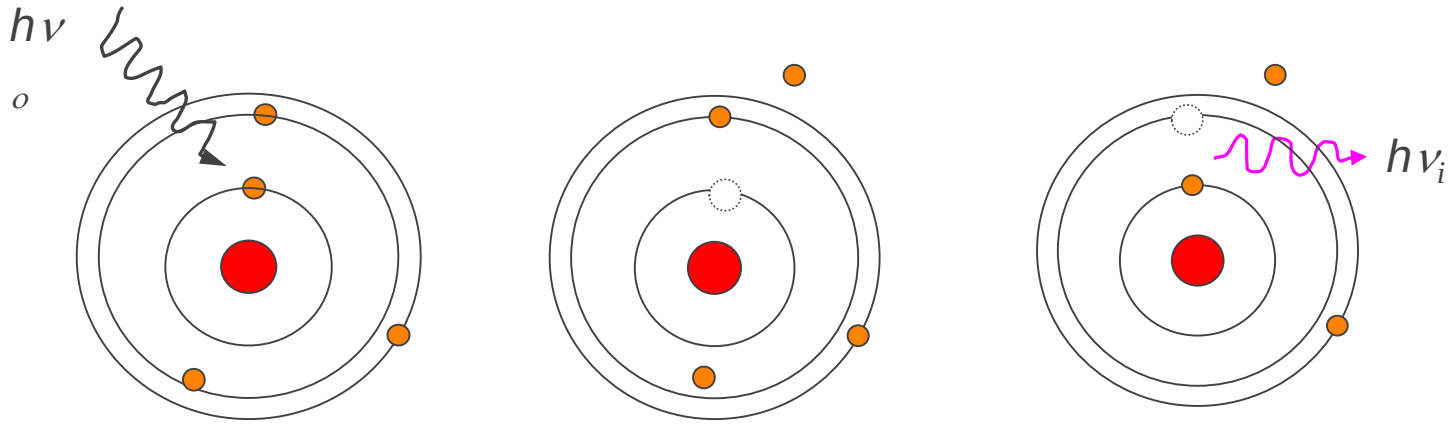
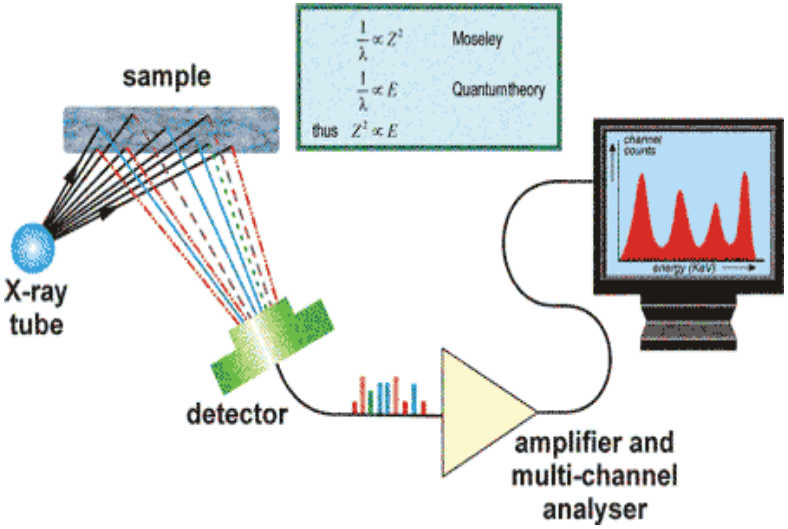
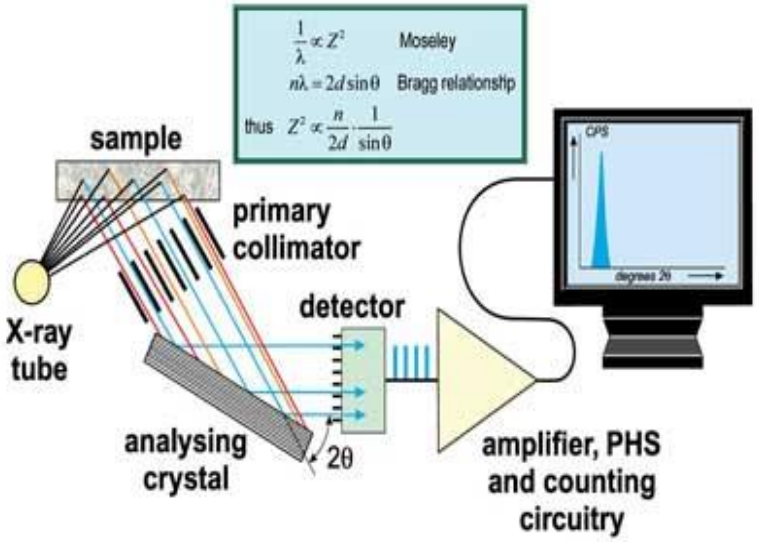
On site heavy metal testing and monitoring using monochromatic XRF methods

X-Ray Fluorescence Analysis

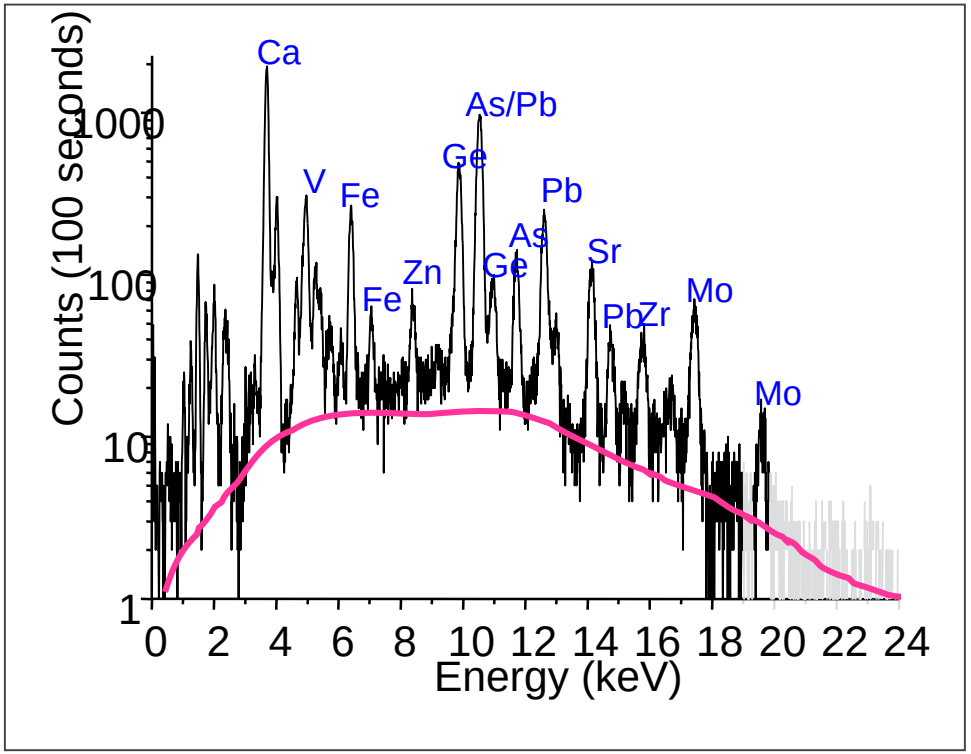






Limitation of XRF

- High scattering background
- Difficult in sub-ppm level
- Matrix effect and interference



Limitation of current field XRF

- Hand Held XRF/Portable XRF
  - Powerful tools for high level contaminations testing
  - Low cost
  - Non-destructive, no sample preparation
- Limitation of HHXRF and Portable XRF
  - Ineffective for Cd, As, and Hg
  - Inability of measure 1-20ppm range for most of metals

Quantitative analysis in Lab

Current State - Certification: Wet Chemistry/ICP

Wet Chemistry/ICP

- High testing costs
- Long time for results
- Sample Preparation
  - Acid Digestion
- Multi-step process increases result variability
  - Scale, moisture determination, microwave, ICP instrument
- Trained operators required
  - Introduces likliehood of operator error
- Requires expensive consumables (Gas, acid, multiple sample tubes)

Needs for Site Testing

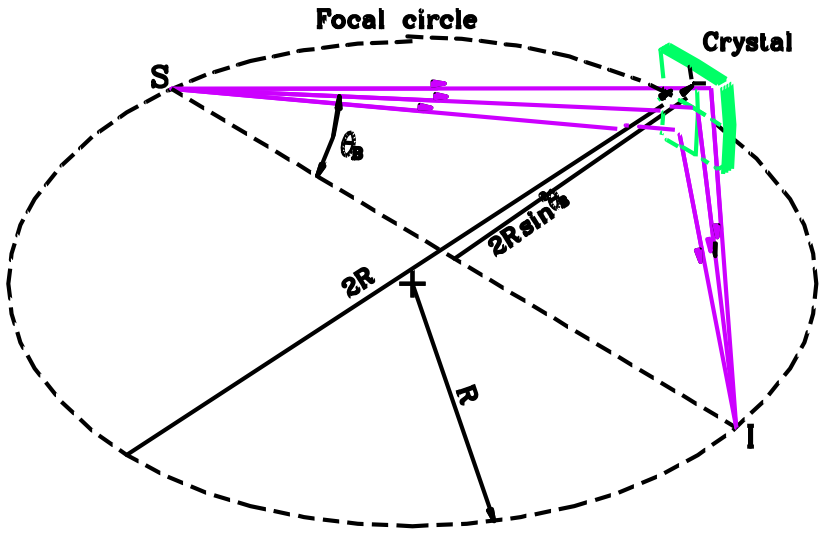
- Accurate assessment of a contaminated site often required a large number of sampling
- Large number of the samples sent to lab for analysis
- Lack of an effective site testing method is a major bottle neck for both economic cost and regulatory enforcement

As and Hg Site Testing

- Meaningful As testing at a contaminated site is difficult if Pb level is relatively high
- Meaningful level of Hg on site testing is almost impossible

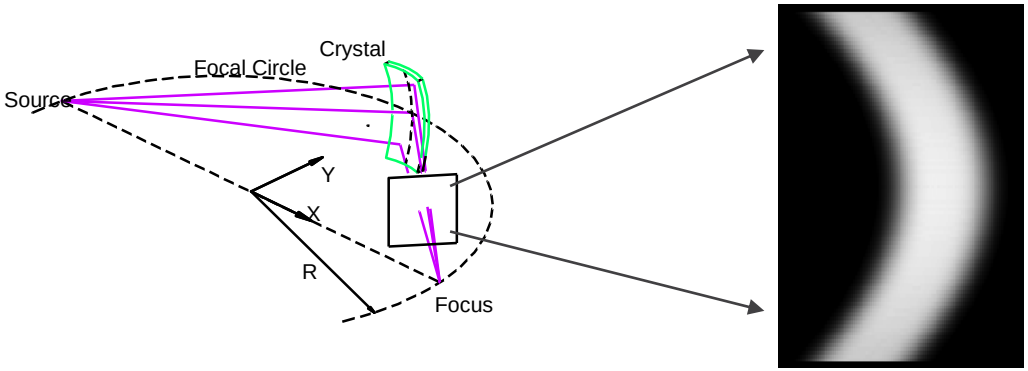
Doubly Curved Crystal Optic

- Point Focusing Geometry



- Solid angle: ~ 0.01 to 0.05 Sr.
- Beam spot size: 50-500μm, depending on the source spot
- Reflection efficiency ~ 10%
- Beam flux: ~ 10^8 -10^{10} photons/s
- Highly monochromatic

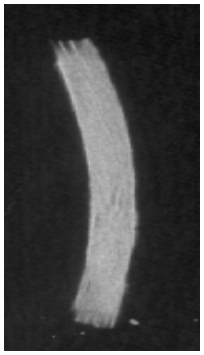
DCC Beam Profile

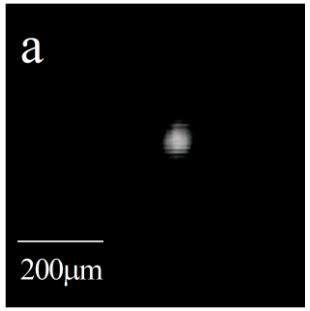


The deviation of incident angle from the Bragg angle

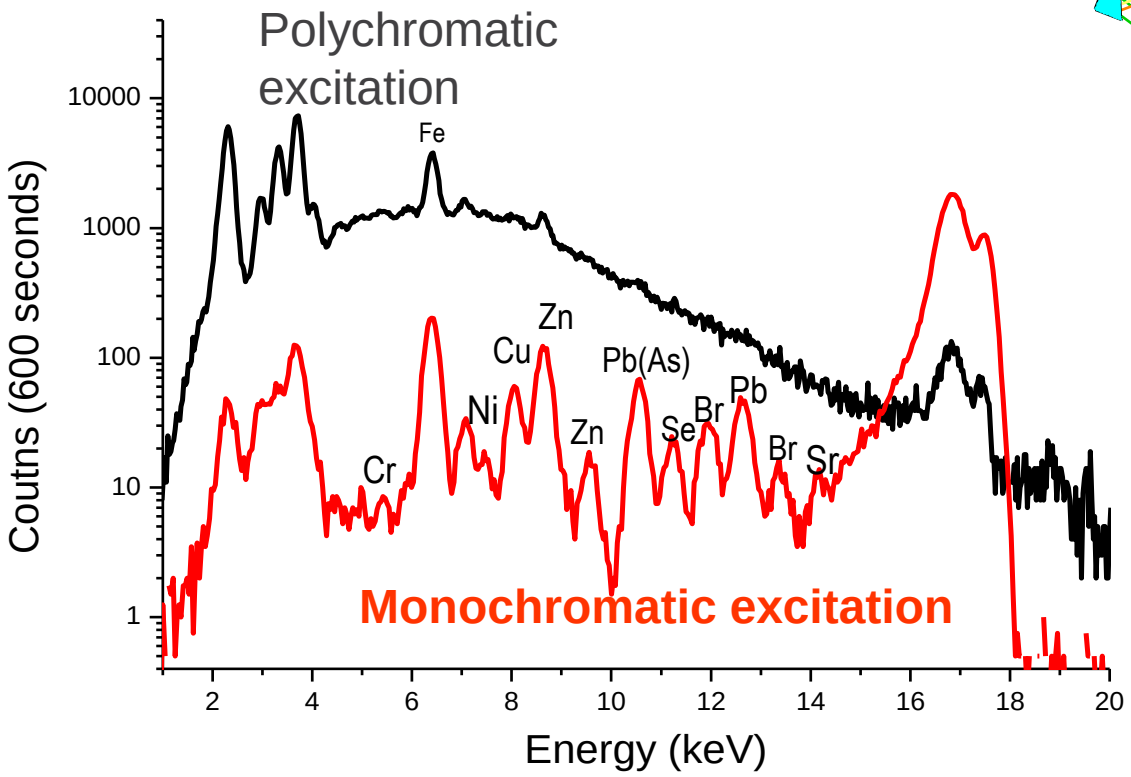
$$\Delta\theta = \theta - \theta_B$$

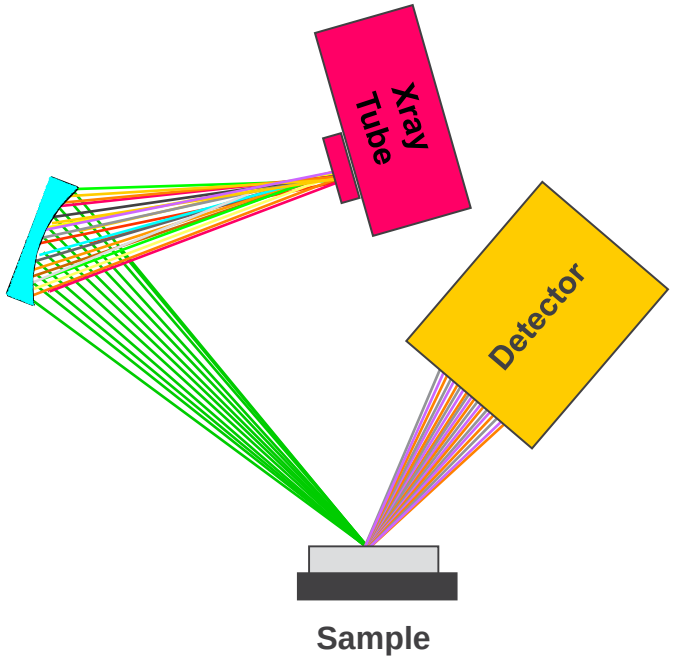
$$\approx 0.5\,(x/2R)^2 \cot\theta_B$$





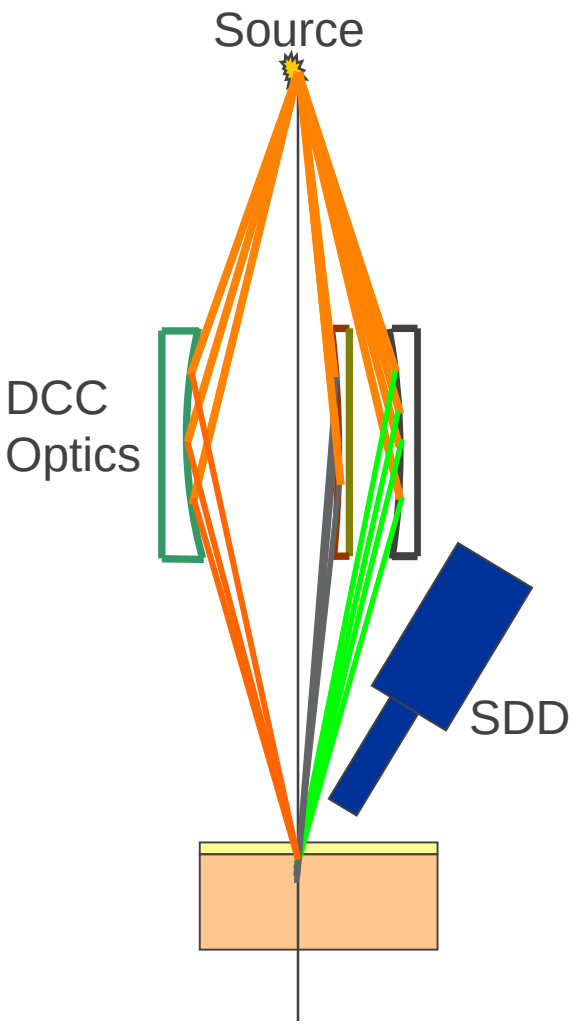
Monochromatic EDXRF--HDXRF





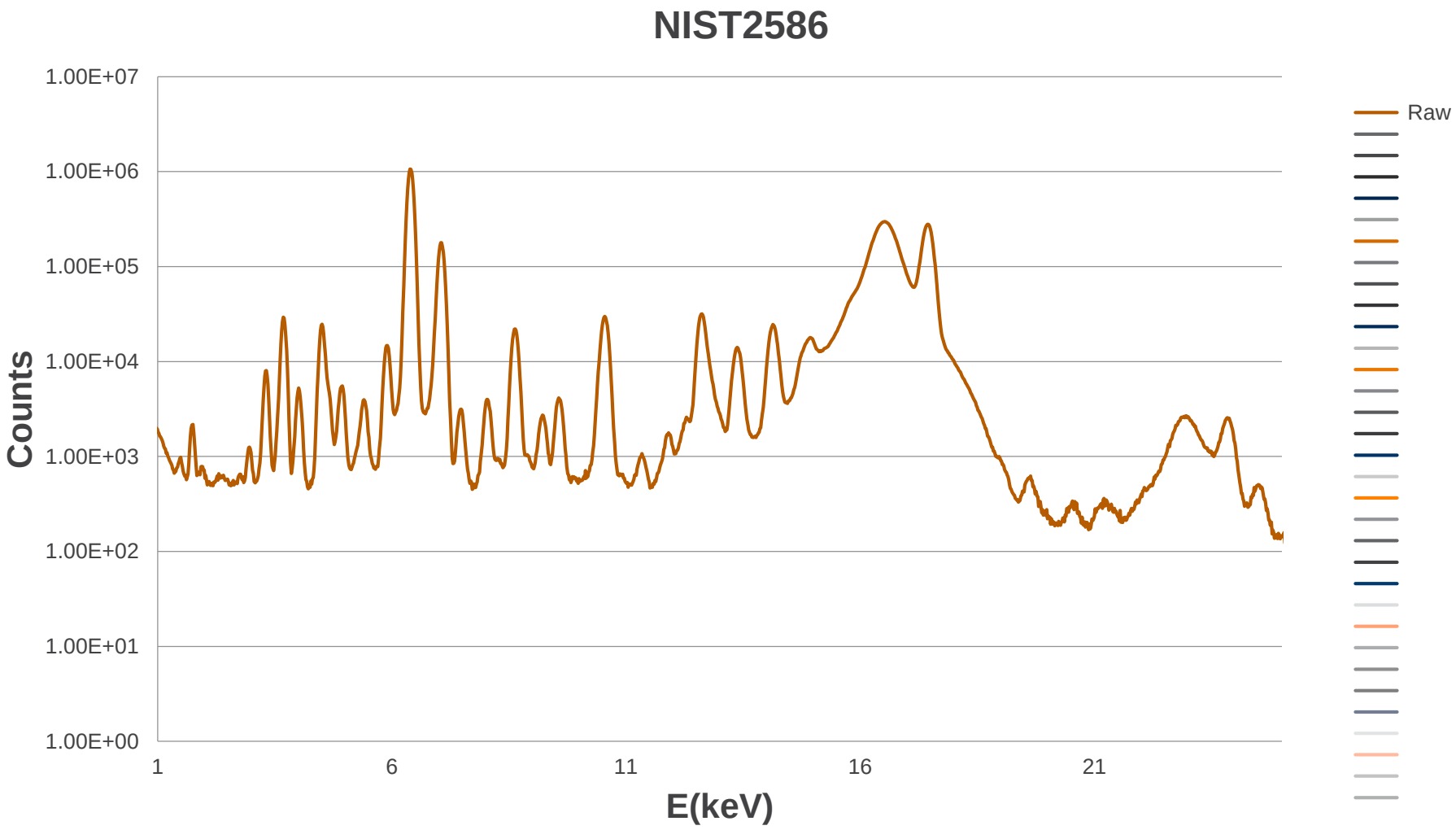
- Very low background
- Clean Spectrum
- Better Precision
- Superior reproducibility

Portable HDXRF

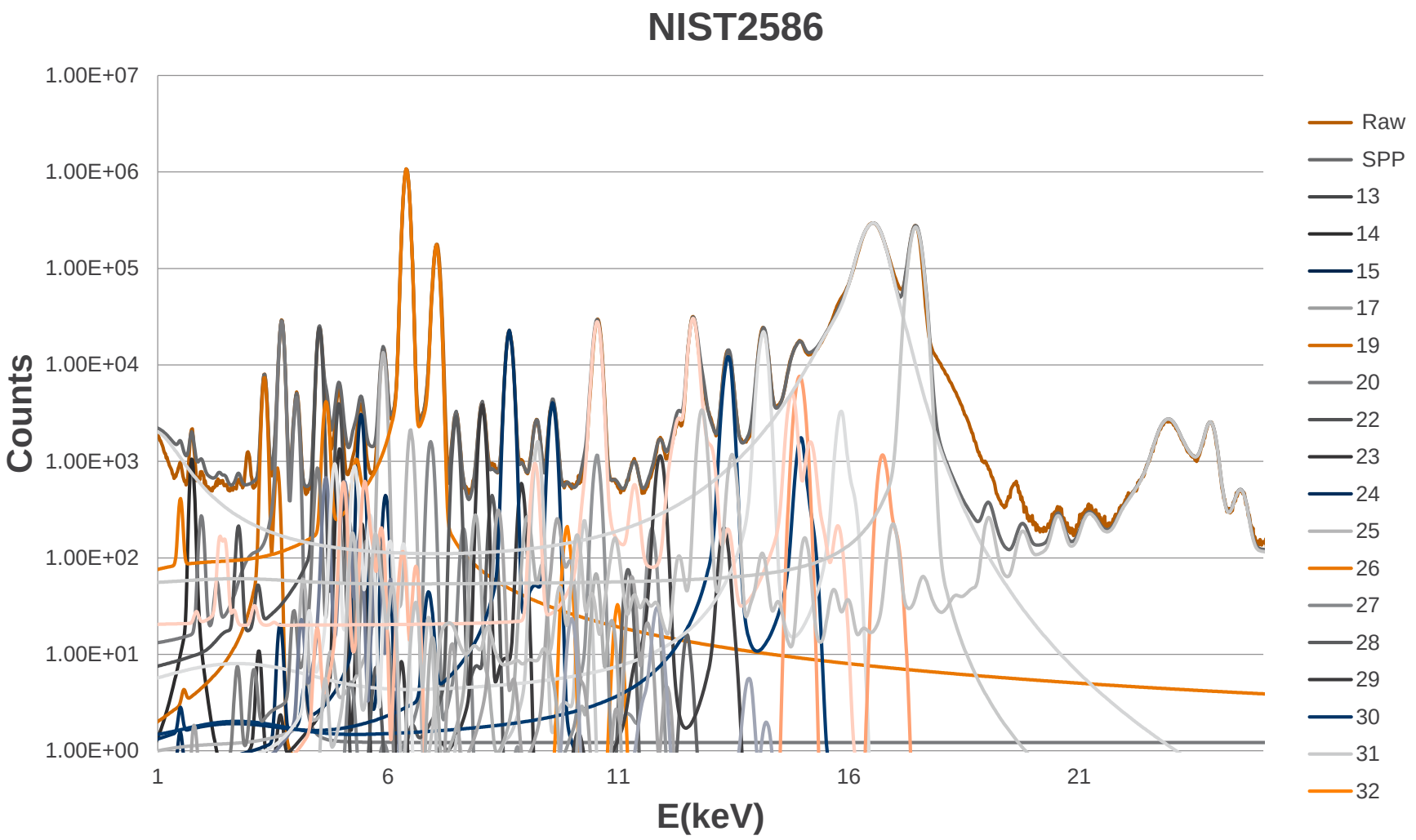


- 3 Monochromatic beams
- Low background
- Selected excitation
- Silicon drifted Detector (SDD)

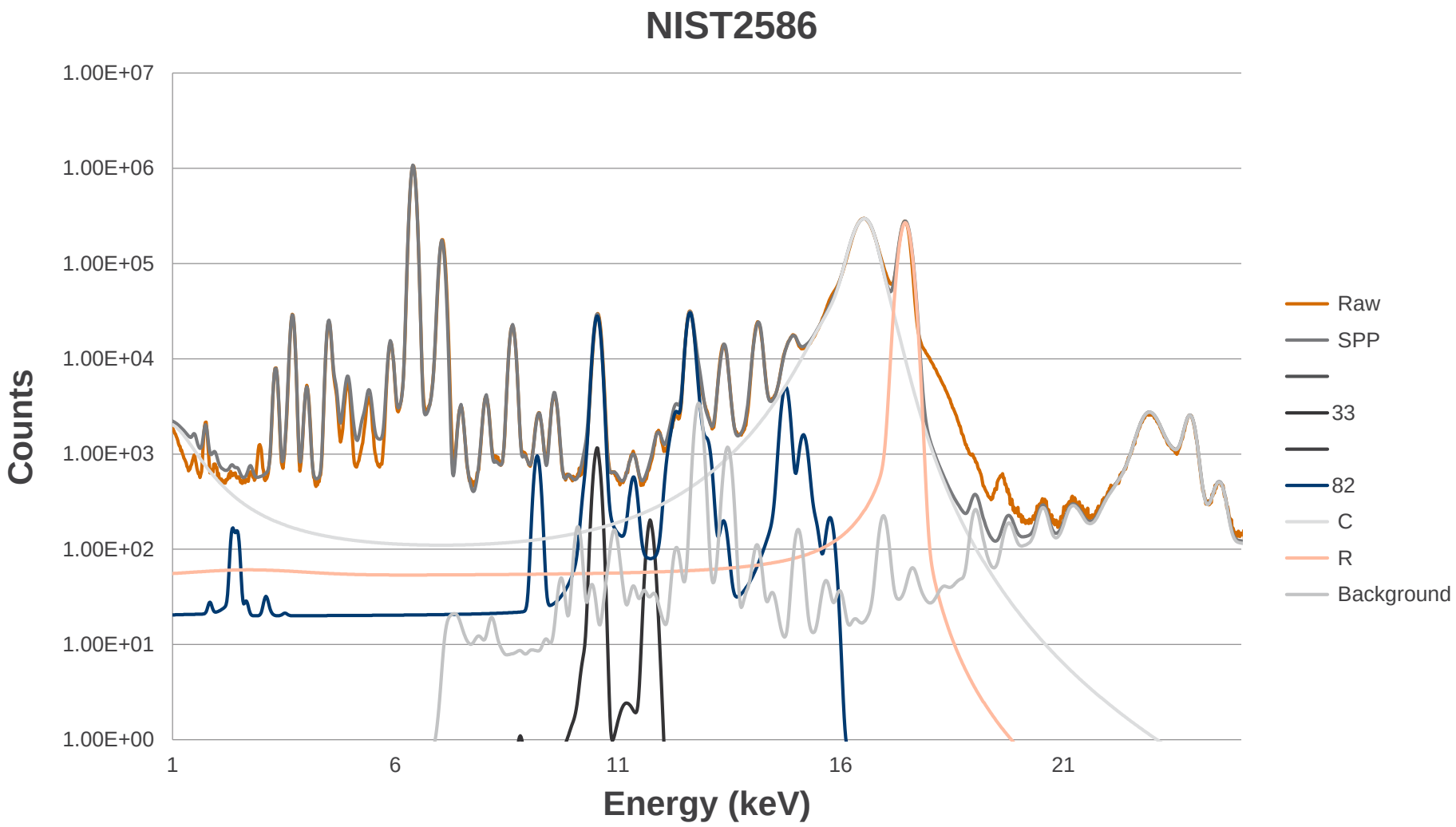
Mid-energy Spectrum



Mid-energy Spectrum

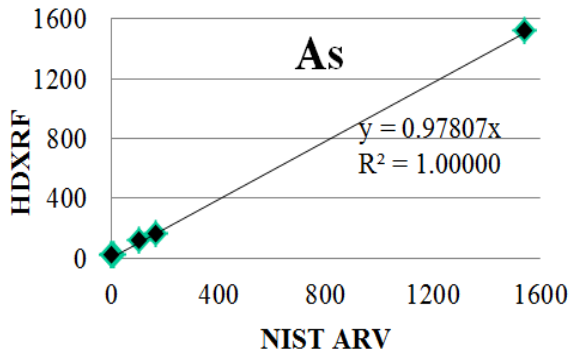


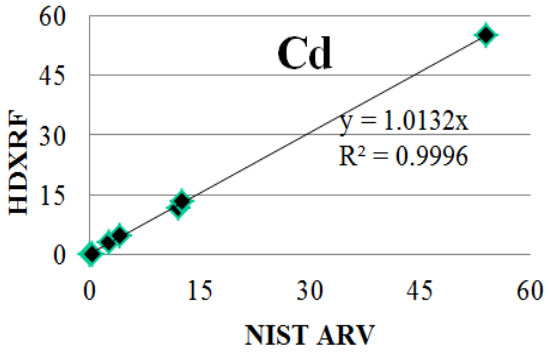
As/Pb in soil

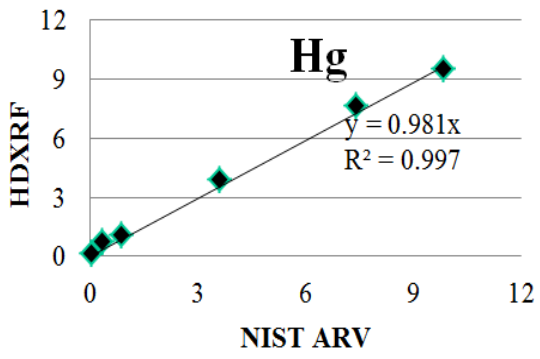

NIST2586
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
Counts
1
6
11
16
21
Energy (keV)
Raw
SPP
33
82
C
R
Background

System Accuracy—NIST Standards

Accepted Reference Values (ARV) (mg/kg) for NIST SRMs Used in Method Precision							
Part #	Description	Cr	Ni	As	Cd	Hg	Pb
1646a	Estuarine Sediment	40.9	23	6.23	0.148	0.04	11.7
2586	Trace Elements in Soil Containing Pb from Paint	301	75	8.7	2.71	0.367	432
2709a	San Joaquin Soil	130	85	10.5	0.371	0.9	17.3
2710a	Montana I Soil	23	8	1540	12.3	9.88	5520
2711a	Montana II Soil	52.3	21.7	107	54.1	7.42	1400
2782	Industry Sludge, Solid Waste	109	154.1	166	4.17	1.1	574
2781	Domestic Sludge, Solid Waste	202	80.2	7.82	12.78	3.64	202



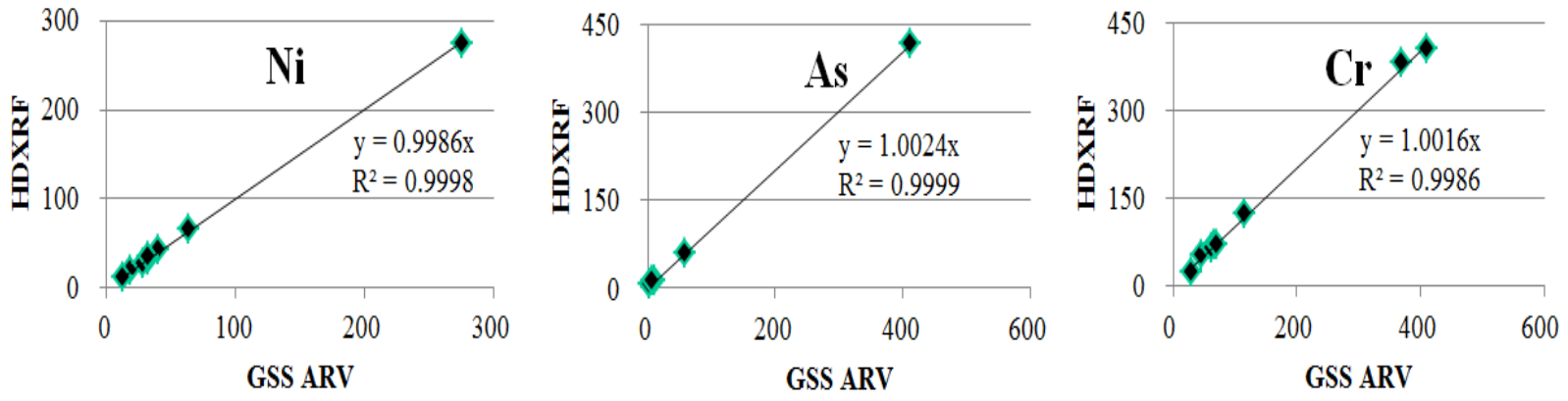




Output from HDXRF soil analyzer measured on NIST soil standard samples

System Accuracy—GSS Standards

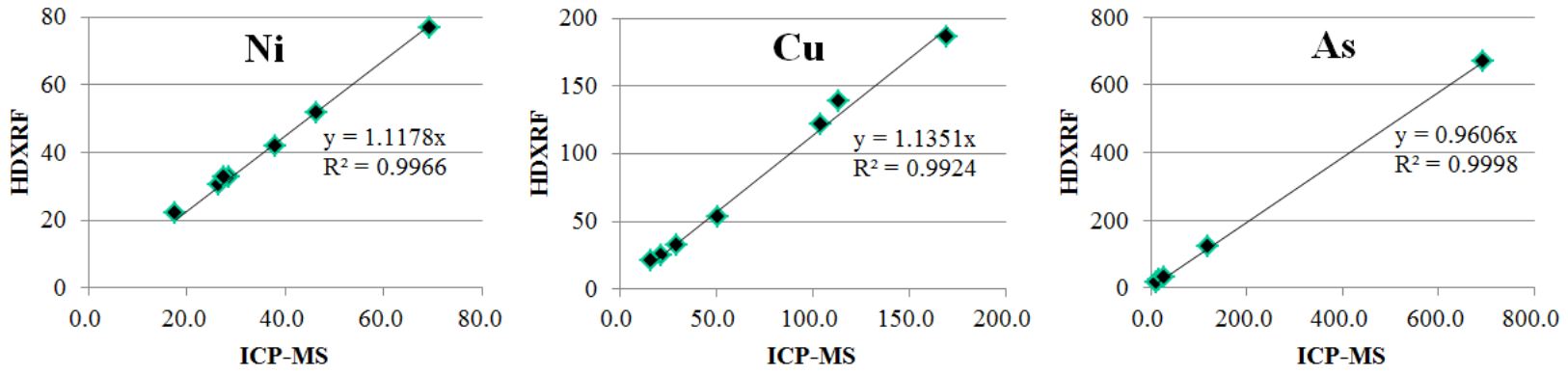
Part #	Description	Cr	Ni	Cu	Zn	As	Pb
GSS2	Chinese National Soil Standard	52.01	19.33	15.77	40.21	12.51	19.71
GSS3	Chinese National Soil Standard	23.22	11.67	11.35	29.47	3.17	26.51
GSS4	Chinese National Soil Standard	377.55	66.05	41.92	214.89	60.17	60.24
GSS5	Chinese National Soil Standard	122.57	41.46	140.59	490.66	412.75	551.77
GSS7	Chinese National Soil Standard	403.72	275.25	101.77	143.41	2.98	14.49
GSS8	Chinese National Soil Standard	68.85	30.19	23.94	65.43	13.02	18.90
GSS13	Chinese National Soil Standard	63.42	27.63	21.89	62.79	10.21	21.51
GSS14	Chinese National Soil Standard	68.33	32.57	27.63	93.11	8.51	30.61



Output from HDXRF soil analyzer measured on GSS soil standard samples

Comparison with ICP

Real-World Samples



Output from HDXRF soil analyzer measured on real-world samples

ASTM D8064

ASTM D8064-16 Standard Test Method for Elemental Analysis of Soil and Solid Waste by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry Using Multiple Monochromatic Excitation Beams

Active Standard(Latest Version)

Abstract

Scope

1.1 This test method is based upon energy-dispersive X-ray Fluorescence (EDXRF) spectrometry using multiple monochromatic excitation beams for detection and quantification of selected heavy metal elements in soil and related solid waste.

1.2 This test method is also known as High Definition X-ray Fluorescence (HDXRF) or Multiple Monochromatic Beam EDXRF (MMB-EDXRF).

1.3 This test method is applicable to various soil matrices for the determination of Cr, Ni, As, Cd, Hg, and Pb in the range of 1 to 5000 mg/kg, as specified in Table 1 and determined by a ruggedness study using representative samples. The limit of detection (LOD) for each element is listed in Table 1. The LOD is estimated by measuring a SiO_2 blank sample (see Table X1.1 in Appendix X1).

Element	LOD (mg/kg)	Method Range (mg/kg)
Cr	5	15 – 500
Ni	1.5	4.5 – 500
As	0.4	1.2 – 2000
Cd	0.8	2.4 – 100
Hg	0.5	1.5 – 50
Pb	0.5	1.5 – 5000

NIST SRM 1646a Estuarine Sediment Results for Single Site Repeatability Study (mg/kg)

SRM 1646a	Cr	Ni	As	Cd	Hg	Pb
1	41.57	24.34	6.70	<1.12	<0.36	11.98
2	39.91	23.91	6.86	<1.16	<0.37	11.68
3	38.20	21.99	6.67	<1.15	<0.37	11.49
4	42.73	22.27	6.53	<1.16	<0.39	11.89
5	41.66	23.30	6.63	<1.14	<0.37	11.81
6	41.95	18.90	6.42	<1.16	<0.39	12.01
7	41.93	21.70	6.63	<1.01	<0.39	11.99
8	40.71	21.72	6.81	<1.16	<0.37	11.58
9	42.93	23.38	6.58	<1.18	<0.36	11.87
10	45.01	19.19	6.79	<1.17	<0.39	12.01
Average	41.66	22.07	6.66	…	…	11.83
Stand. Dev.	1.83	1.84	0.14	…	…	0.19
RSD	4.39%	8.33%	2.05%	…	…	1.58%
ARV	40.9	23	6.23	0.148	0.04	11.7
Bias	1.86%	-4.04%	6.90%	…	…	1.11%

Low As and Cd level with high Pb

SRM 2586	Cr	Ni	As	Cd	Hg	Pb
1	311.7	72.09	7.38	2.89	<0.35	422.6
2	319.8	72.52	6.92	2.95	0.62	416.3
3	318.2	73.51	8.52	2.97	0.36	426.8
4	310.2	72.51	8.33	2.37	0.39	424.5
5	311.0	73.01	8.70	2.87	1.00	423.1
6	331.4	72.89	7.79	2.75	<0.75	421.8
7	310.4	72.39	9.44	2.29	0.68	424.0
8	310.2	73.73	8.73	3.34	0.71	421.3
9	303.3	72.81	8.42	3.34	0.42	424.2
10	306.1	73.66	7.36	3.18	0.92	423.2
Average	313.2	72.91	8.16	2.89	0.63	422.8
Stand. Dev.	8.02	0.57	0.77	0.36	0.24	2.75
RSD	2.56%	0.78%	9.49%	12.31%	37.70%	0.65%
ARV	301	75	8.7	2.71	0.367	432
Bias	4.06%	-2.79%	-6.21%	6.64%	71.66%	-2.13%

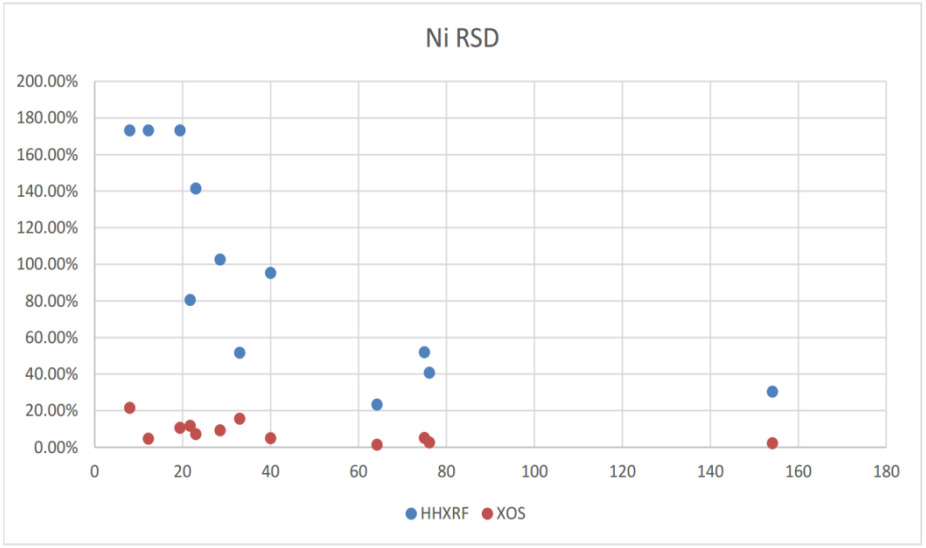
Hg contamination

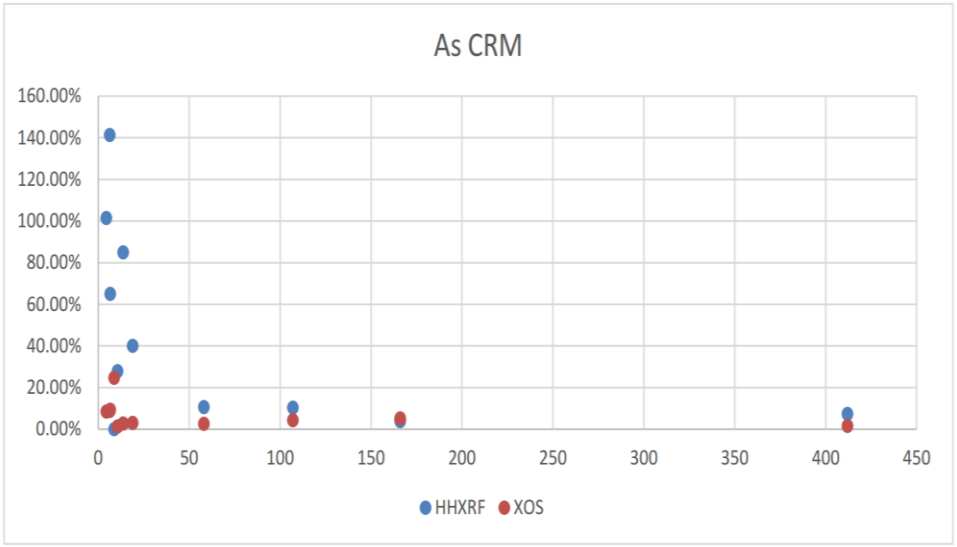
SRM 2711a	Cr	Ni	As	Cd	Hg	Pb
1	57.57	18.67	100.9	56.35	7.49	1404.0
2	56.97	18.69	107.2	55.54	7.01	1407.3
3	49.53	19.13	105.8	55.05	7.27	1403.9
4	53.98	17.97	107.5	55.21	8.00	1404.8
5	54.38	18.29	103.7	55.03	7.32	1405.0
6	54.78	19.00	102.6	55.63	7.61	1402.0
7	52.26	19.47	105.0	54.21	7.30	1403.8
8	54.6	18.65	106.6	53.44	7.21	1406.6
9	57.85	18.65	104.9	54.44	7.74	1404.1
10	51.09	19.12	101.2	55.48	7.93	1404.7
Average	54.3	18.76	104.5	55.04	7.49	1404.6
Standard Deviation	2.75	0.43	2.37	0.83	0.33	1.49
RSD	5.06%	2.32%	2.27%	1.50%	4.37%	0.11%
ARV	52.3	21.7	107	54.1	7.42	1400
Bias	3.82%	-13.55%	-2.30%	1.74%	0.94%	0.33%

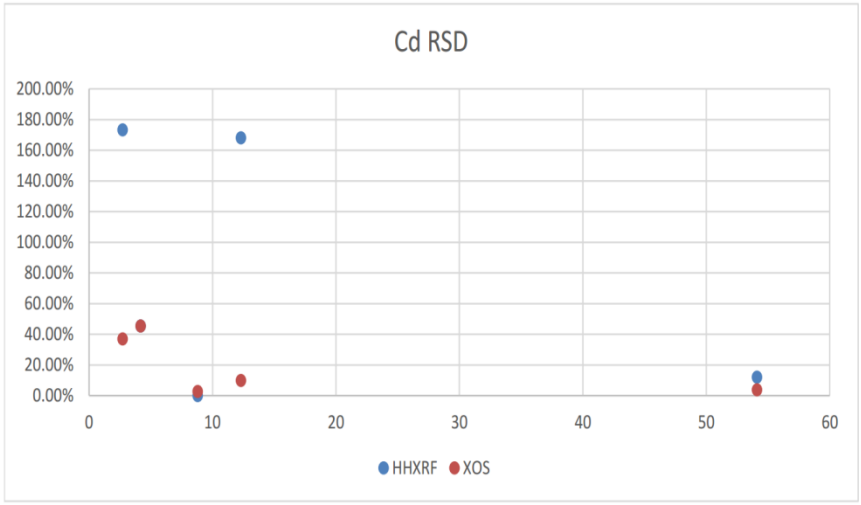
Screening Hg at 1 ppm level

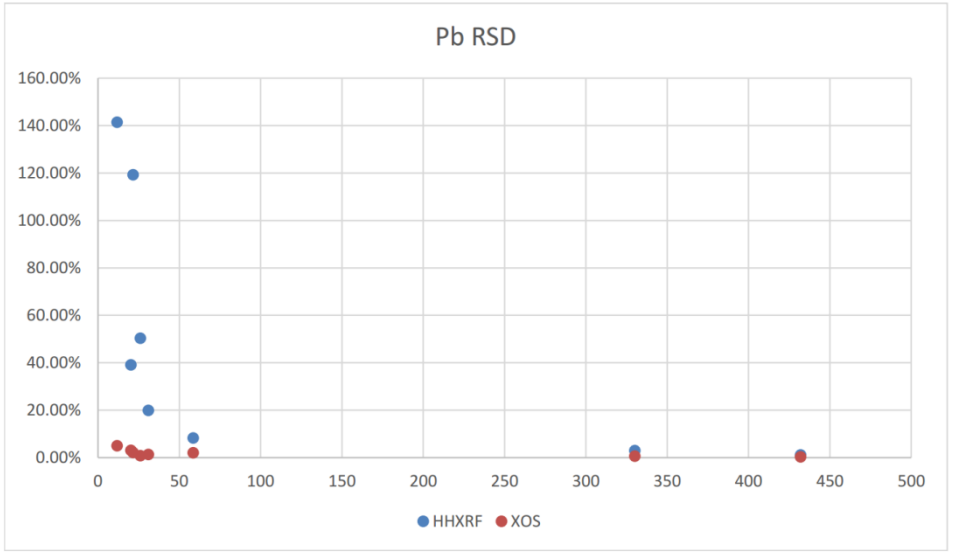
SRM 2709a	Cr	Ni	As	Cd	Hg	Pb
1	137.3	88.50	12.23	<1.36	1	18.09
2	135.3	87.03	12.24	<1.34	0.72	18.35
3	130.1	86.37	10.73	<1.33	0.90	18.02
4	134.2	86.30	10.90	<1.32	1.05	18.03
5	133.7	86.57	11.93	<1.34	1.20	18.02
6	132.3	87.37	11.44	<1.32	1.11	18.36
7	130.3	87.66	11.27	<1.35	0.86	17.99
8	130.5	86.67	11.90	<1.35	1.27	18.17
9	134.5	86.95	11.21	<1.37	1.09	17.91
10	138.5	86.66	12.40	<1.36	0.37	17.77
Average	133.7	87.01	11.63	…	0.96	18.07
Stand. Dev.	2.91	0.68	0.59	…	0.26	0.18
RSD	2.18%	0.78%	5.10%	…	27.47%	1.02%
ARV	130	85	10.5	0.37	0.9	17.3
Bias	2.82%	2.36%	10.76%	…	6.67%	4.45%

Comparison with HHXRF





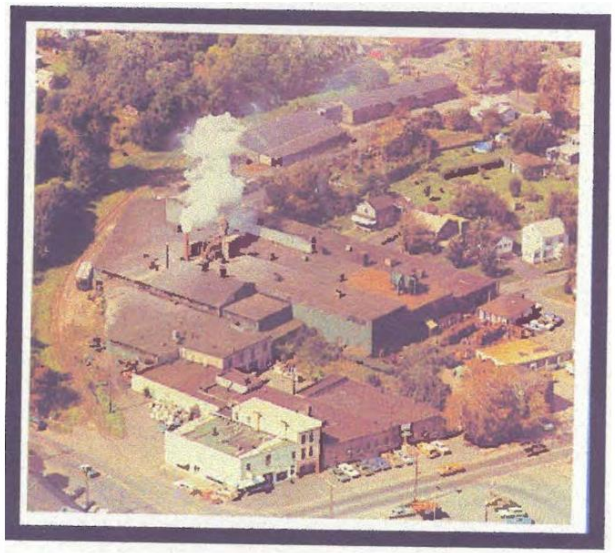




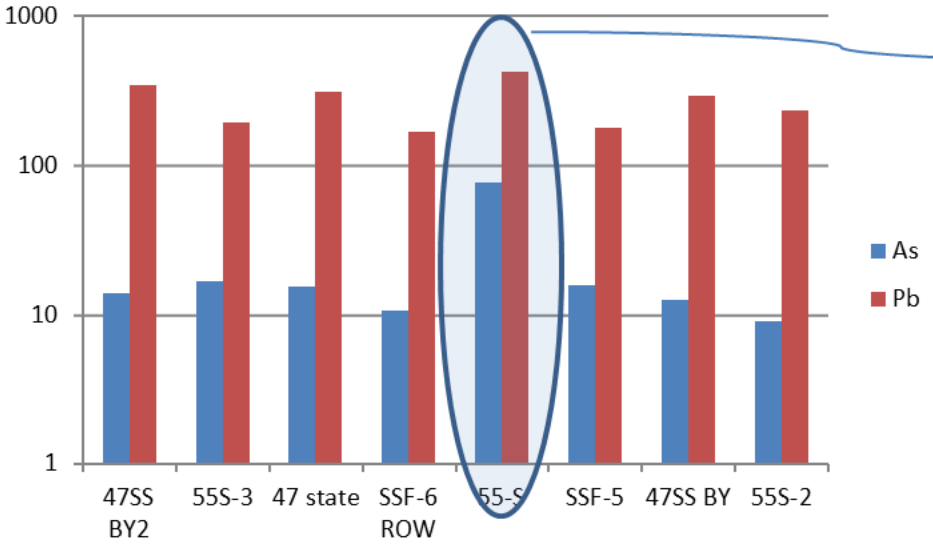
Case Study—Upstate NY As Site

Soil Sampling Strategy/Plan

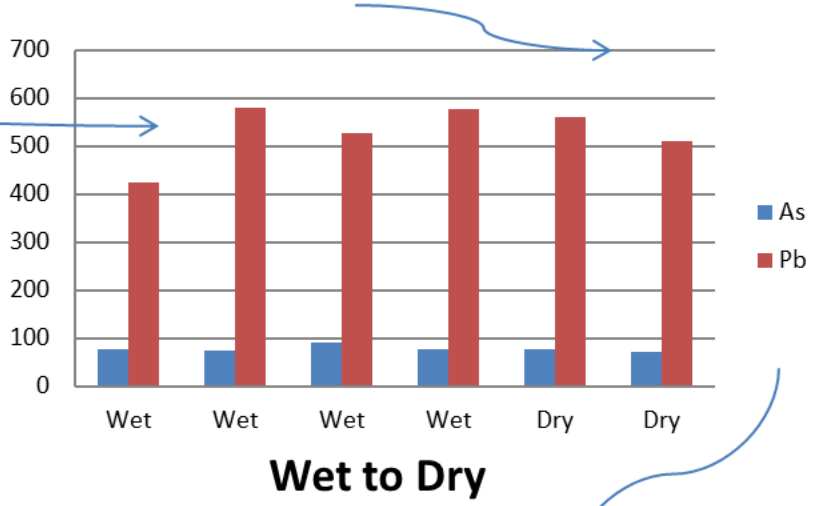
Former Geneva Foundry (site #B00019) – 43 Jackson St. – Geneva, NY



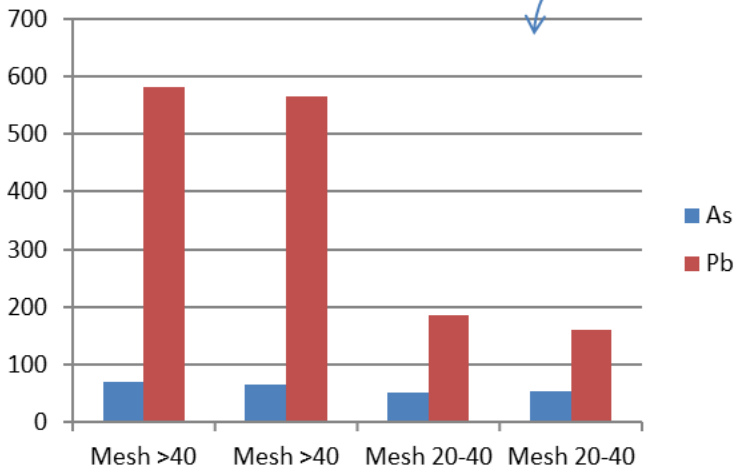
Case Study—Geneva NY As Site



Direct Measurements



Wet to Dry



20-40 Mesh

Matrix Spiked

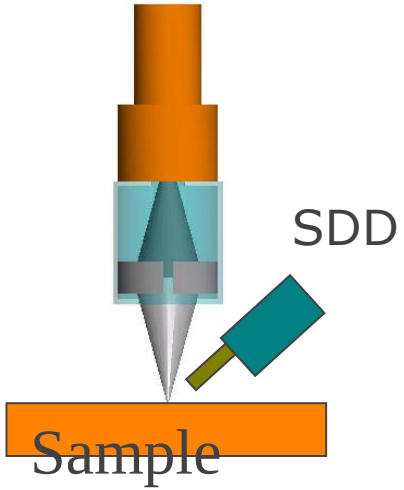
NY Geneva Soil Result and Matrix Spike Recovery

	Pb	As	Ni	Cr
unspiked				
1	347	25.2	51.7	71.2
2	362	27.1	53.6	83.7
3	397	19.2	48.7	85.9
4	394	20.6	58.1	84.7
5	346	20.3	53.7	78.7
mean	369.2	22.48	53.16	80.84
spiked				
1	754	48.7	130	179
2	753	48.7	123	155
3	812	45.4	133	179
4	702	38.2	118	183
5	773	50.8	122	200
mean	758.8	46.36	125.2	179.2
STD	39.73	4.95	6.14	16.07
R STD (%)	5.24	10.68	4.9	8.97
Recovery (%)	102.53	91.85	127.64	122.95

The Cd problem

- Cd is highly toxic element
- Cd contamination in agriculture soil and can be transported from soil to plants and crops
- The safety limits for wheat are at level of 0.2ppm
- The critical limits for soil is at 0.3ppm
- The only effective testing method for Cd at such level is ICP/MS at sophisticated labs

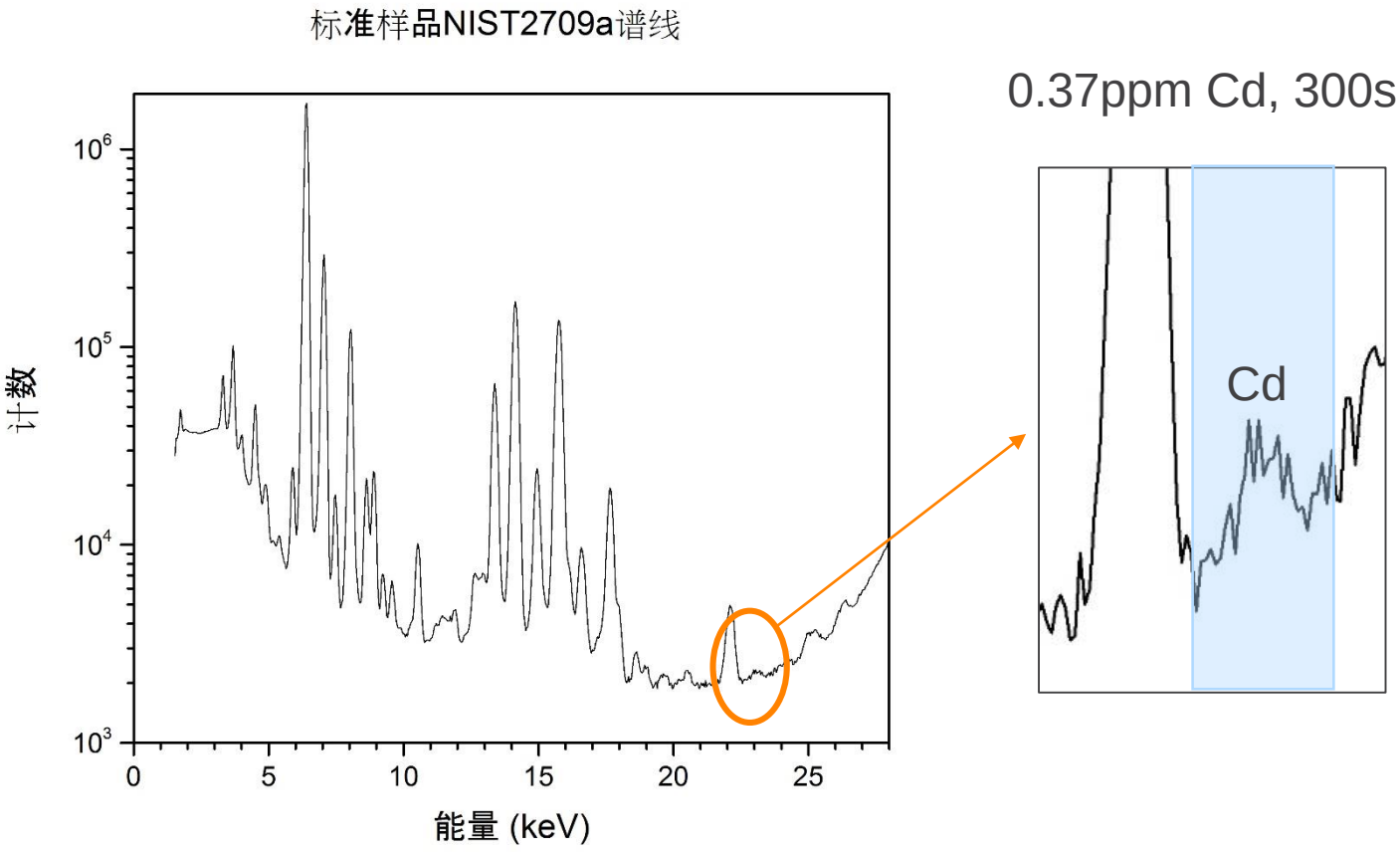
MXRF solution



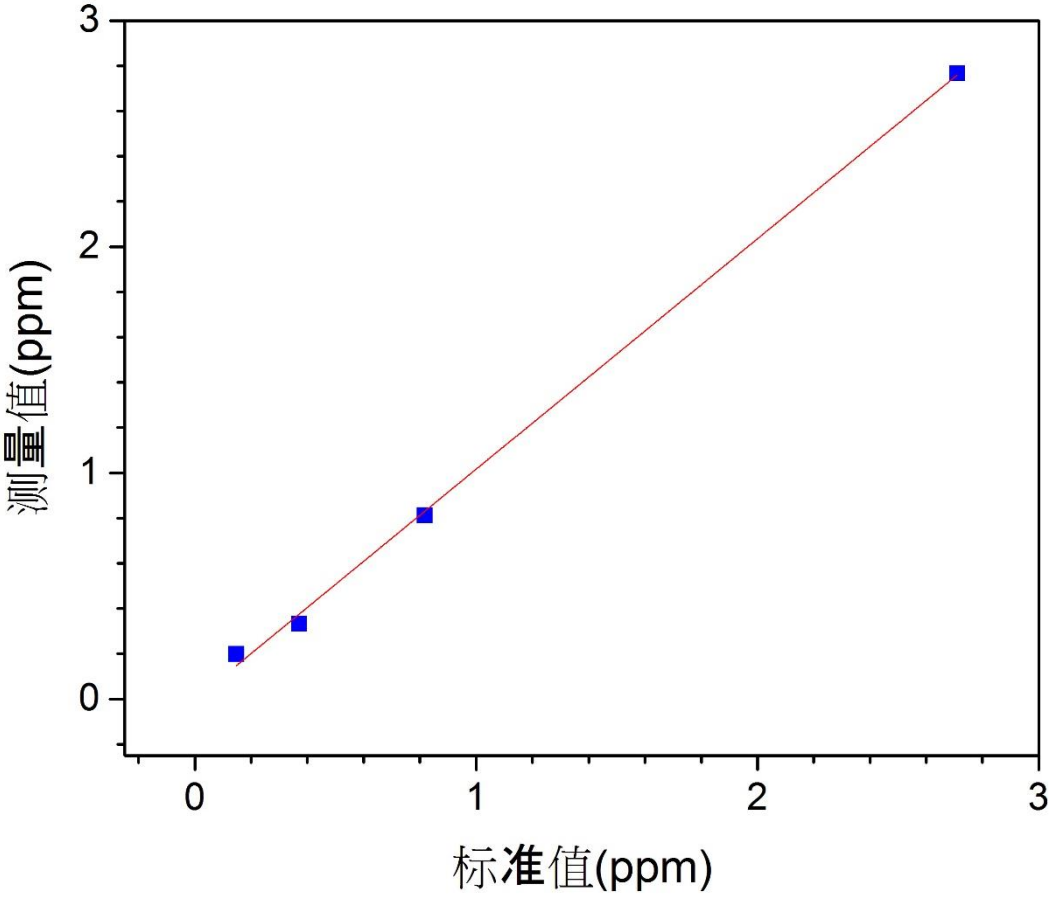
- High energy monochromatic beam excitation
- Low power x-ray tube
- Small and transportable system

Spectrum of low Cd sample

- NIST2709a



Cd calibration and detection limit



Sample	ARV (ppm)	Measured (ppm)
NIST1646	0.148	0.199
NIST2709a	0.371	0.333
NIST2702	0.817	0.813
NIST2586	2.71	2.767

Limit of Detection(LOD) = 0.09 ppm

Repeatability

NIST SRM2702 Soil	
# test	C(ppm)
1	0.894
2	0.801
3	0.820
4	0.780
5	0.790
Aver.	0.817
ARV	0.045
Stdev.	0.817

NIST SRM2709a Soil	
# test	C(ppm)
1	0.378
2	0.337
3	0.385
4	0.360
5	0.386
Aver.	0.369
ARV	0.021
Stdev.	0.371

NIST SRM1646a Soil	
# test	C(ppm)
1	0.143
2	0.121
3	0.156
4	0.152
Aver.	0.143
ARV	0.016
Stdev.	0.148

Limit of Detection(LOD) = 0.05 ppm

Repeatability

NIST SRM1573a Leaf	
# test	C(ppm)
1	1.45
2	1.48
3	1.47
4	1.48
Aver.	1.47
Stdev	0.02
ARV	1.52

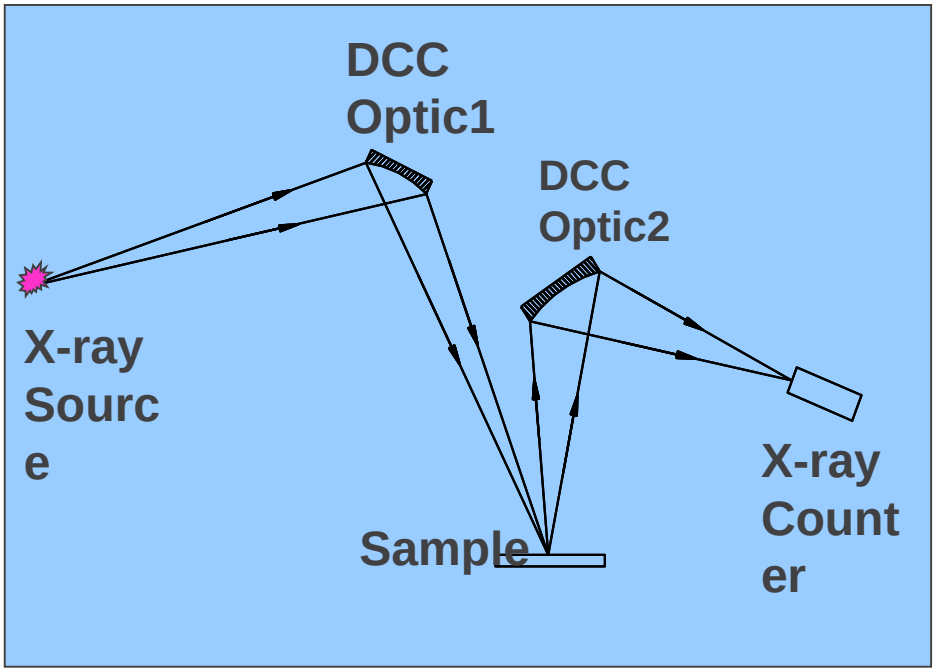
NIST SRM1568b rice powder	
# test	C(ppm)
1	0.034
2	0.019
3	0.041
Aver.	0.031
Stdev	0.011
ARV	0.0224

Limit of Detection(LOD) = 0.03 ppm

Power Plant discharging Se problem

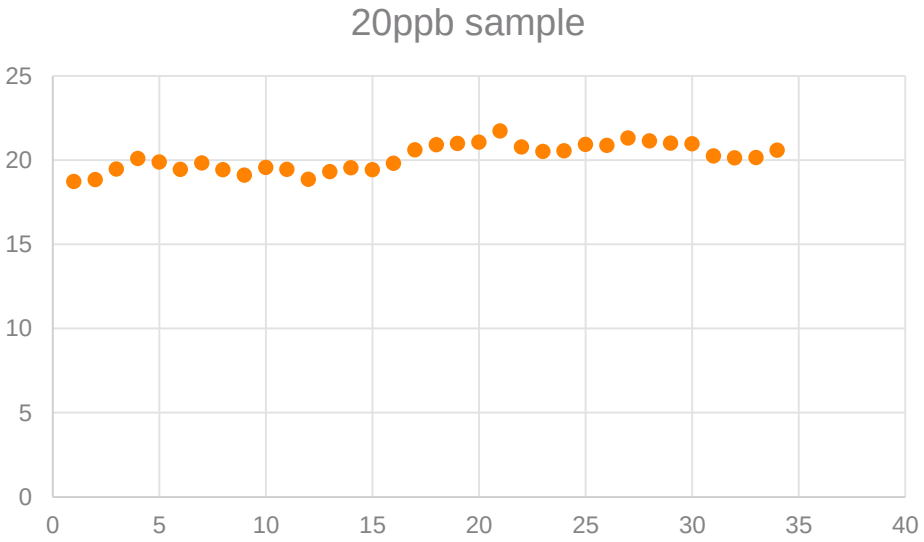
- Power plant can discharge harmful level of As and Se
- No effective on-site/online testing of Se discharge

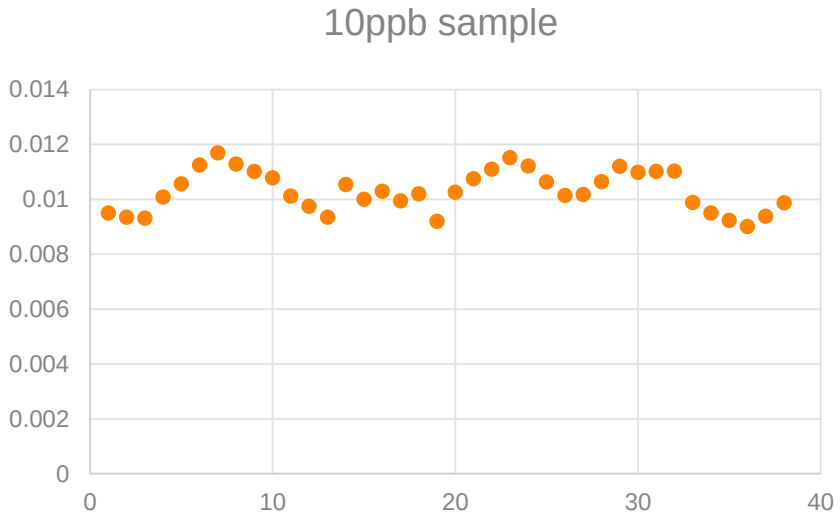
Monochromatic WDXRF Solution



- Low Power
- Single/dual Elements
- Ultra-low Background
- High E Resolution

Preliminary As testing results





LOD=2ppb

On-going work

- Improve optic sensitivity
- Improve source efficiency
- Achieve ~1ppb LOD for Se feasible

Conclusion

- A breakthrough development for heavy metal analysis in soil for contaminated sites
- First time to achieve non-destructive analysis at site in 1-10ppm concentration range for metals in soil with portable HDXRF method
- Quantitative analysis of NIST and other national standards show excellent accuracy
- Successfully achieve low level Cd analysis in agriculture soil and crops
- Demonstrate a path for on-site monitoring of low ppb level of Se or As in discharging water