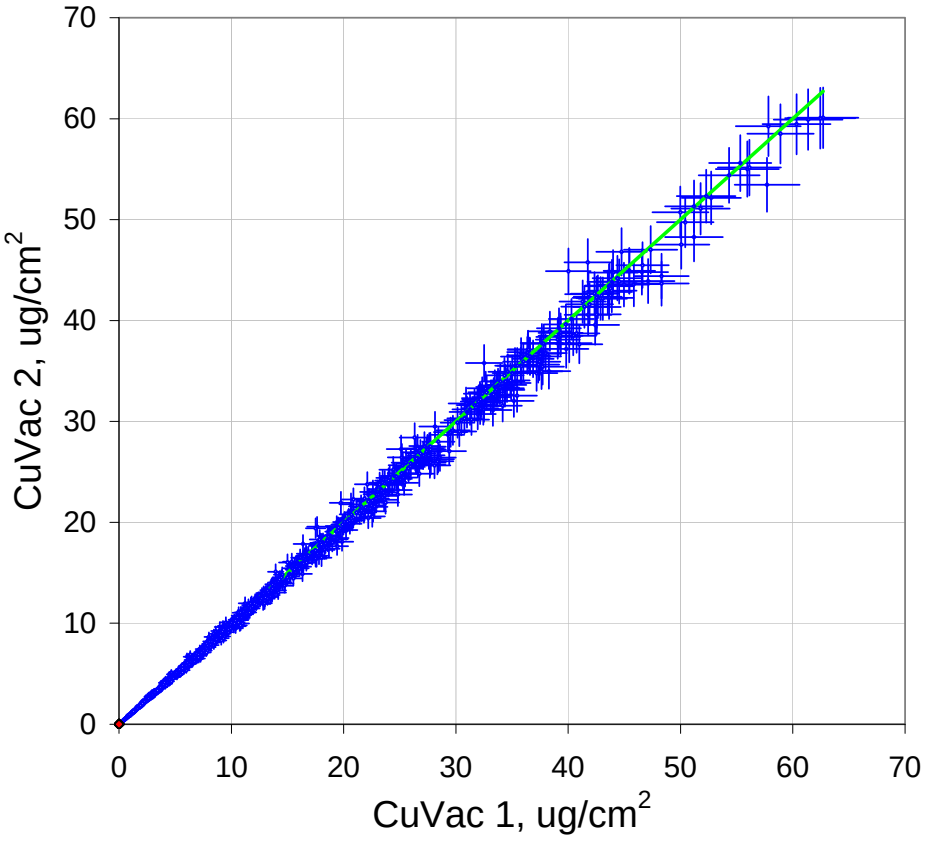


Figure 7. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems.

The detector in the Mo system was replaced (and the system was accordingly recalibrated) during the analysis of May 2005 samples. The samples analyzed after this change, which were from QURE1, QUVA1, RAFA1, and REDW1, exhibited better (lower) MDL's.

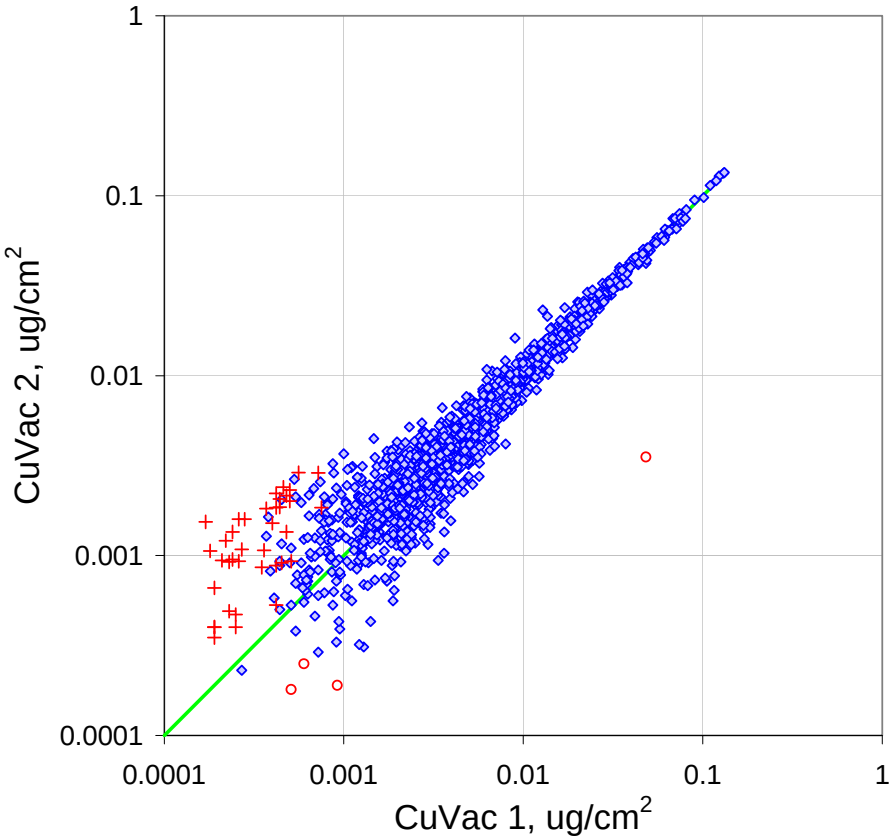
S, July 2005

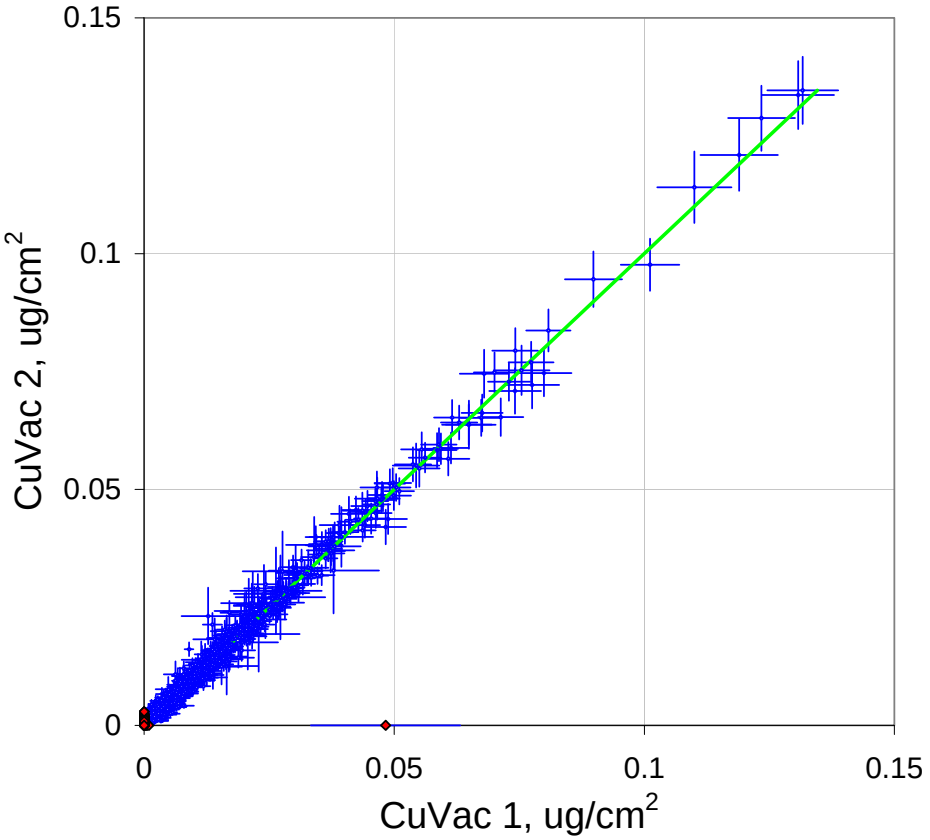




The introduction of a duplicate Cu-anode system made new comparisons possible.

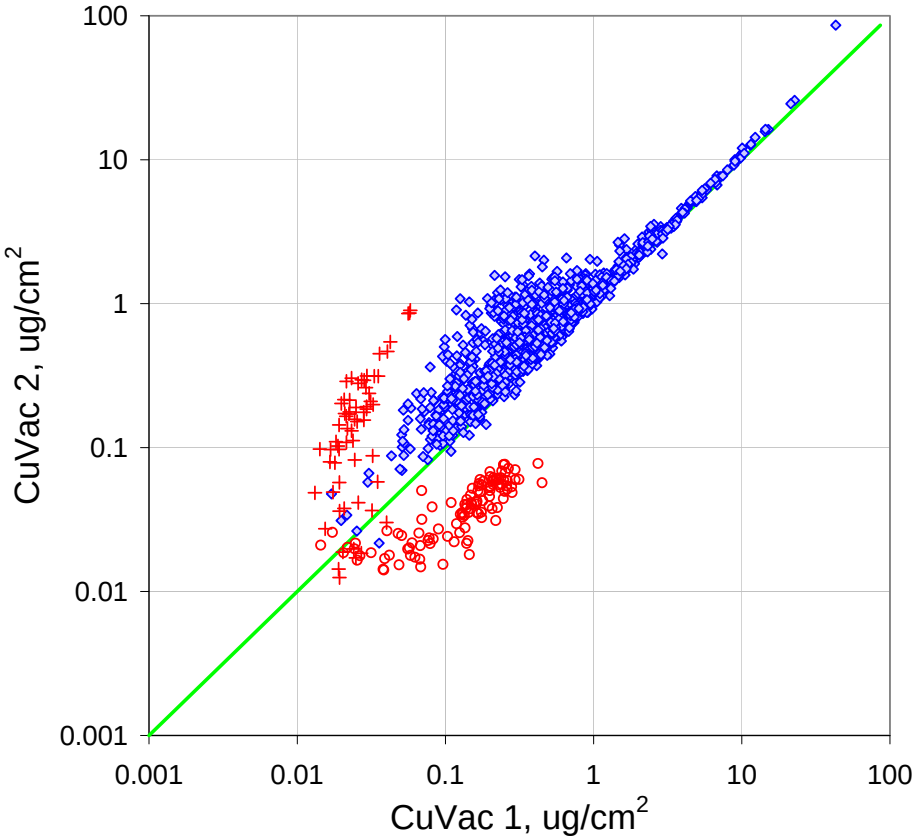
V, July 2005

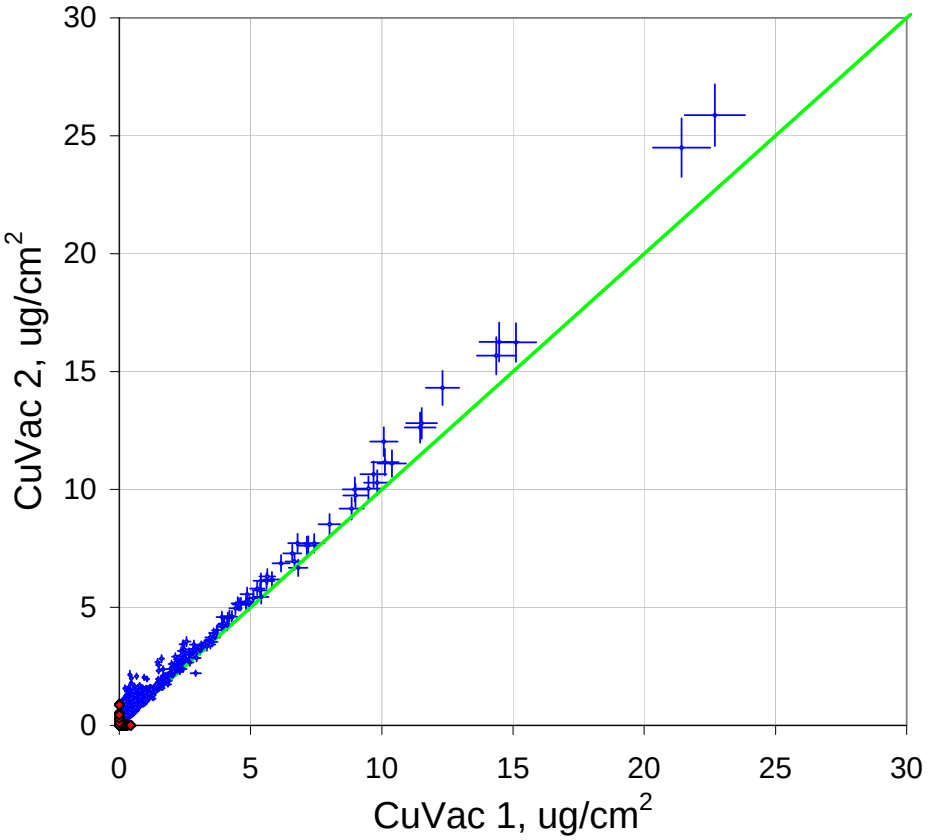




Vanadium is closer than sulfur to the detection limit, but the uncertainty is similar in both systems and is adequately characterized.

Al, July 2005





The “interference-free” detection limit reported for Al is known to be unrepresentative of actual performance,

as is now documented:

http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory/da0010/da0010_Almdl.pdf

Posting type	Advisory
Subject	Elemental concentrations above the MDL can go undetected
Module/Species	A/ Al
Sites	entire network
Period	entire record
Recommendation	Estimate undetected Al from Si (*e.g.* Eldred, 2003)

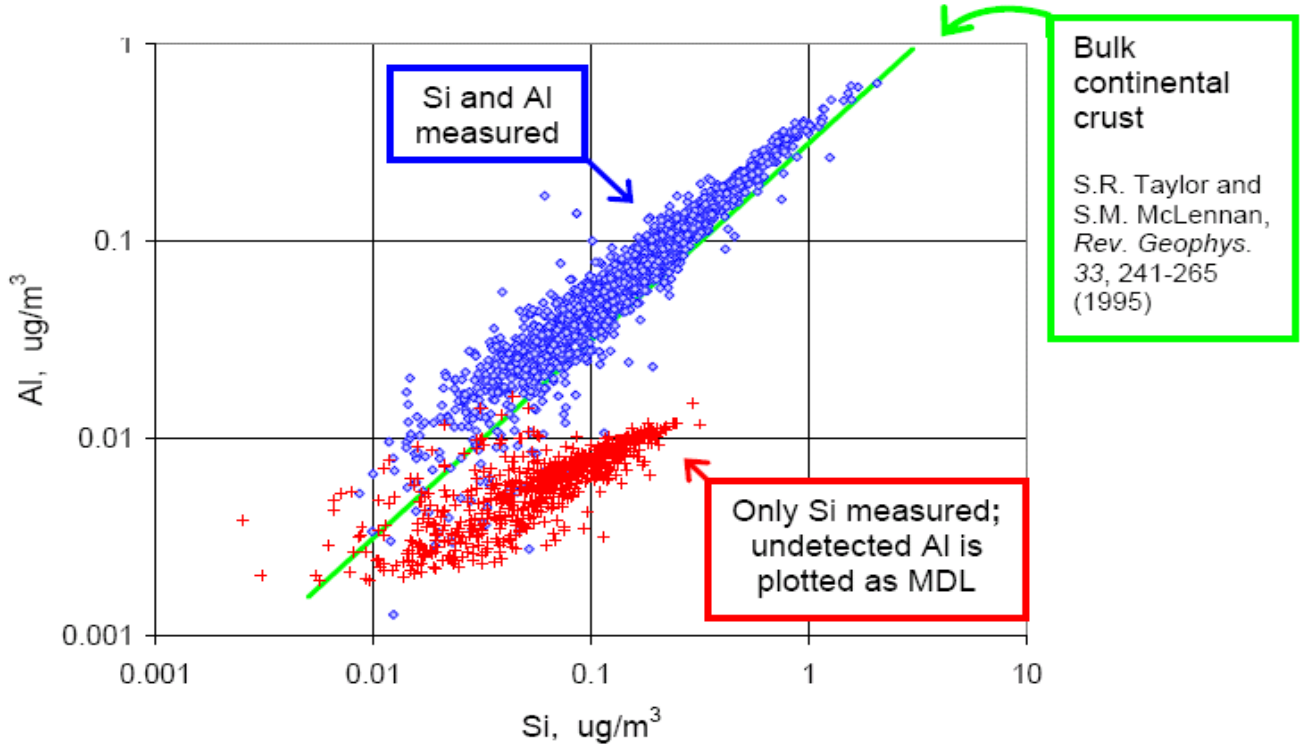
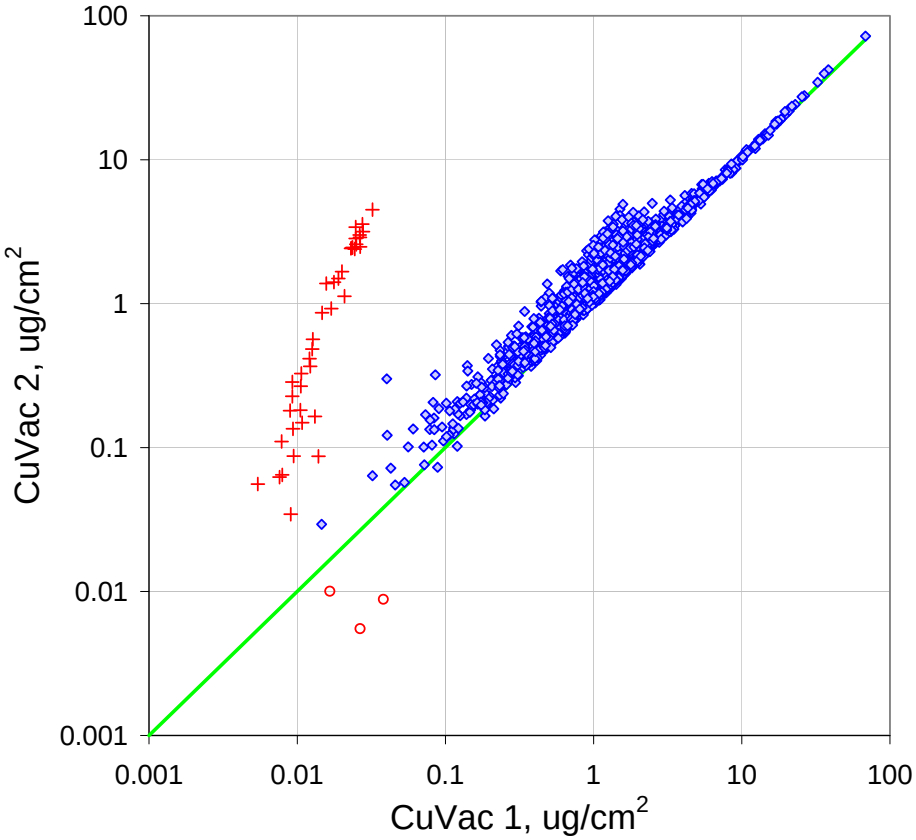
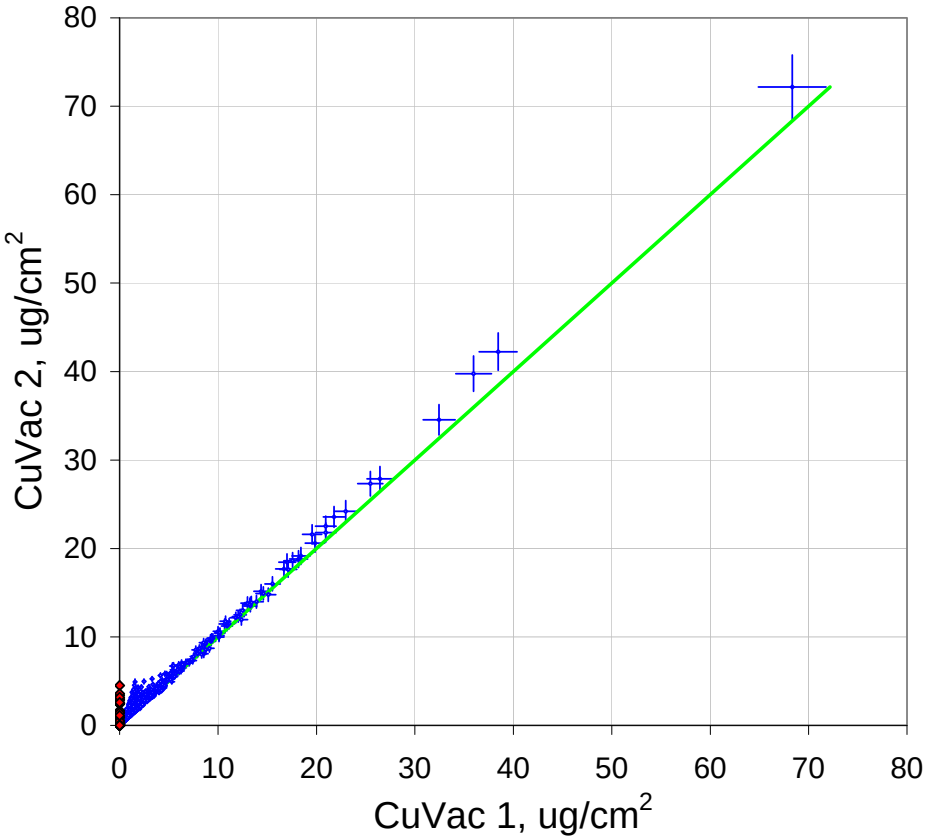


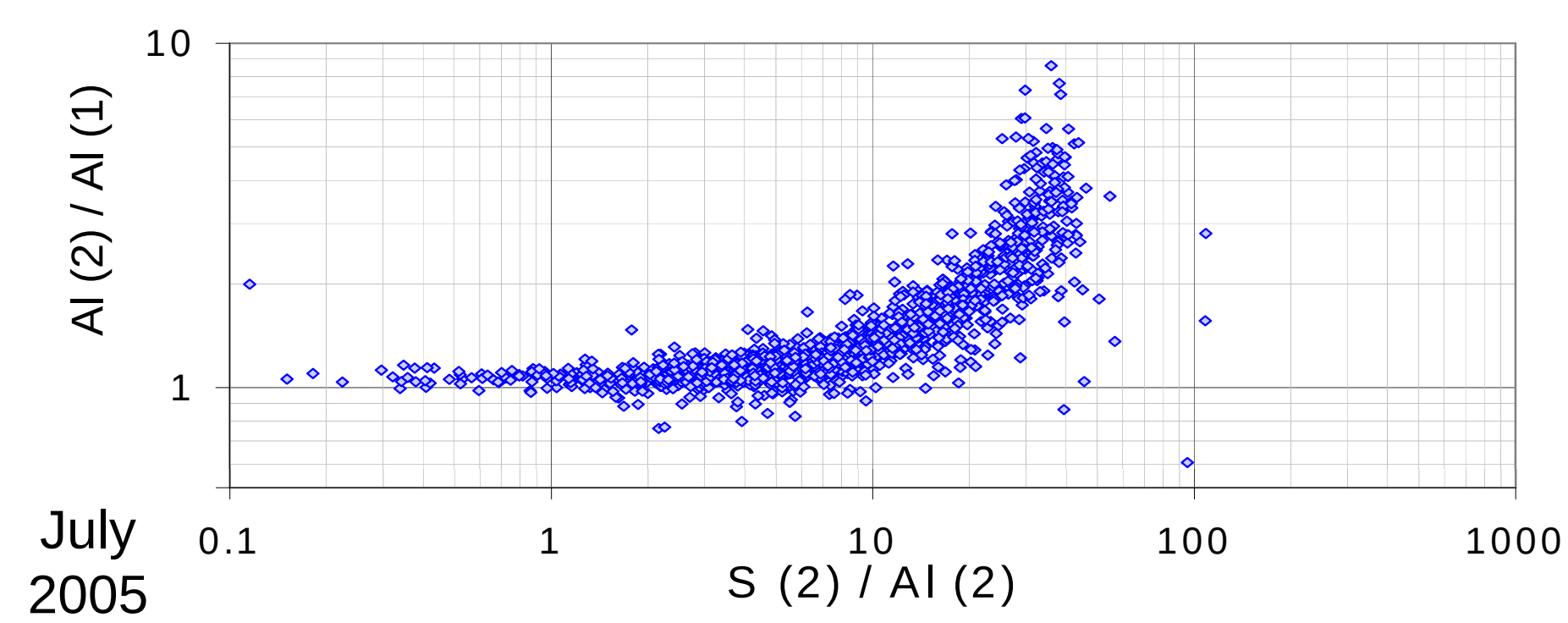
Figure 1. Aluminum and silicon concentrations from all non-urban sites in the network during March-April 2004.

Si, July 2005

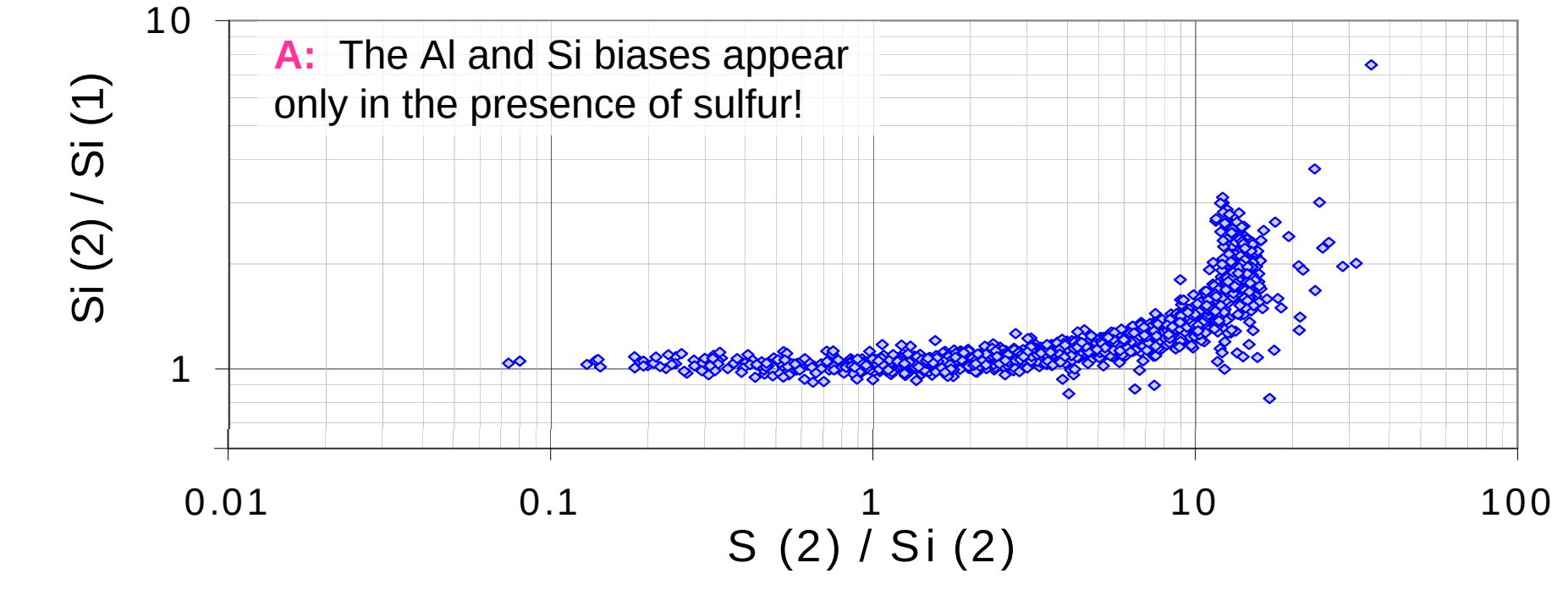




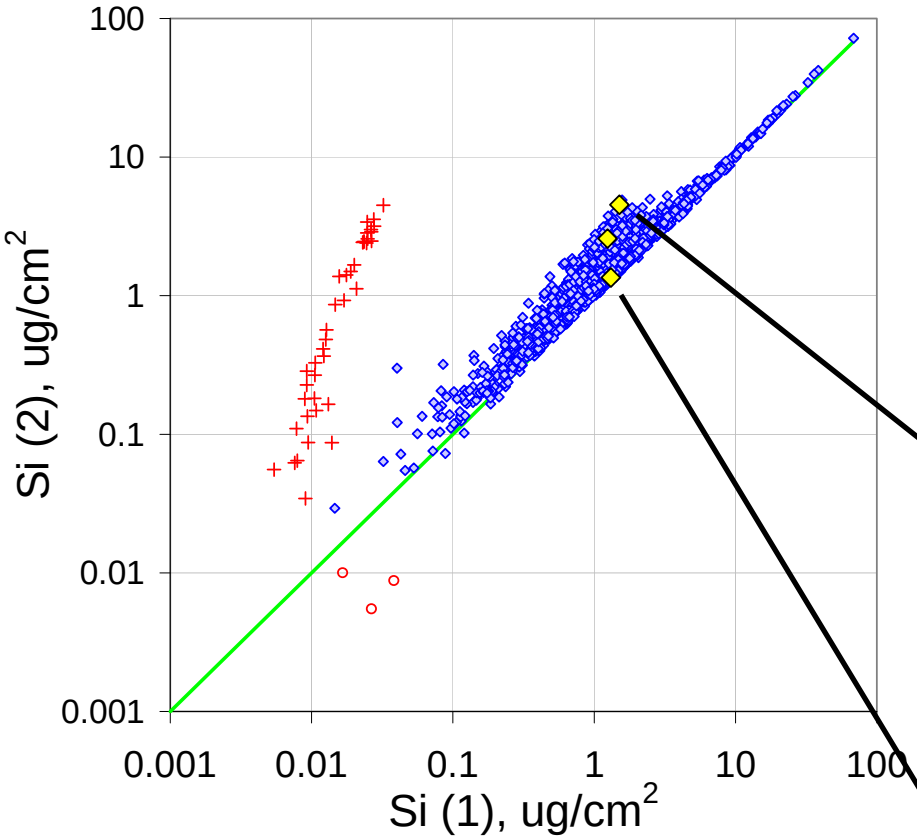
Q: How can the two systems show such relative bias for Si and Al when they are both calibrated to the same standards?

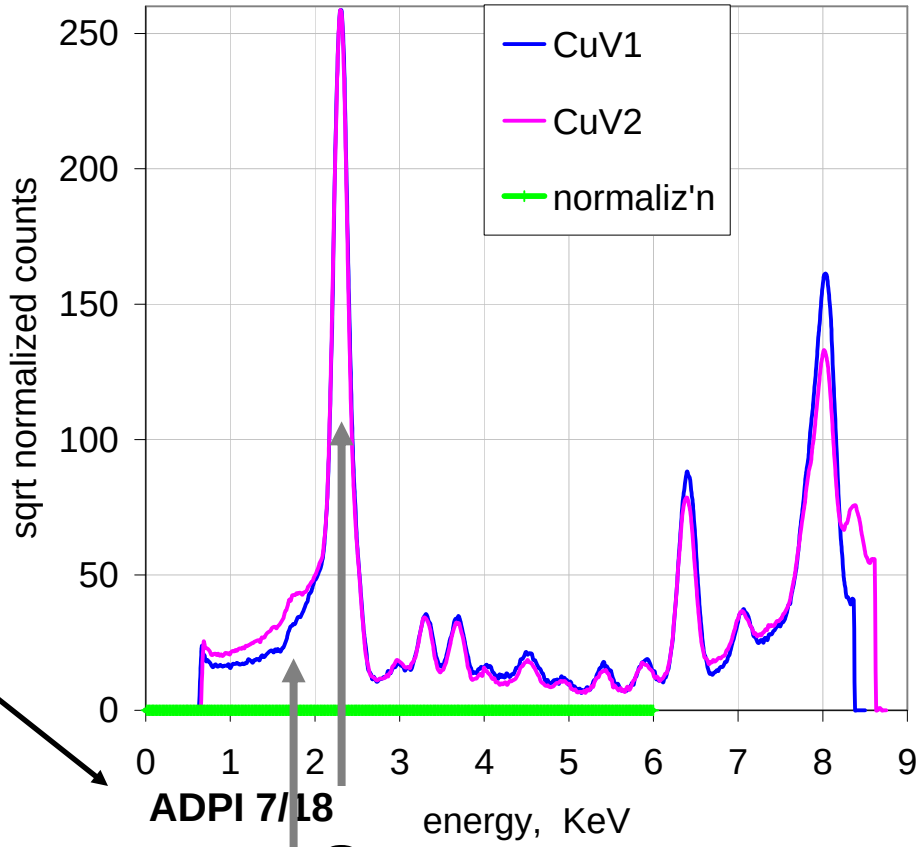

10
1
Al (2) / Al (1)
0.1
1
10
100
1000
S (2) / Al (2)

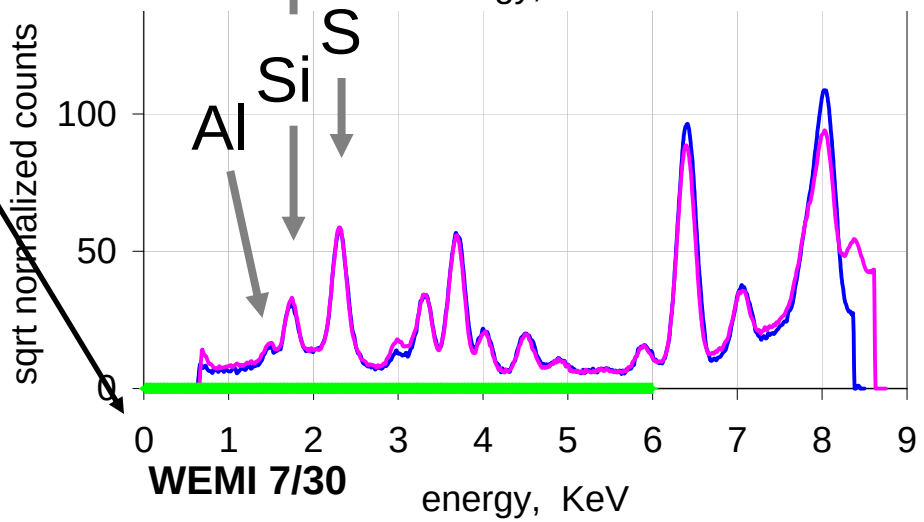
July 2005


10
1
Si (2) / Si (1)
A: The Al and Si biases appear only in the presence of sulfur!
0.01
0.1
1
10
100
S (2) / Si (2)

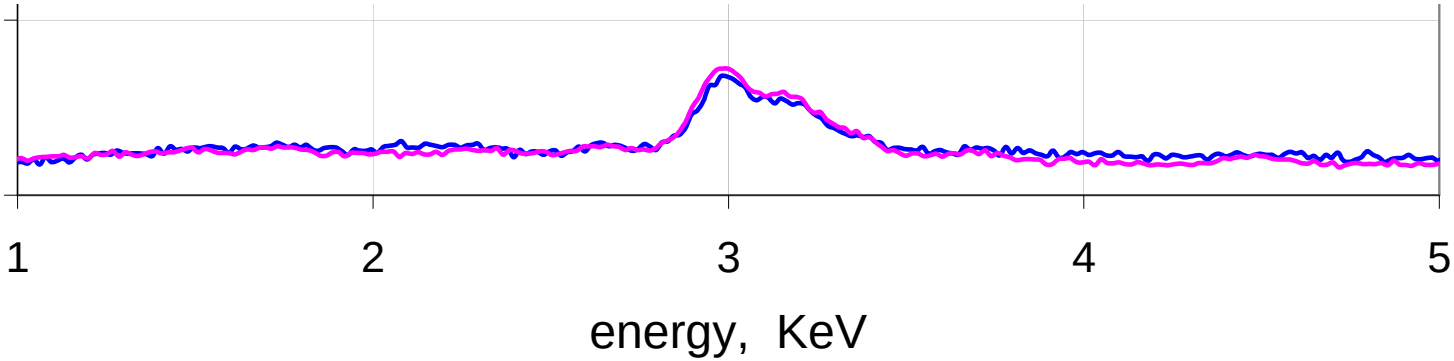
July 2005


100
10
1
0.1
0.01
0.001
0.001
0.01
0.1
1
10
100
Si (2), ug/cm2
Si (1), ug/cm2

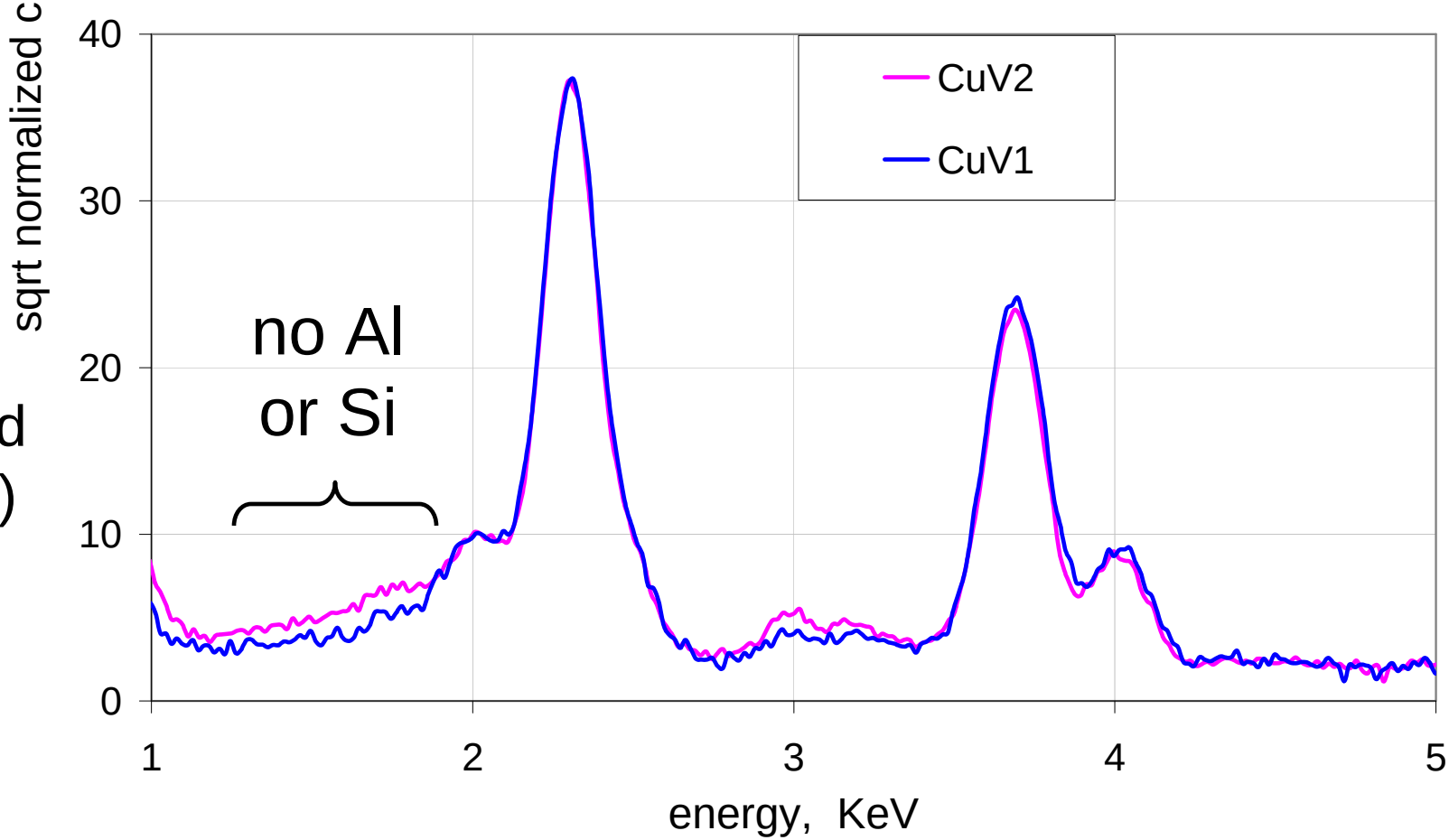

CuV1
CuV2
normaliz'n
sqrt normalized counts
250
200
150
100
50
0
0 1 2 3 4 5 6 7 8 9
energy, KeV
ADPI 7/18


S
Si
Al
sqrt normalized counts
100
50
0
0 1 2 3 4 5 6 7 8 9
energy, KeV
WEMI 7/30

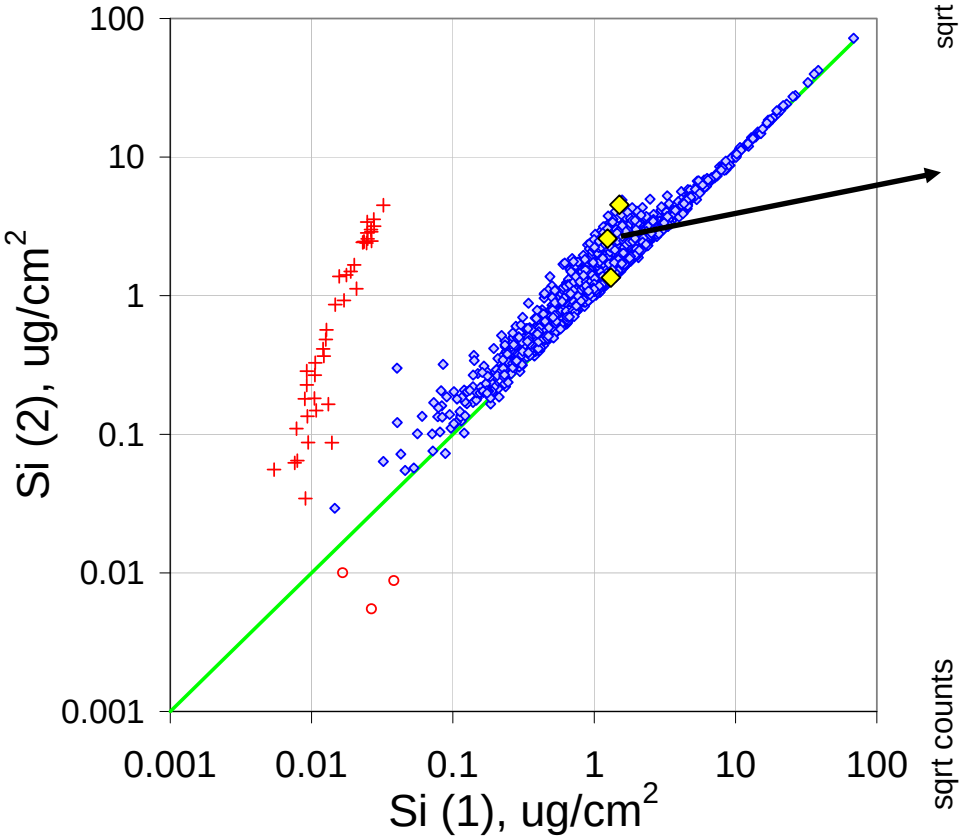
Teflon blank

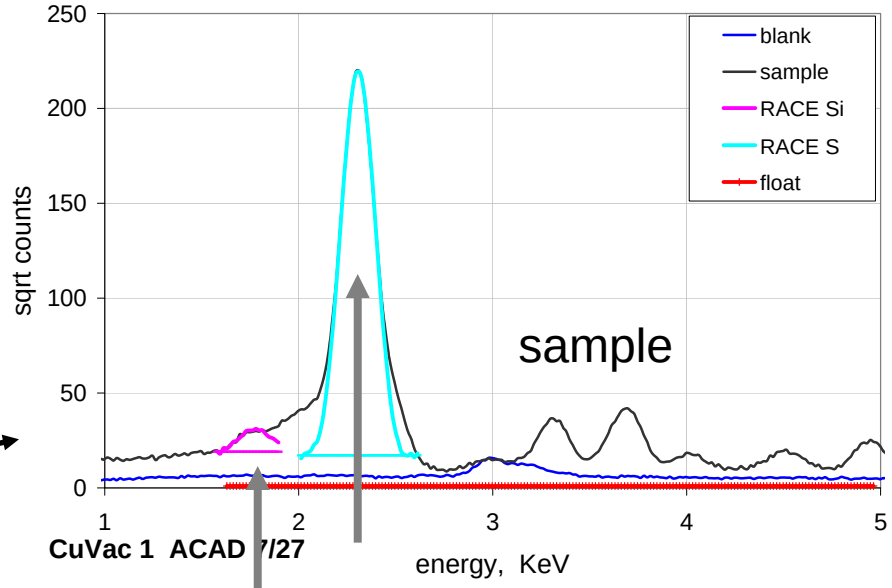


S standard (on Mylar)



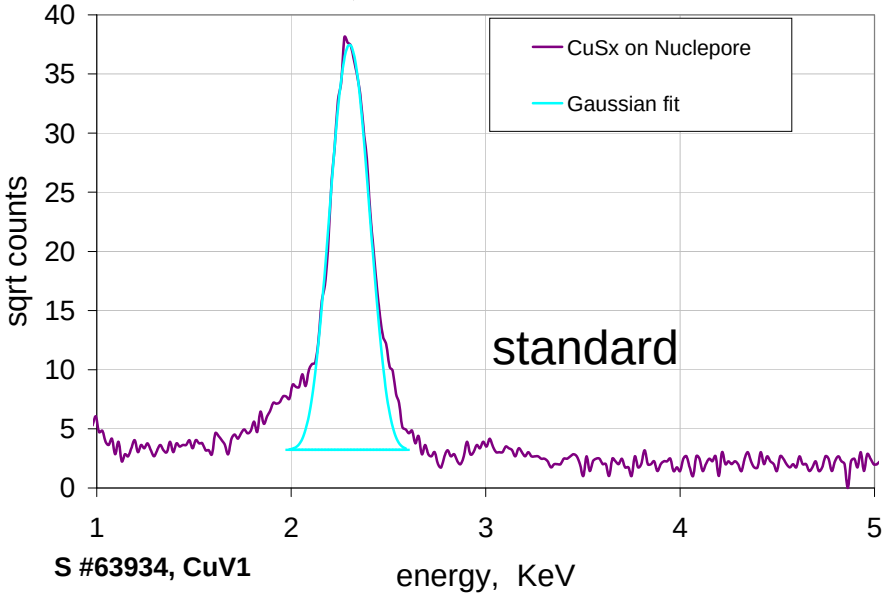
July 2005

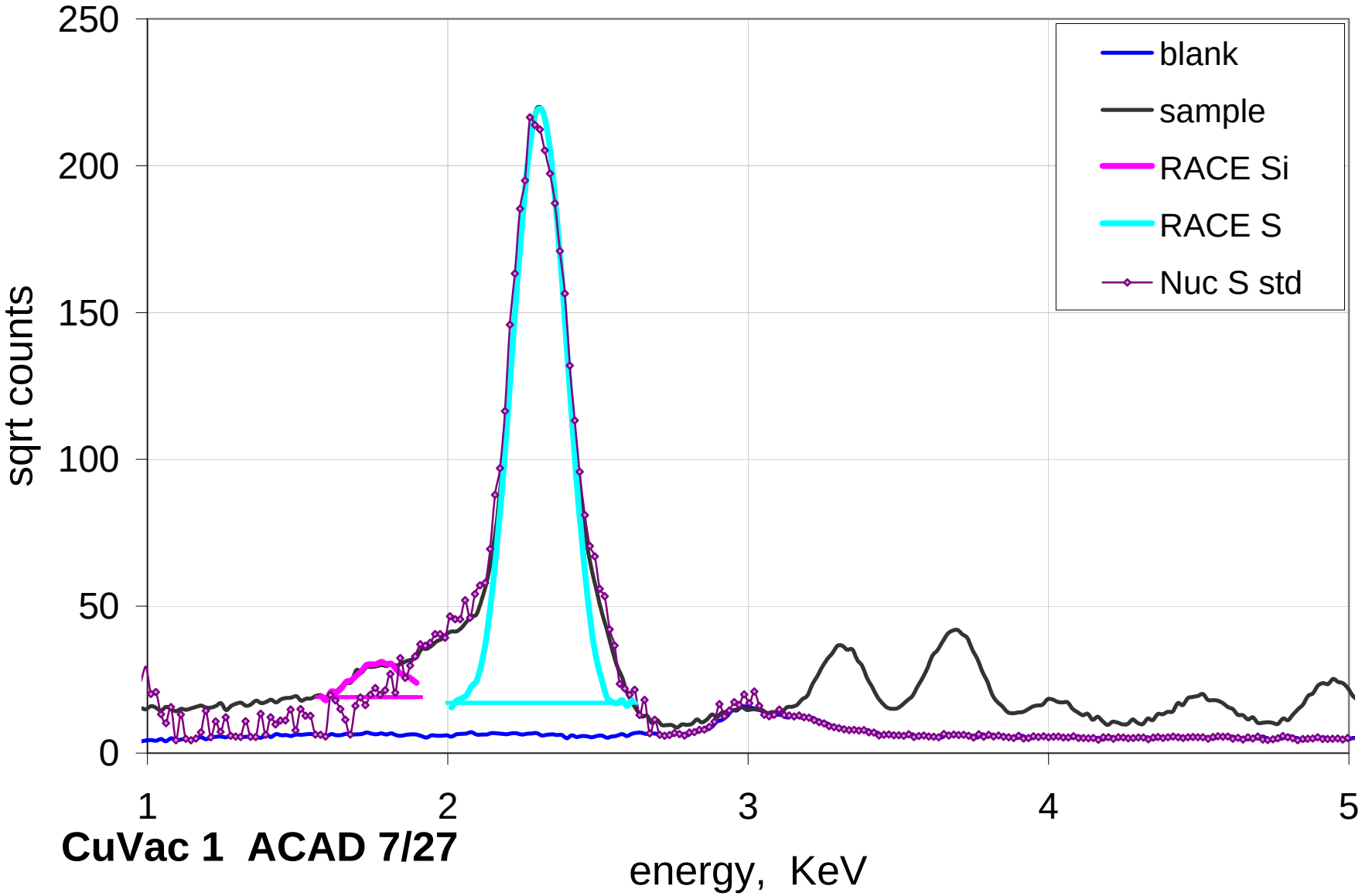


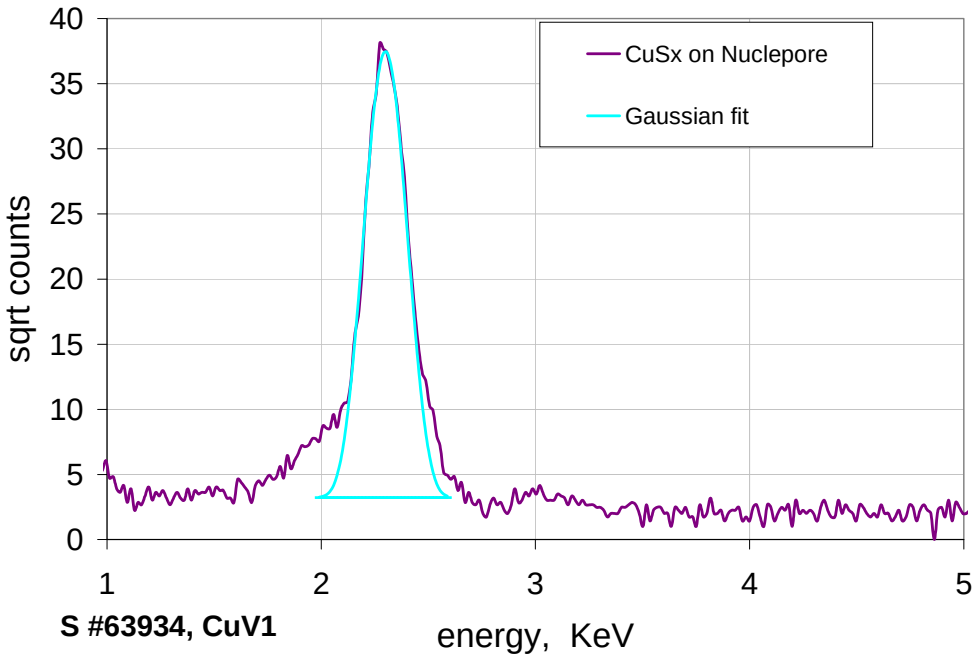


S

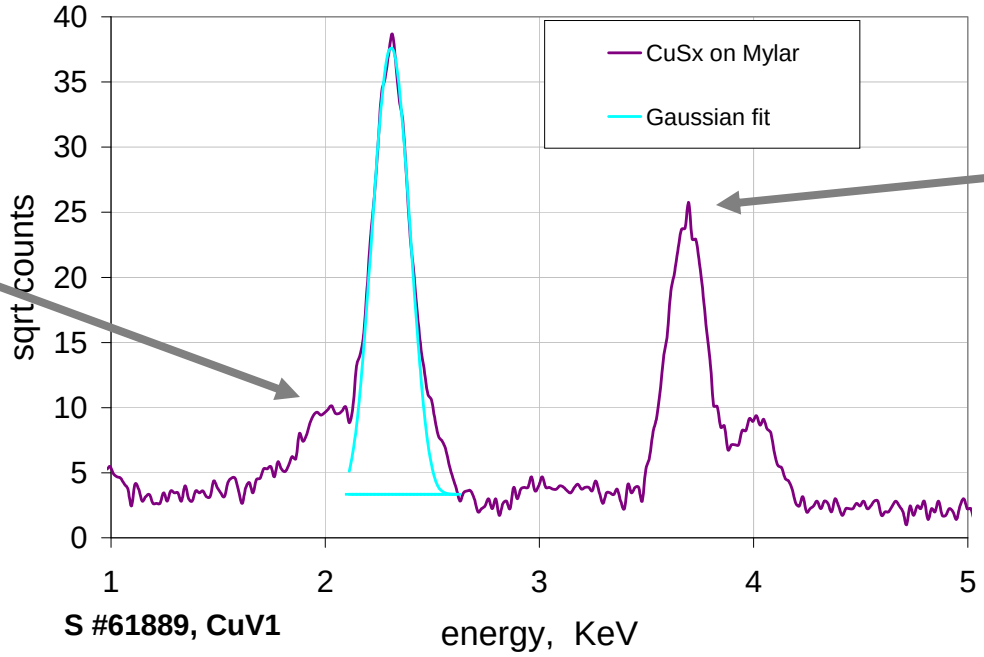
Si




250
200
150
100
50
0
sqrt counts
1
2
3
4
5
energy, KeV
blank
sample
RACE Si
RACE S
Nuc S std
CuVac 1 ACAD 7/27



Nuclepore backing, under consideration



Si escape peak:

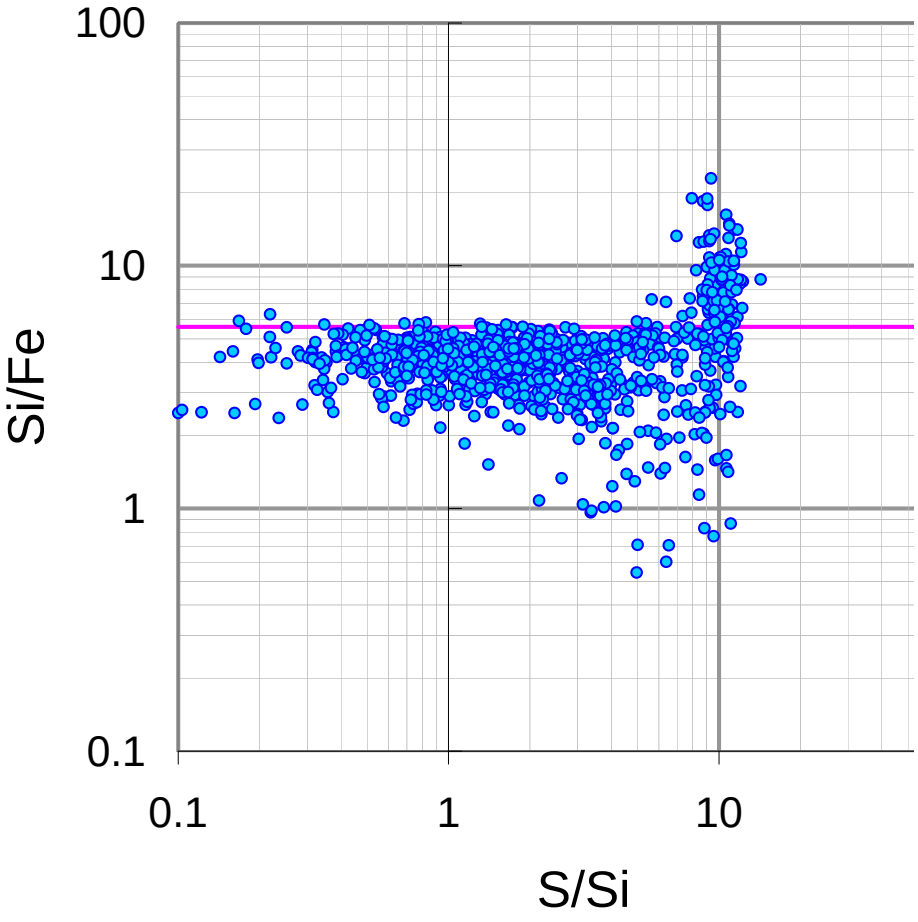
3.69 KeV
- 1.74 KeV
=1.95 Kev

Ca

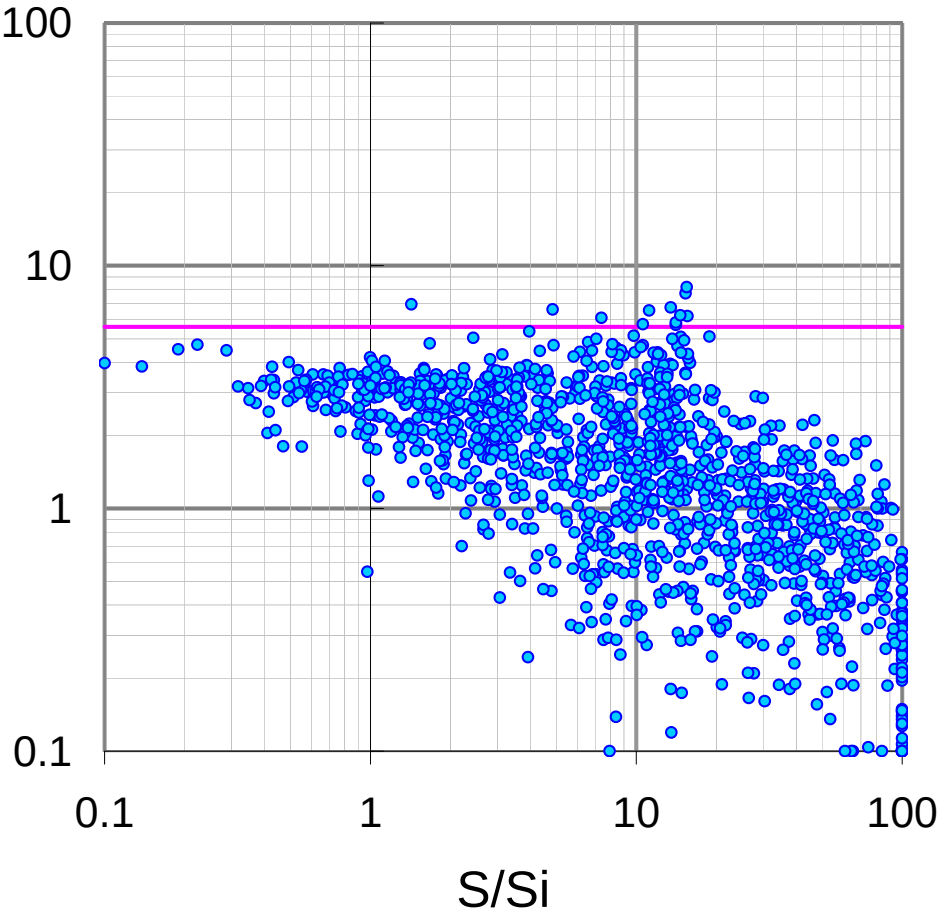
Mylar backing, historical choice

July, 2004,

Fe > 0.025 ug/m^3



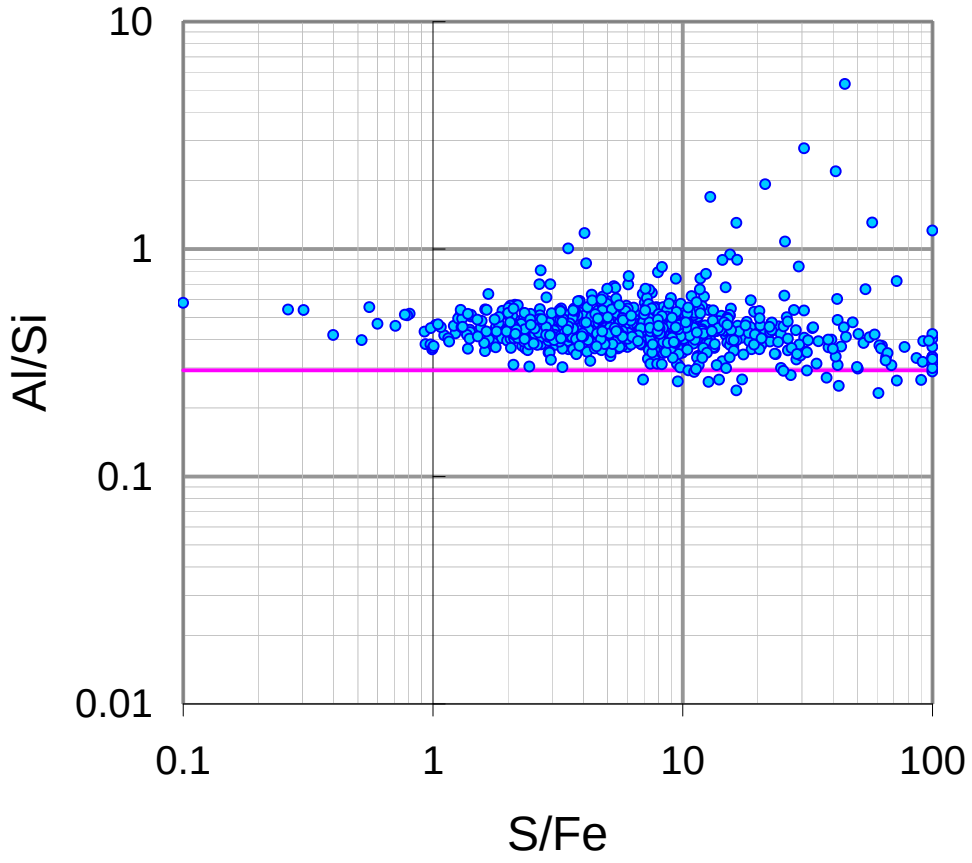
IMPROVE, Cu (He)



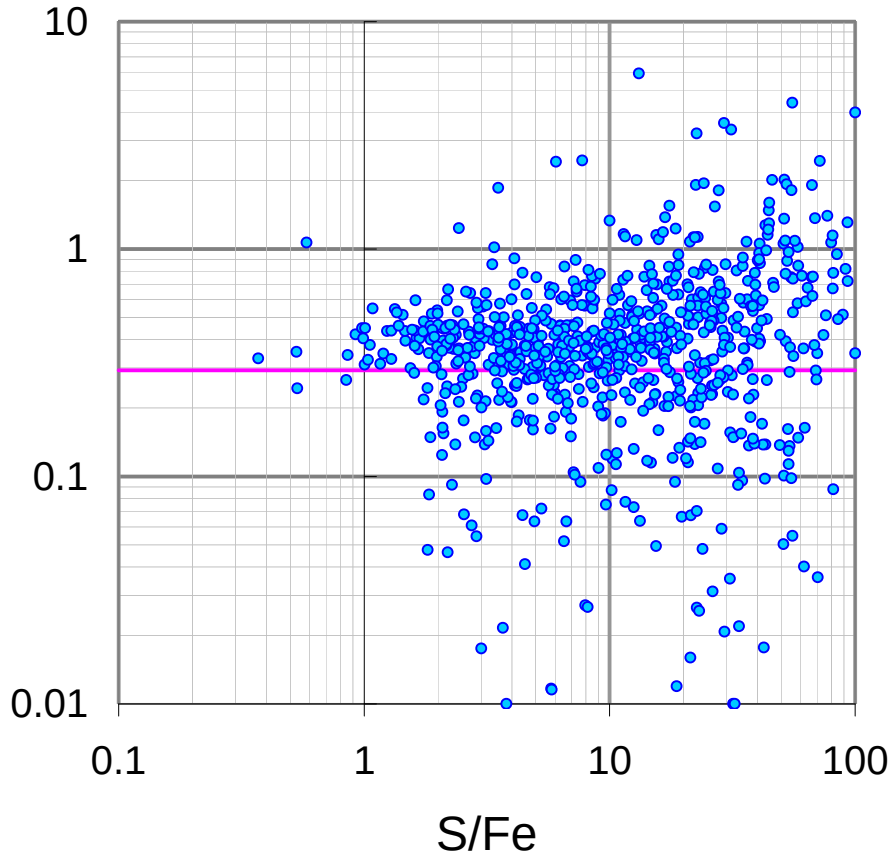
Chemical Speciation Network

July, 2004,

Fe > 0.025 ug/m^3

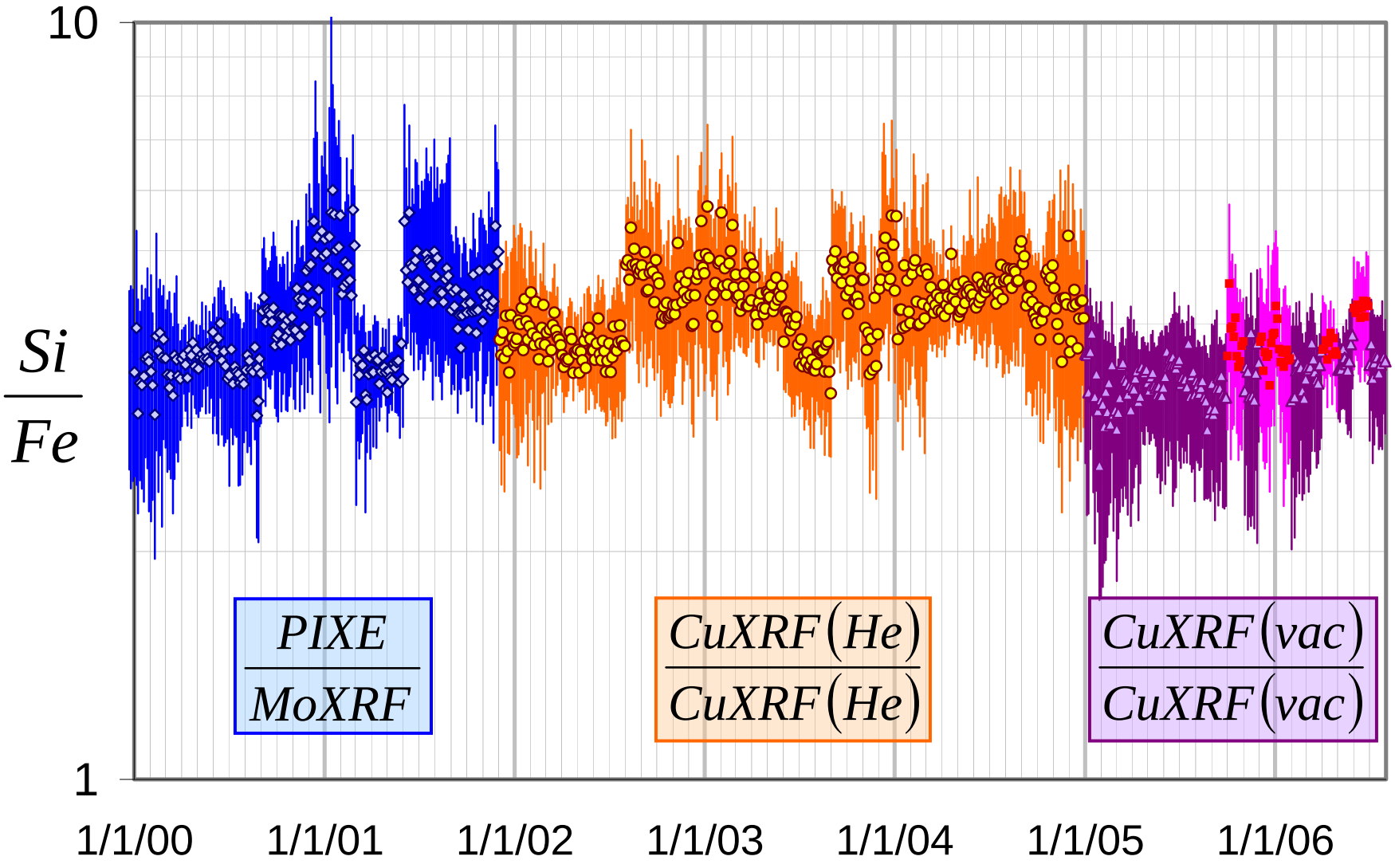


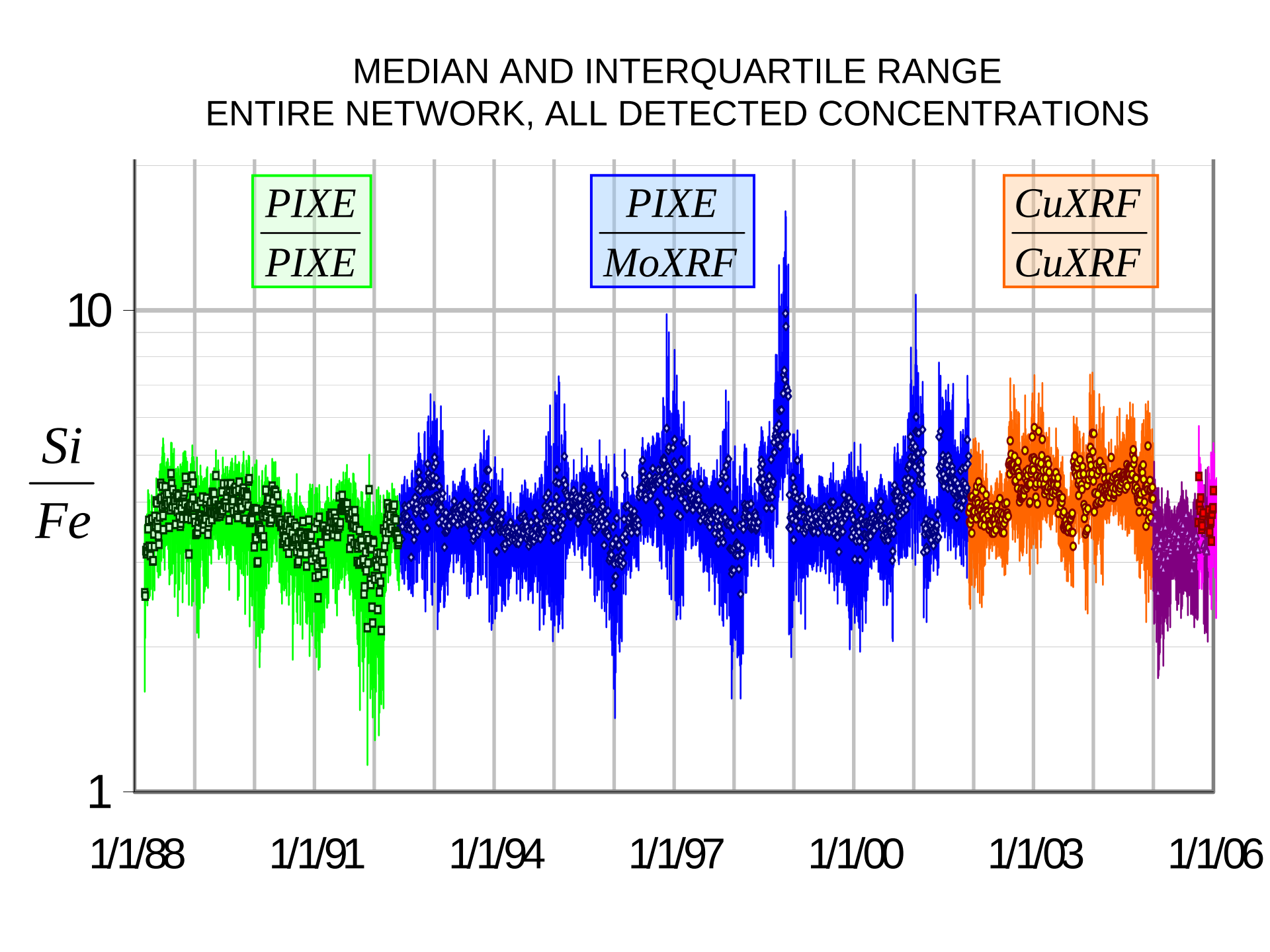
IMPROVE, Cu (He)



Chemical Speciation Network

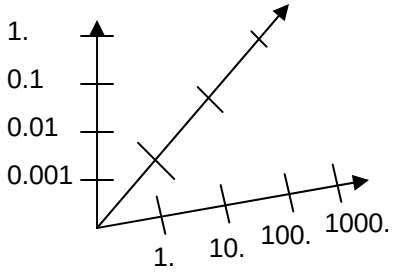
MEDIAN AND INTERQUARTILE RANGE
ENTIRE NETWORK, ALL DETECTED CONCENTRATIONS




MEDIAN AND INTERQUARTILE RANGE
ENTIRE NETWORK, ALL DETECTED CONCENTRATIONS
PIXE / PIXE
PIXE / MoXRF
CuXRF / CuXRF
10
1
Si / Fe
1/1/88
1/1/91
1/1/94
1/1/97
1/1/00
1/1/03
1/1/06

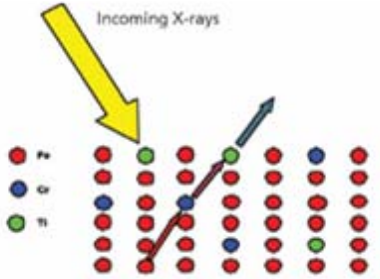
EDXRF is a bountiful measurement method.

It can simultaneously determine a dozen elements in each sample, at concentrations ranging over orders of magnitude. It can be automated to process samples of diverse compositions with a single set of calibration parameters.



Its bounty challenges calibration.

The disparate environments represented in the network span a huge volume in the space of concentrations. Calibration tolerances that are more than adequate in one region may yield unacceptable errors in another.



My personal conclusion: "Of whom much is given, much is expected."

The <u>user</u> of routine EDXRF data must therefore accept some of the responsibility for assessing its quality.