Recent Advances in Handheld XRF for Site Remediation

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IEC

International Electrotechnical Commission

Creator of international standards for electrotechnical equipment

TC45 – Nuclear Instrumentation

PT 62495 – Portable X-ray Fluorescence Analysis Equipment Utilizing a Miniature X-ray Tube

Outline

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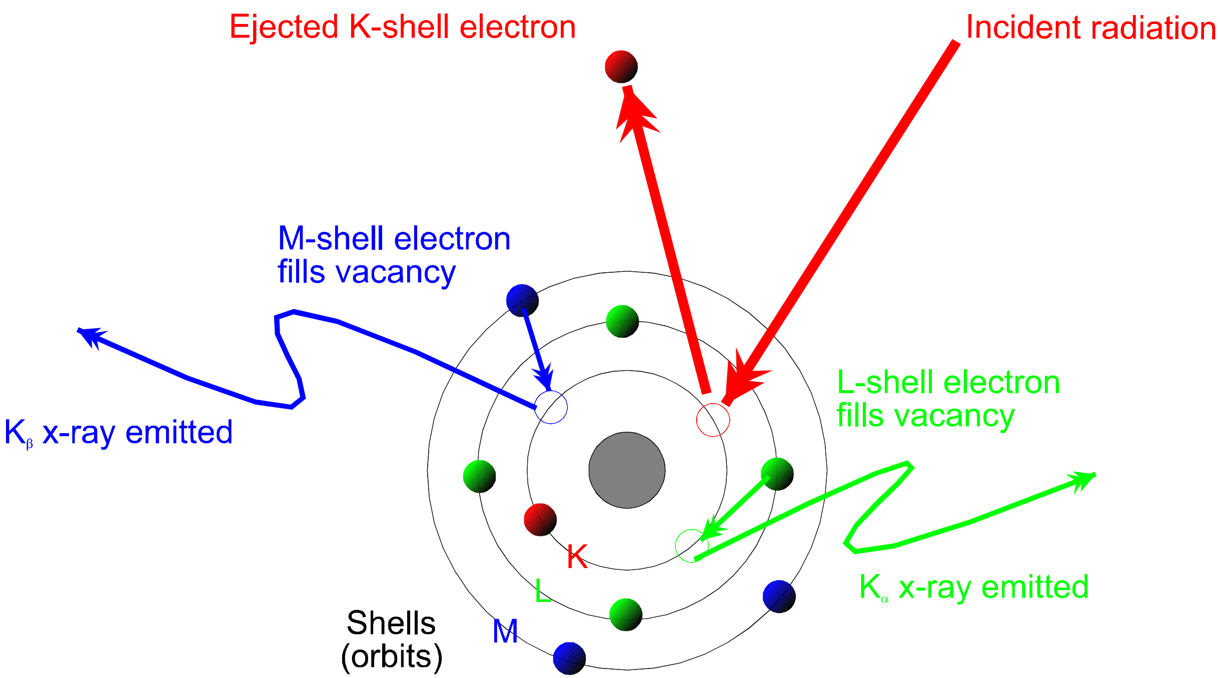
- XRF Theory
- EPA 6200
- Hardware Advances
  - Miniature X-ray tubes
  - Silicon Detectors
  - GPS
- Software Advances
  - Mapping
  - User Empirical Calibrations
  - Type Standardization
- Limits of Detection

Characteristic x-ray production



K shell x-rays analyzed up to about 30 kV AN ~30;
ex. Ti (Ka @ 4.5 kV), Ag (22.2 kV), Sb (26.3 kV)

L shell x-rays analyzed for elements above AN ~30
ex. Hf (Ka @ 55.8, La @ 7.9); Pb (Ka 75.0, La 10.5)

XRF Rules

1. Energy of X-ray tells you what element is present
2. Number of X-rays tells you how much is present
3. Measurement precision increases with increased number of counts
4. Energy decreases with atomic number (Z)
5. Absorption increases with decreasing energy

EPA 6200

EPA 6200

- Field work 1997
- Published 1998
- Updated 2007

Covers

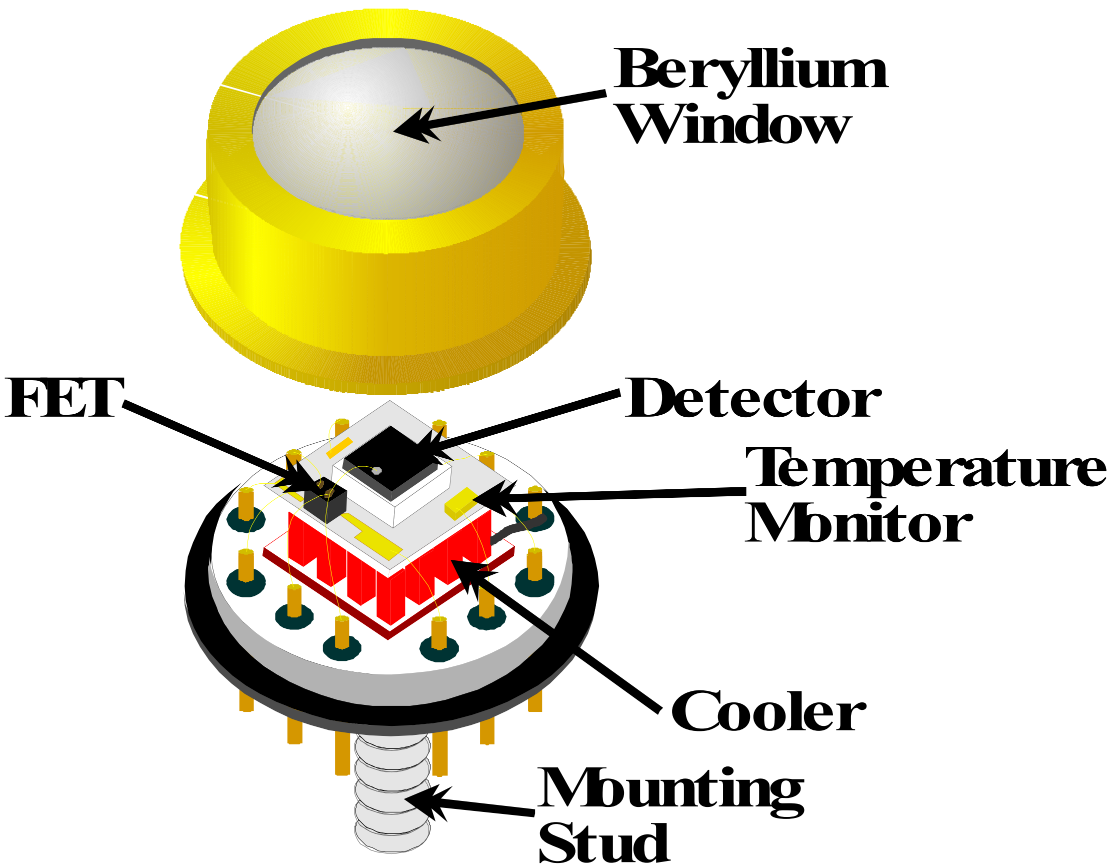
- Radioactive Sources
- Proportional counters
- Early solid state detectors

	EPA 6200
	LOD
	mg/Kg
Arsenic (As)	40
Cadmium (Cd)	100
Chromium (Cr)	150
Lead (Pb)	20
Mercury (Hg)	30
Silver (Ag)	70
Strontium (Sr)	10

Miniature X-ray Tubes

Up to 50 kV
Completely Adjustable
No Radioactive Material
Weight ~10-15 grams

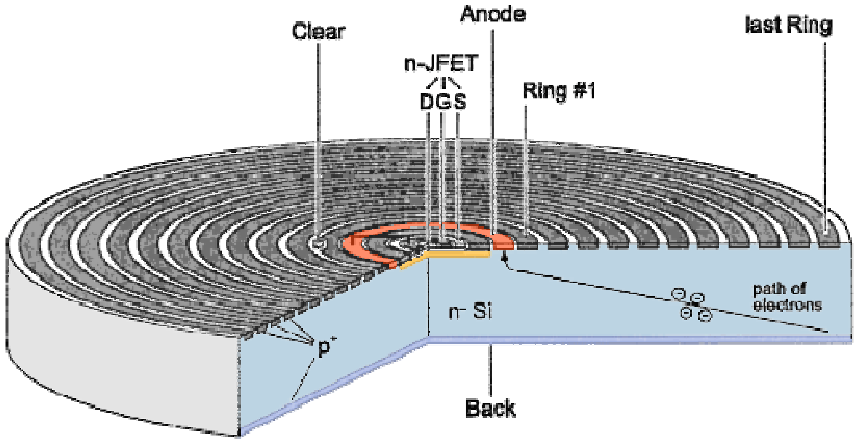
SiPIN Detector



Detector capacitance increases with increasing area

Detector resolution decreases with increasing area

Silicon Drift Detector



SDD

- ❖Integrated drift structure results in electron capture at center electrode
- ❖Small contact means low capacitance
- ❖Thin entrance window

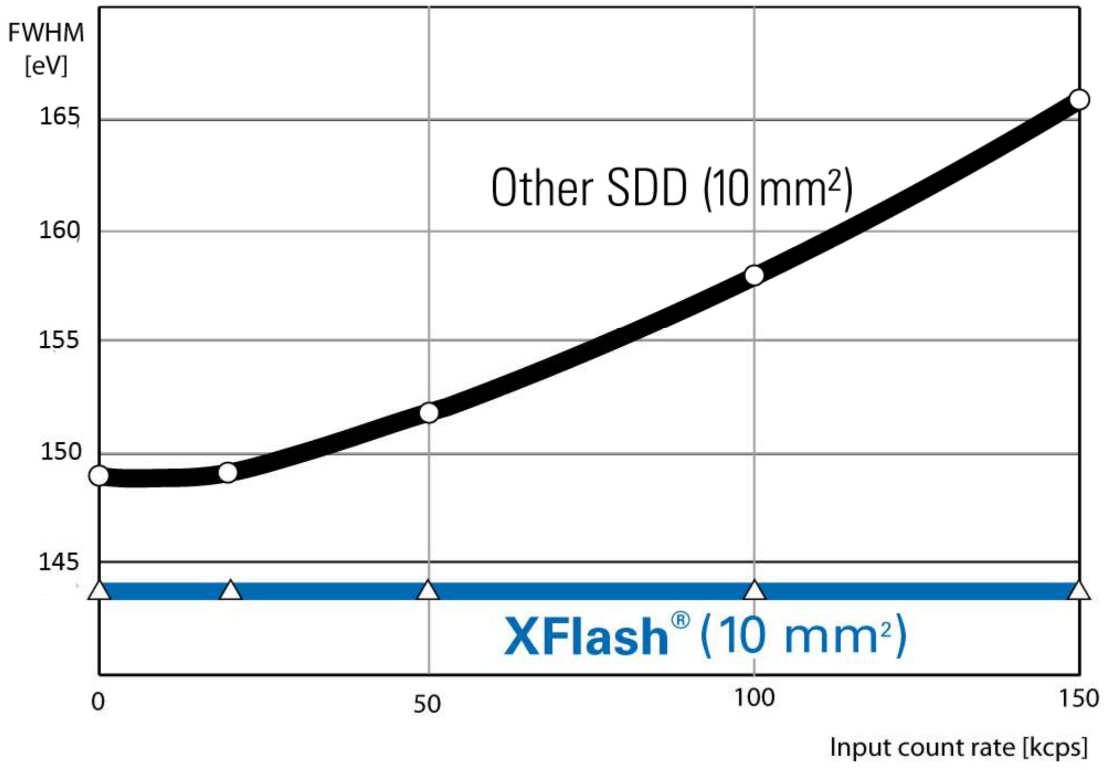
SDD Offers

- ❖Improved Resolution
- ❖High Count Rate
- ❖Low Z sensitivity

SDD Resolution

Comparison XFlash® / other SDD

Typical energy resolution at Mn Kα vs. input count rate



Results of SDD

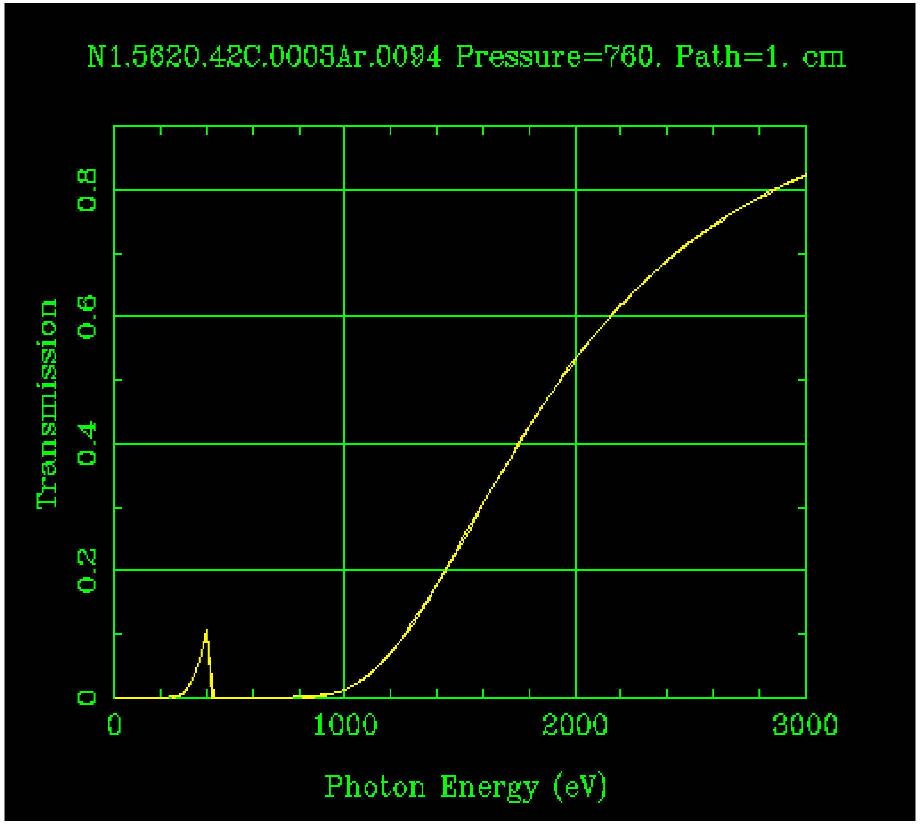
High Count rate means better precision in a given counting time

Better resolution means better signal to noise thus further improving the precisions

Resolution is especially important at low Z where neighboring peaks are ~250 eV apart

Transmission of 1 cm Air Path

	Energy	Trans.
Mg	1.3	11.9%
Al	1.5	24.0%
Si	1.7	36.6%
P	2.0	53.2%
S	2.3	65.5%

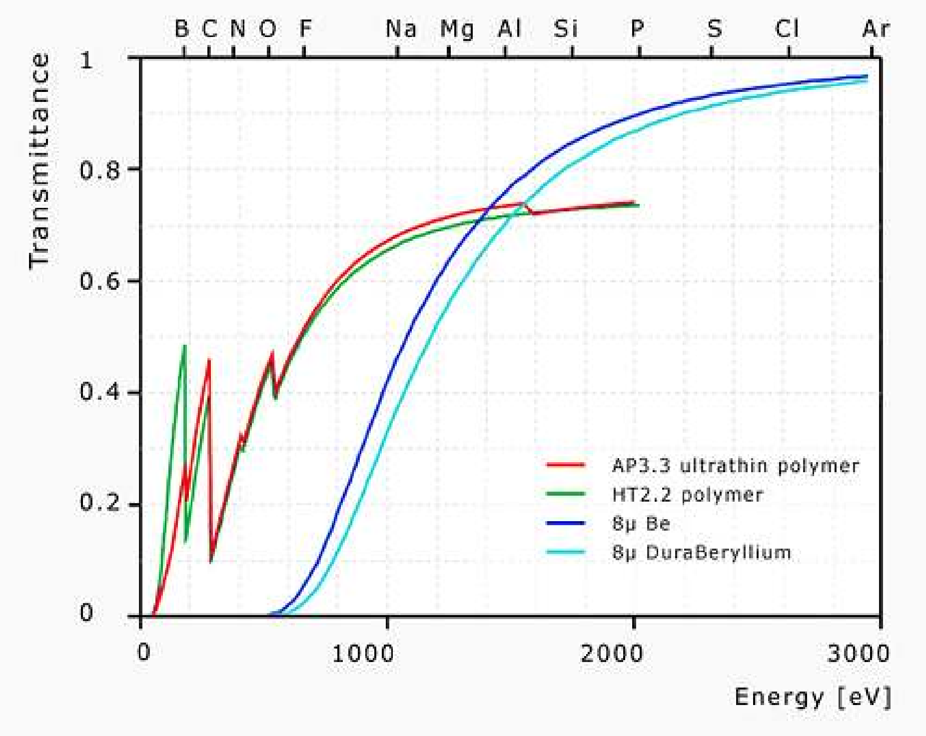


Careful Design for Low Z Detection

Thin Detector window

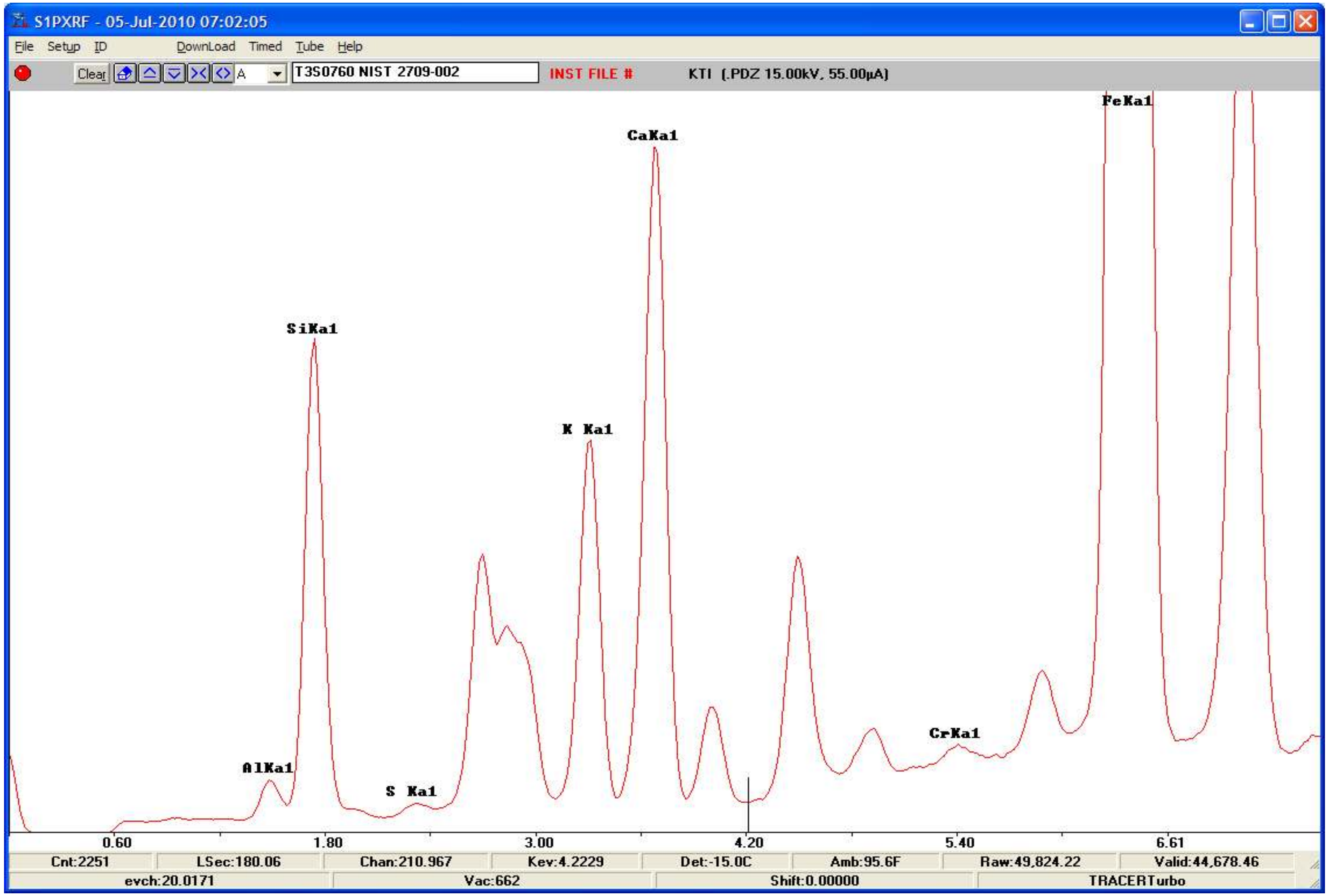
Thin Be window

Minimize distance between sample and detector



Low Z Spectrum

Al @ 7.5%; Si @ 29.7%; K @ 2.0%



Low Z Detection

SiPIN Detectors

- Low Z limit ~TI (22)
- Some Detection at Ca (20)

SDD

- Low Z limit ~Si (14)
- Some Detection as Mg (12)

AN	Element	LOD mg/Kg
12	Mg	6600
13	Al	1050
14	Si	790
16	S	90
20	Ca	50
30	Zn	4

Low Z detection

Why does it matter?

- **Allows selection of proper calibration**

  Ex. if not Si matrix then substantial error will occur, the software can select a S based matrix or others

- **Provides a more complete and accurate analysis**

Typical SDD Analyzers

Typical Specifications:

Weight: ~2 Kg

Batteries: 4-8 hours

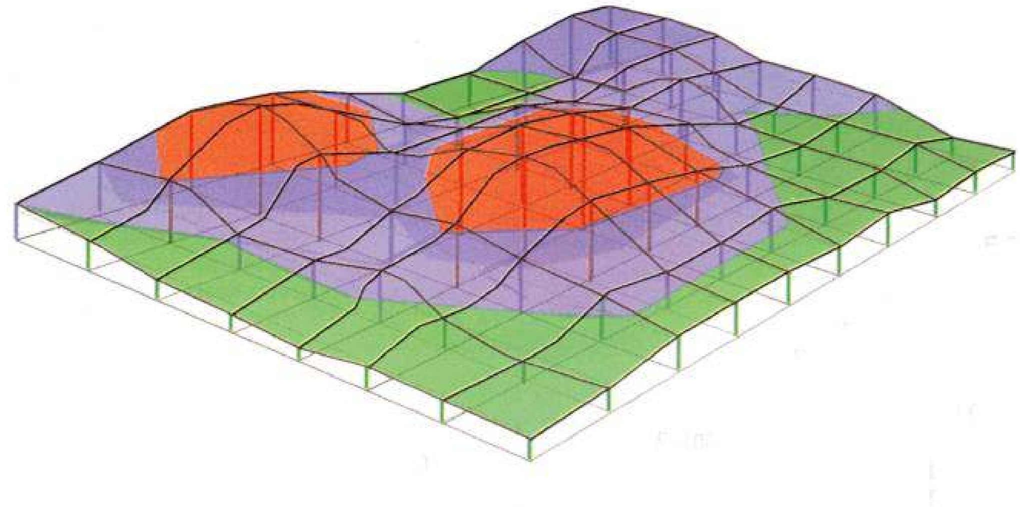
Voltage: 40-50 kV

Input Count Rates: 200 kcps

Heavy Metal LOD: 2-10 mg/kg

Factory Supplied Calibration

GPS/GIS



GPS is easily integrated to handheld XRF analyzer

Differential GPS can achieve spatial resolution of ~10 cm

Data can be exported with the assay data and all GPS coordinates to a mapping program

Sample Preparation

XRF is a surface measurement (depth of a few mm depending on Z).

Precision and accuracy will depend on the level of sample preparation

Sample preparation required depends on you data quality objectives

Quantitative results can be achieved in situ

Almost lab grade quantitative can be achieved with on site sample preparation

Sample Preparation

In situ measurements

- Remove any possible surface debris, stones, vegetation, and excess moisture from measurement area.
- Select a test area where soil particle-size is small and which looks homogeneous.
- Position the nose of the analyzer against the ground and start the measurement.
- After each measurement, clean the nose of the instrument with a soft cloth or tissue.
- Send 5 – 10% of samples to laboratory

Sample Preparation

On Site Sample Preparation (any part improves results)

- Dry sample
  - Absorbent paper
  - Dry overnight in shallow pan
  - Heat in oven until constant weight (care must be taken to prevent volatile compounds escape)
- Grind/Sieve
  - Sieve out large debris
  - Grind to 60 mesh (better 120 mesh)
  - Sieve
- Prepare homogeneous sample in XRF cups.

XRF Sample Cups and Holder

Sample Cups

Sample Bags

Sample Table and cover with Sample Cup

Analyzer in Stand

Site Specific Calibration

Empirical – based on standards which are representative of samples to be measured

Advantage –

Can exactly match the site conditions

For homogeneous samples give quantitative results

Disadvantage –

Requires understanding of XRF

Number of standards required

Time required to create calibration

Site Specific Calibration

Fundamental Parameters – based on measurement of a few standards, assumptions about the nature of the sample and theoretical understanding of XRF

Advantage -

Ready "out of the box"

Disadvantage –

Does not represent site conditions

Probably gives "semi-quantitative" results

Site Specific Calibration

Factors which affect the calibration

- Matrix
- Particle size
- Density
- Moisture content

Typical FP calibration assumptions

- SiO_2
- Small particle size (120 mesh)
- Very low moisture content

Type Standardization
“Calibration Correction”

Most differences between measured assay and actual are from difference between calibration assumption and reality

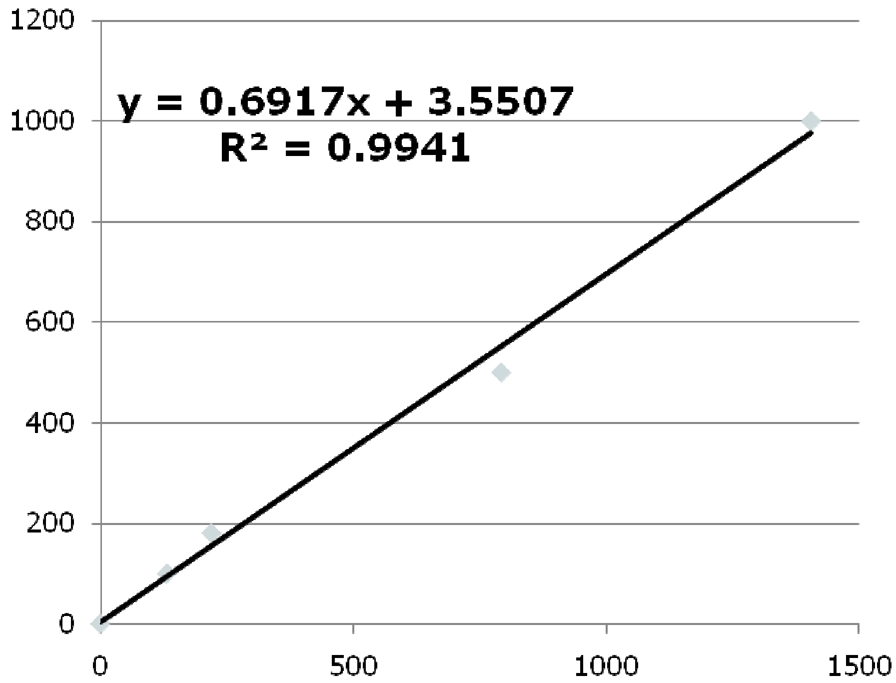
Most of these differences are linearly related to the concentration

Actual = Slope * Measured + Offset

Type standardization allows correction of measured data

Correction Calculation

Element 1	Ni	
SLOPE	0.6917	
OFFSET	3.5507	
CORR	99.7%	
Reference values	S1 Meas. Results	Adjusted S1 Result
0	0	3.55
100	131.1	94.24
180	219.45	155.35
500	792.17	551.53
1000	1404.84	975.33



What to Do for Site Specific Assay

Always try Type Standardization first

- Measure 5-10 well characterized samples
- Plot Actual vs. Measured
- If the result is a straight line plot with a correlation coefficient > 0.9 use Type Standardization

If not or if the element of interest in not in the basic calibration then Site Specific calibration will be required

Limit of Detection

How LOD is calculated

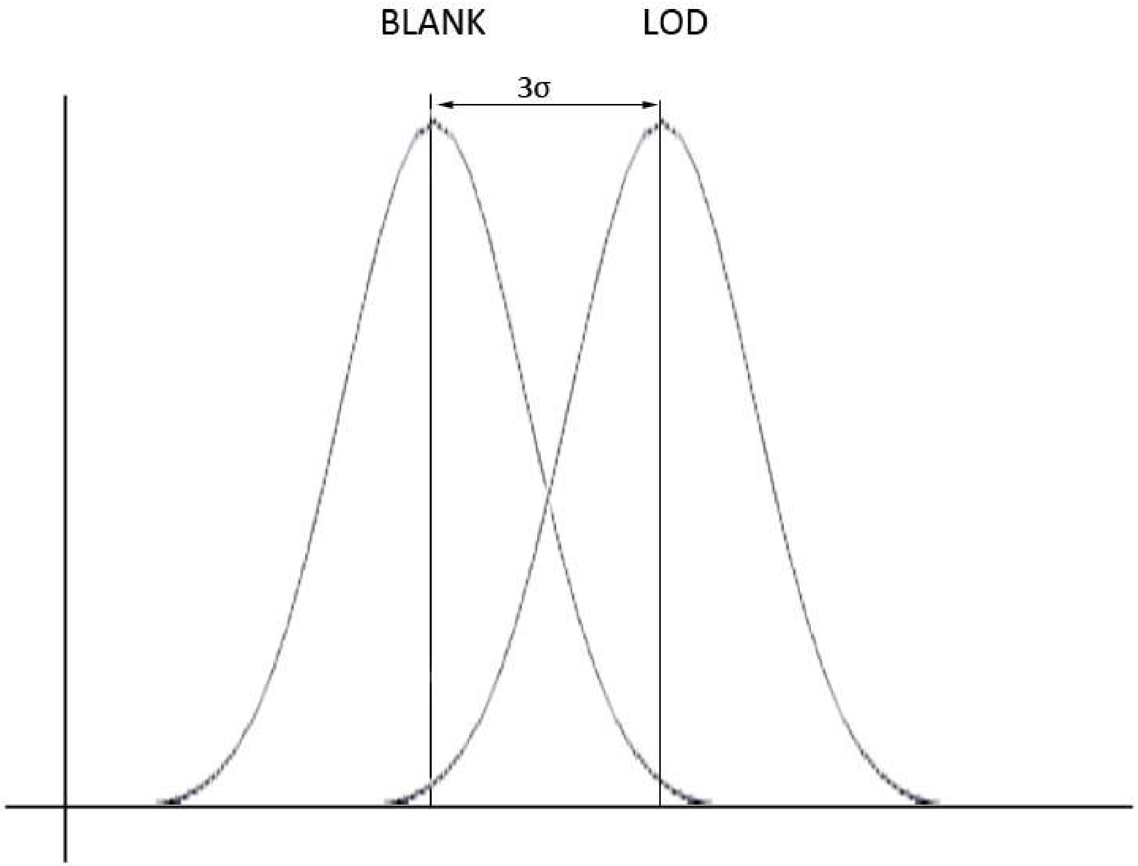
$$LOD = 3 * \sqrt{BKG} * SENS$$

Where:

BKG = average counts in the region of interest in counts/second

SENS = slope of the calibration curve in ppm/cps

Result



LOD Issues

LOD= Concentration

If sample at exactly LOD is measured a result will be calculated only about 50% of the time

This does not indicate a concentration which can be measured

Good for comparing one instrument (or calibration to another)

Limit of Quantification

Limit of Quantification

LOQ=3*LOD

Good indicator of concentration which can be measured accurately

LOD and LOQ

	EPA 6200 LOD mg/Kg	Current LOD mg/Kg	Current LOQ mg/Kg
Arsenic (As)	40	4	12
Cadmium (Cd)	100	21	63
Chromium (Cr)	150	40	120
Lead (Pb)	20	12	36
Mercury (Hg)	30	5	15
Silver (Ag)	70	8	24
Strontium (Sr)	10	4	12

Data is specifically for Bruker S1 TURBO^{SD}

Representative of state of the art

Conclusions

In situ Handheld XRF

- Offers rapid measurement (1-2 minutes)
- Can easily transfer data along with GPS coordinates
- With proper calibration and sample preparation will give quantitative results
- Has LOQ for most heavy metals on the order of 10 to 25 mg/kg

Thank You For Your Attention