Real-Time Techniques for Beryllium Analysis in Soils – A Case Study

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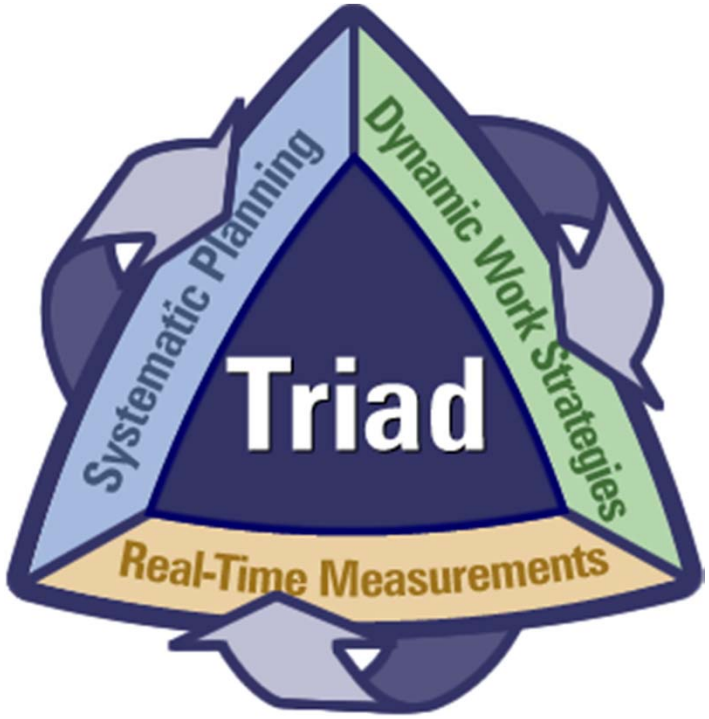
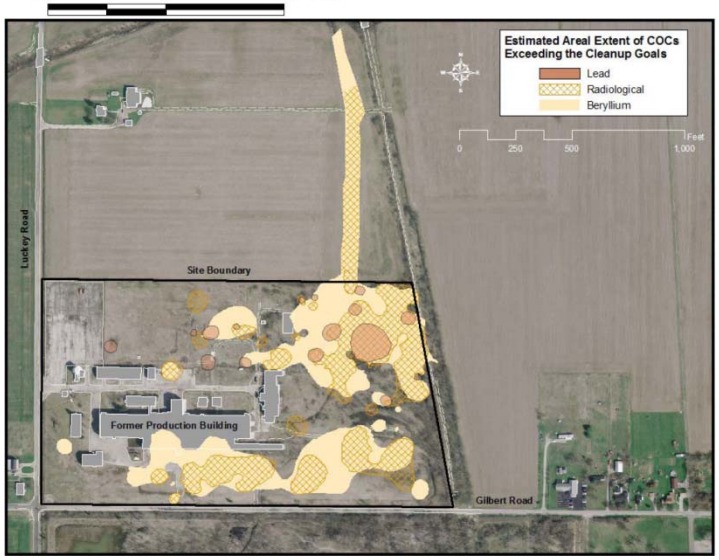
Real-Time Systems Facilitate Dynamic Work Strategies



- Systematic Planning
- Dynamic Work Strategies
- Real-Time Measurement Systems

Luckey Site

- Part of the USACE FUSRAP Program
- ~40 acre inactive facility
- Final Record of Decision (ROD)
- Beryllium, lead, and radiological contamination in soils
- Beryllium has the most extensive footprint and will drive cleanup activities (clean-up level - 131 ppm)
- Beryllium real-time techniques that could support dynamic data collection (pre-design, remedial support, site closure)

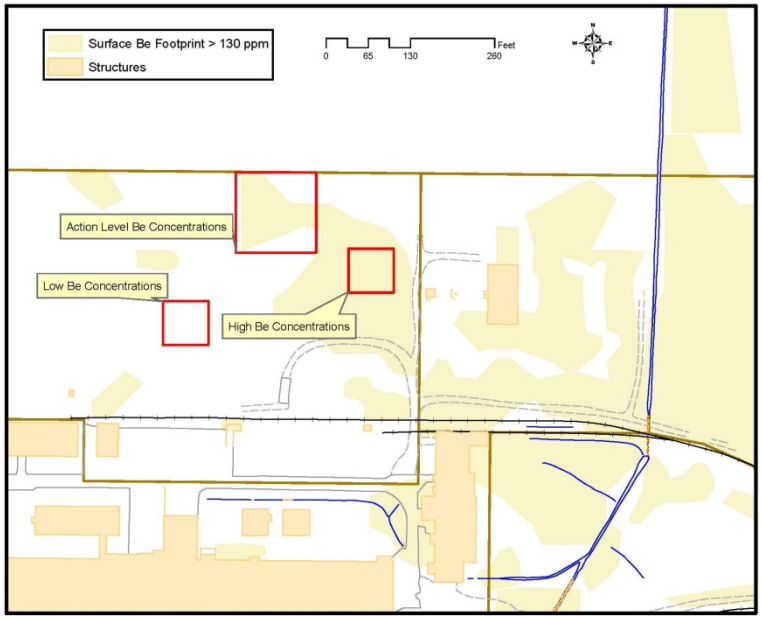


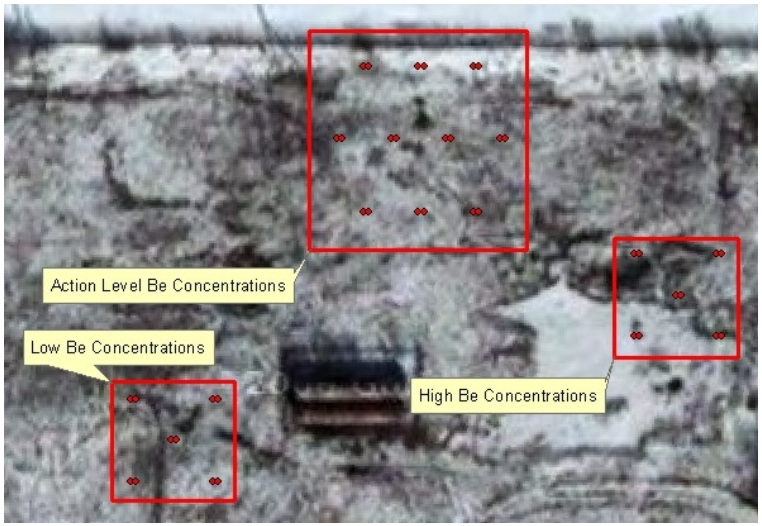
Study Objectives

- Evaluate two potential real-time techniques for beryllium analysis
  - Optical Fluorescence (BeFinder)
  - Laser-Induced Breakdown Spectroscopy (LIBS)
- Evaluate comparability with standard laboratory analyses
- Determine detection limits
- Estimate precision
- Evaluate range of linear calibration
- Identify cost and implementation issues
- Explore beryllium spatial variability and implications for sampling program design

Study Design

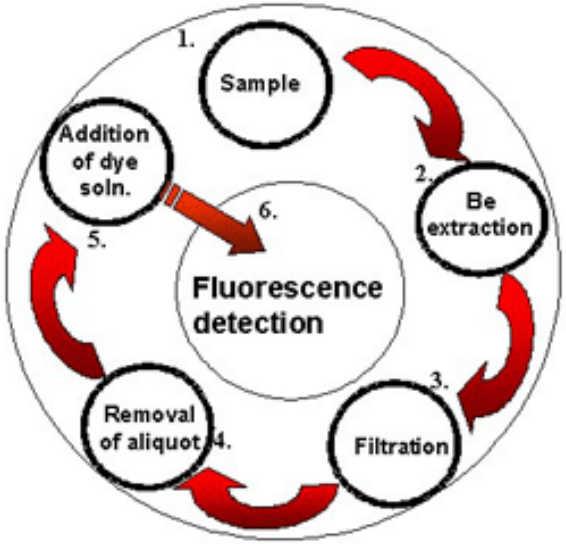
- Three areas selected for sampling
  - Radiological concerns avoided
  - Low, medium, and high beryllium impacts
- 10 samples (5 pairs) collected from low and high areas of beryllium concentrations
- 20 samples (10 pairs) from medium area (range of the beryllium clean-up criterion)
- Paired samples separated by 1 m
- Samples homogenized and analyzed by ICP-MS
- Sample closest to beryllium clean-up level re-subsampled and re-analyzed 5 times (analytical variability)
- Sub-samples sent for BeFinder and LIBS analysis





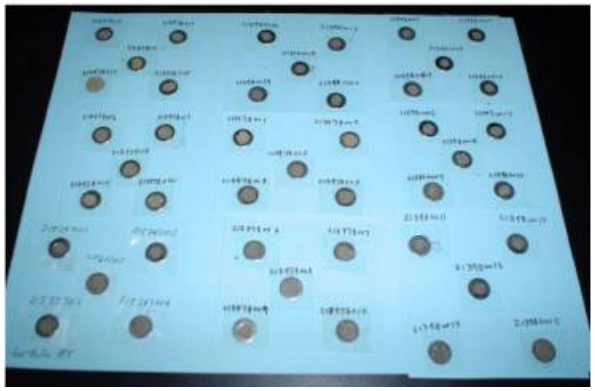
BeFinder

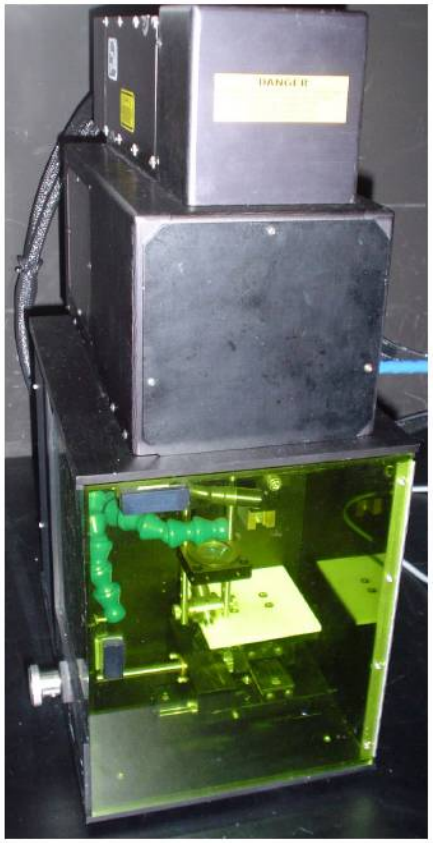
- Optical fluorescent technique
- Developed by LANL
- Commercially available from Berylliant, Inc.
- NIOSH method for beryllium wipe analyses
- Soil protocol requires:
  - 0.5 mg soil sample
  - Ammonium bifluoride dissolution step
  - Proprietary fluorphore added
  - Fluorescence is measured by the fluorometer
- Expected detection limits ~ 0.1 ppm
- Background soil concentrations ~ 1 ppm



LIBS

- Prototype system demonstrated at Luckey in late 1990s
- Early performance not great, but data proved useful
- No commercial systems currently available specifically for Beryllium
- Ocean Optics system adapted for this study
- Soil samples compressed into “pucks”
- Samples “shot” by laser, small amount of soils turned into plasma
- Plasma spectra analyzed to identify elements
- Element/matrix-specific calibration required for quantification

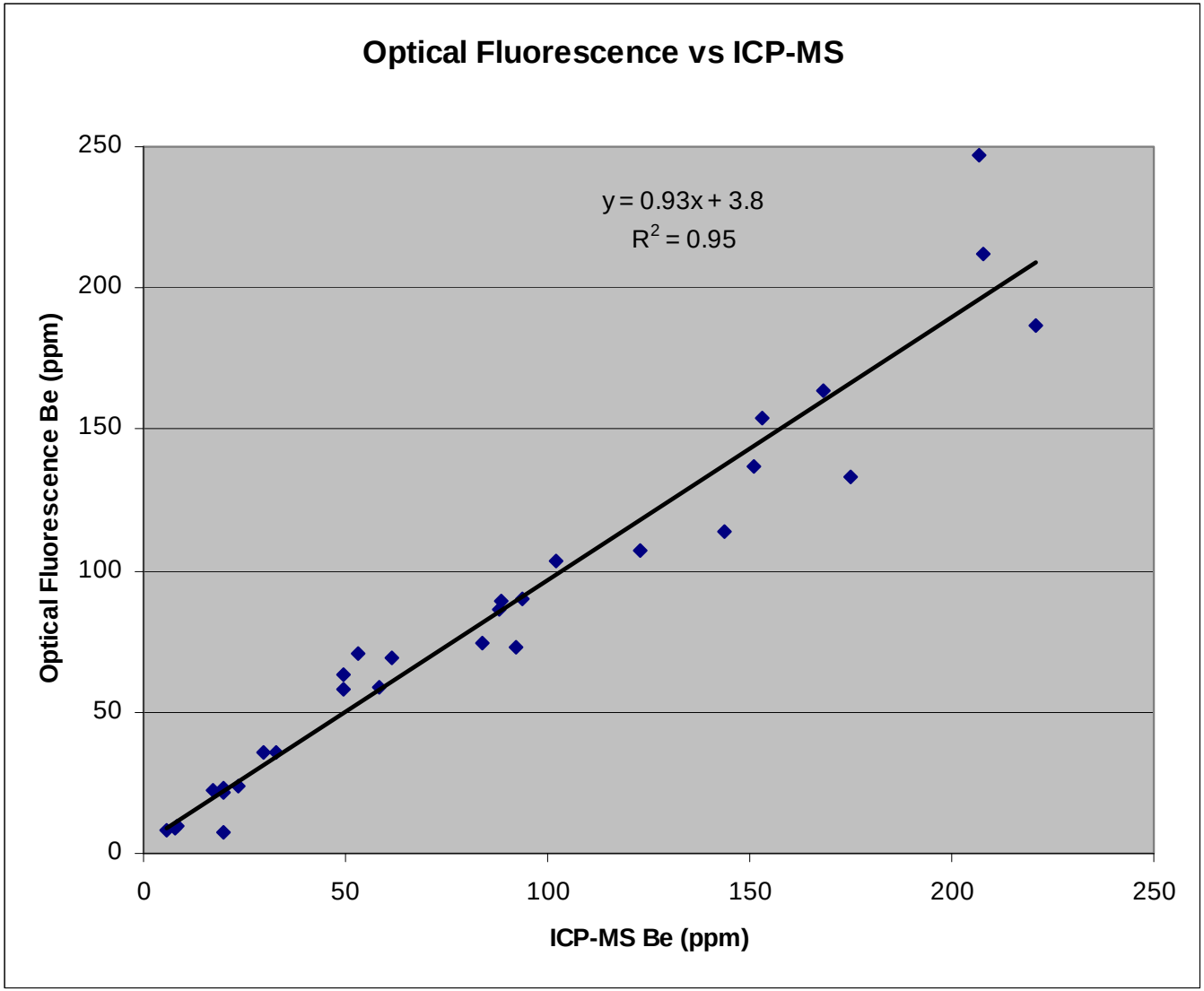




BeFinder Performance

- 45 samples analyzed in all
- ICP-MS beryllium concentrations ranged from 5 to 6,000 ppm
- Evidence of BeFinder beryllium underestimation for high concentrations
- Excellent correlation from 5 to 500 ppm
- Approx. 10% systematic bias (under-reporting) for BeFinder
- Precision (measured by 5 replicate measurements for sample at the Clean-up level) the coefficient of variation was 3% – better than ICP-MS
- Experimented with dissolution times
  - Standard is 40 hours
  - 4 samples done with 2 hour dissolutions
  - Approximately 10% loss in extraction efficiency

BeFinder Performance (cont.)



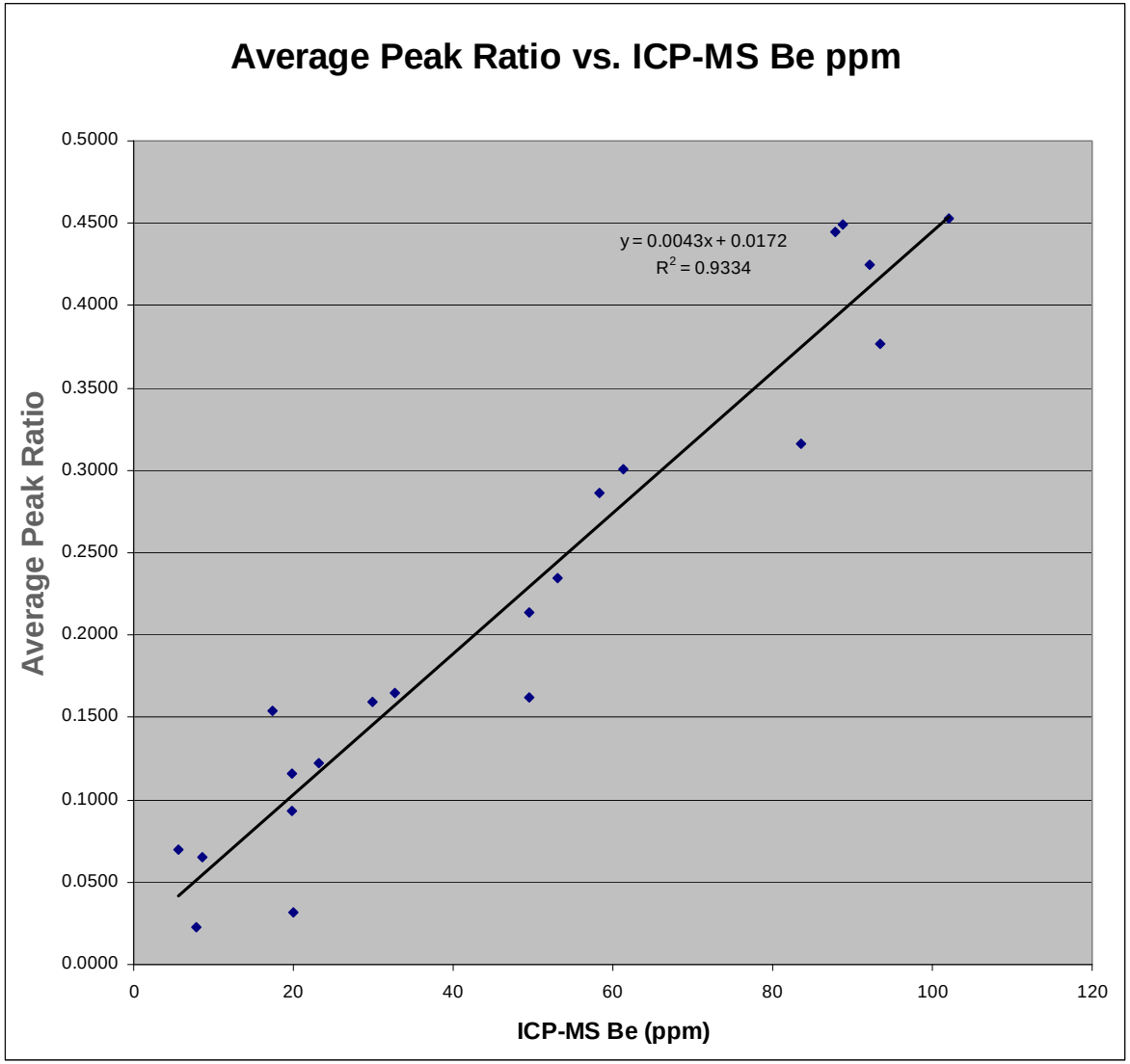
BeFinder performance with reduced extraction times

Sample	40 hr. Result	2 hr. Result	% Recovery
L6	22.34	18.83	0.81
M14	133.55	126.07	0.94
M1	35.97	33.39	0.93
H7	683.55	589.61	0.86

LIBS Performance

- 45 samples analyzed in all
- Each puck shot 5 times in succession; results average of the 5
- LIBS had a much more limited linear calibration range than BeFinder
- Strong linear relationship between 5 and 130 ppm
- At higher concentrations LIBS grossly underreported beryllium
- LIBS beryllium detectability extended down to the lowest concentrations encountered (5 ppm)
- LIBS precision in the range of the action level around 15% coefficient of variation (compared to 3% for BeFinder and 5% for ICP-MS)
- Current LIBS performance much better than the prototype system originally deployed

LIBS Performance (cont.)



Summary of BeFinder, LIBS, and ICP-MS Be results by area

Area	# of Samples	ICP-MS Beryllium (ppm)				
		Min	Average	Max	StdDev	Coefficient of Variation (COV)
Low	10	5.62	35	88	30	0.86
Medium	20	7.93	110	221	65	0.59
High	10	178	1978	6120	2053	1.04
Overall	40	5.62	558	6120	1290	2.31

Area	# of Samples	BeFinder Beryllium (ppm)				
		Min	Average	Max	StdDev	Coefficient of Variation (COV)
Low	10	7.94	36	86	27	0.75
Medium	20	7.55	106	247	64	0.60
High	9	215	1853	4773	1651	0.89
Overall	39	7.55	491	4773	1071	2.18

Area	# of Samples	LIBS Beryllium (ppm)				
		Min	Average	Max	StdDev	Coefficient of Variation (COV)
Low	10	13.6	37	96	26	0.72
Medium	20	4.3	83	148	40	0.49
High	10	33	334	707	197	0.59
Overall	40	4.3	134	707	155	1.16

Pros/Cons

- Optical Fluorescence
  - Relatively low capital costs (~$10K)
  - Excellent precision, comparability, and detection limits
  - Recurring per sample costs (~$30)
  - Extra work in sample prep/analysis (wet chemistry method)

- LIBS
  - Fast analyses
  - No recurring costs/minimal sample handling
  - High capital costs (~$80K)
  - Precision, detection limits, comparability not as good

(2009)

Deployment of the BeFinder for Beryllium Detection in Soils at the Luckey Site – Advantages and Lessons Learned

USACE Buffalo District incorporated the BeFinder as part of a pre-remedial characterization effort at the site.

Advantages of the BeFinder

- Field deployable and rapid turnaround
- Comparable detection limits to ICP-MS
- Good accuracy and precision

Limitations and Lessons Learned

- Required trained and experienced laboratory personal and support team
- Per sample analysis costs is on average higher in comparison to off-site laboratory analysis
- Extended sample preparation time
- Challenges managing interferences
- Variability in dissolution efficiency

Conclusions

- Both methods had performance adequate for Luckey characterization needs.
- Both methods had their unique strengths and weaknesses.
- Sample homogenization will be key to the success of either method (and is a concern for standard laboratory analyses as well).

Thank You