High Throughput Analysis of Environmental Samples-A Case Study for Determining Beryllium

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Presentation Outline

- Why beryllium- Industrial applications and regulatory actions to prevent beryllium exposure in industry.
- Test methods to determine presence of beryllium, comparison and cost, brief discussion of fluorescence method.
- Introduction to high throughput (HT) methods.
- Adaptation of HT methods for quantifying beryllium by Fluorescence.
- Possible extension to other analytical methods and determination of other materials of environmental concern.

Applications of Beryllium

- Industrial uses of beryllium are mainly in metallic form (including alloys) or as its oxide.
  - Pure beryllium metal is used in defense, aerospace, X-ray imaging and nuclear applications.
  - High thermal conductivity and transparency to microwaves of beryllium oxide (BeO) ceramics has led to its use in electronics, microwave and communication equipment.
  - Most beryllium is used as an alloying element in copper. The high strength alloys retain copper's electrical conductivity, heat dissipation and impart corrosion resistance, low creep resistance leading to many electronic and specialty tool applications.

Regulatory Actions to Prevent Exposure from Beryllium Particles

- **1940s** – Acute disease is associated with occupational exposures over 100 µg/m^3, proposal to regulate at below 25 µg/m^3
- **1950s** – Exposure monitoring and control programs instituted
- **1970s** – Personal versus DWA monitoring.
- **1990s** – CBD cases associated with exposures <2 µg/m^3 OSHA PEL.
- **1999**- DOE adopts < 0.2 µg/m^3 TWA over 8 hours and surface contamination levels < 0.2µg/100cm^2 for equipment release.
- **2009**- ACGIH adopts a threshold value of 0.05 µg/m^3 .

One 50µm particle of BeO contains 0.07µg of beryllium

*DWA-Daily weighted Average, CBD-Chronic Beryllium disease, TWA-Time weighted Average, PEL-permissible exposure limits

Examples of Metals Analyzed and Test Methods used in Industrial Hygiene

Metal	Air Std (OSHA, DOE or NIOSH)	Test Methods	Instrumentation
Lead	0.05 mg/m^3	OSHA-ID125G NIOSH 7700, 9100 and 7702	ICP-AES, ICP MS, AA, XRF, colorimetric
Mercury	0.1 mg/m^3	OSHA-ID140 NIOSH 6009	AA
Cadmium	0.1mg/m^3	OSHA-ID125G NIOSH 7300	ICP-AES, ICP MS, AA
Hexavalent Cr	0.001 mg/m^3	OSHA ID215 NIOSH 7600	Optical absorption
Beryllium	0.0002 mg/m^3	OSHA-ID125G, NIOSH 9110 ASTM D7202	ICP-AES, ICP MS, AA, Optical Fluorescence

Conventional Sample Preparation and Analysis

- NIOSH Method 7300 (ICP-AES)

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.
   NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120 °C) until ca. 0.5 mL remains.
   NOTE 1: Recovery of lead from some paint matrices may require other digestion techniques. See Method 7082 (Lead by Flame AAS) for an alternative hotplate digestion procedure or Method 7302 for a microwave digestion procedure.
   NOTE 2: Some species of Al, Be, Co, Cr, Li, Mn, Mo, V, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [5-10]. For example, aqua regia may be needed for Mn [6,12].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150 °C and take the sample to near dryness (ca. 0.5 mL).
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 25-mL volumetric flasks.
11. Dilute to volume with dilution acid.
    NOTE: If more sensitivity is required, the final sample volume may be held to 10 mL.

- **Sample Analysis**
  - Calibration 1-3 hours
  - Sample Analysis time 6 hours for 100 samples with auto-sampler

Maximum 45 samples/shift/person,

Cost at DOE facilities to Quantify Beryllium in Air or Surfaces

- Direct analytical cost estimated at $60/sample.
- Turn-around time 4 (urgent) to typical 24 to 48 hours.
- An increasing number of samples from wipes due to clean up and D&D operations. Some DOE facilities processing upwards of 50,000 samples/year.
- The above cost does not include waiting time for crew and equipment.

How are Samples Analyzed by Biologists in High Throughput (HT) mode?

- Automation of Sample Preparation using a liquid handling system
- Analysis conducted using a plate reader. Each plate to comprise of samples and standards. Full plate analysis time- few minutes

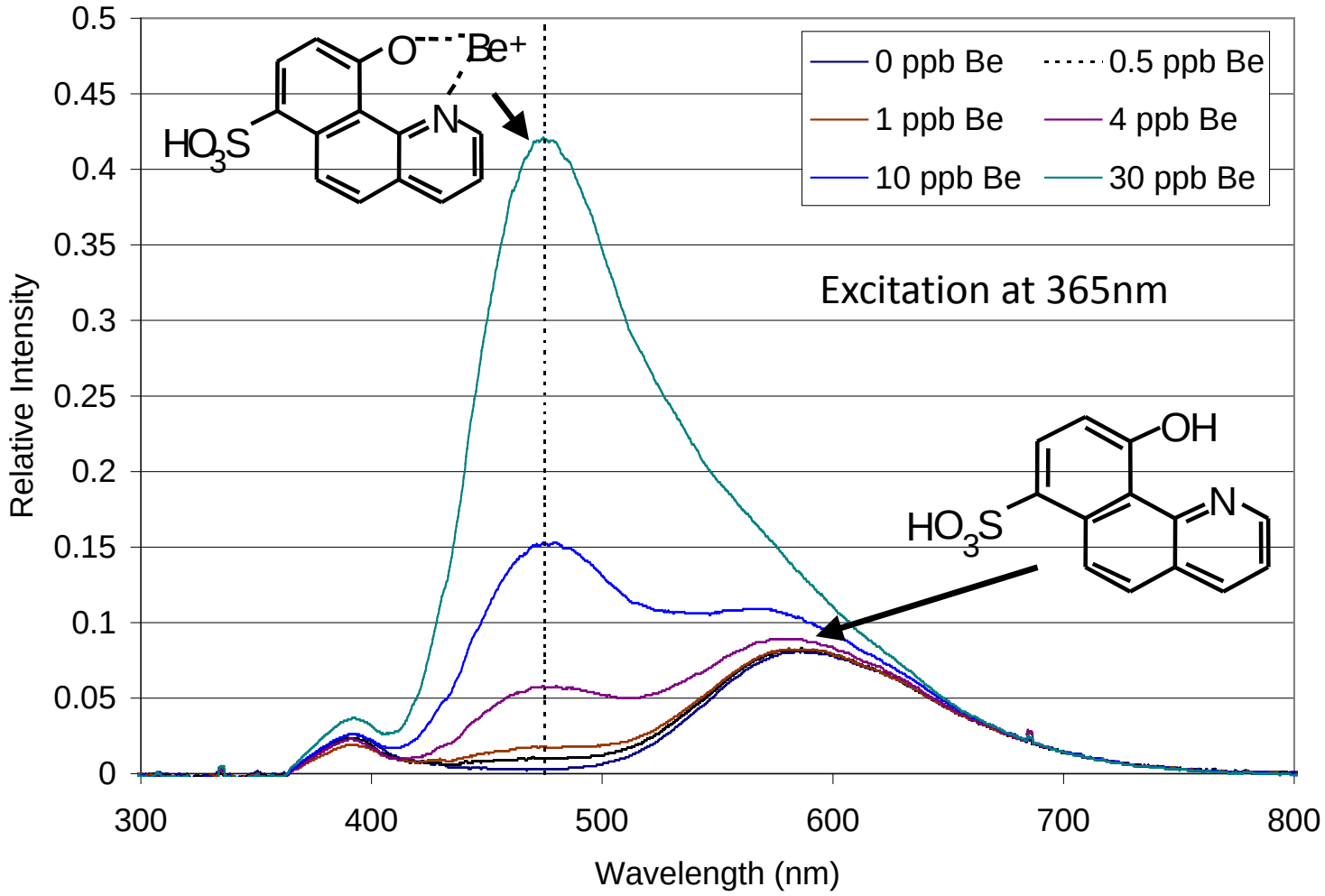
Advantages-High Throughput Methods

- Reduced Cost
  - Reduced labor.
  - Reduced turn-around time.
  - Reduced capital- Less number of analytical instruments and less laboratory space is needed.
  - Less chemical waste, as small quantities are handled.
- Increased safety
  - Reduced worker injury from repetitive motions.
  - Less interaction between humans and chemicals.
- Improved consistency

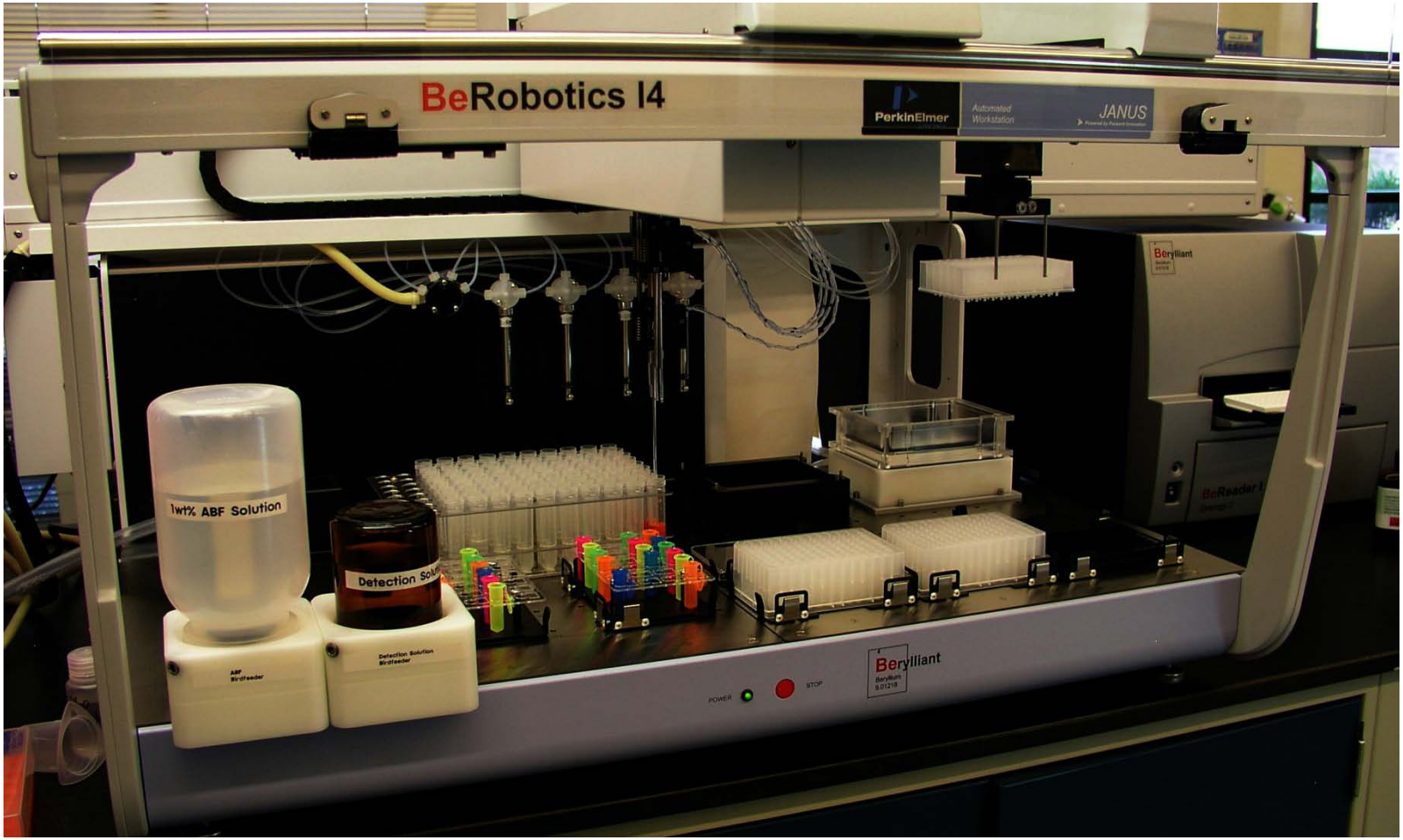
Fluorescence Method for Beryllium Analysis

- Method used NIOSH 9110 (wipes)or 7704 (air) ASTM D7202 (wipes and air)
- Sample Preparation
  - **Dissolve sample in 5ml** of 1% aqueous ammonium bifluoride (ABF solution) at elevated temperature for one hour.
  - **Remove 0.1ml** of sample and **mix** with **1.9ml Fluorescent dye** solution.
  - **Filter** (measurement solution).
- Analysis
  - **Prepare calibration** solutions, **calibrate.**
  - **Measure** (measurement solution).

Principles of Fluorescence Analysis



BeRobotics* HT System



*Available from Berylliant Inc

Challenges

- Considerable tubing and hardware changes were required to handle highly acidic and basic solutions.
- Larger volumes had to be dispensed.
- Since large amount of data is generated, checks and balances had to be incorporated in order to flag potential issues.
- Calibration and sample-check issues had to be implemented differently.

QC Protocol from Y12

- Initial calibration verification (ICV) using a second source standard
- Blank level checking: calibration (CCB) and method blanks
- Reporting limit verification
- Duplicate lab controls (aqueous or BeO)
- Method precision from LCS duplicates
- End-of-plate calibration verification (CCV)

96 Well-Plate Layout from Y12

	1	2	3	4	5	6	7	8	9	10	11	12
A	Blank	Blank	ICV									
B	Std #1	Std #5	ICB									
C	Std #2	Std #6	RLV									
D	Std #3	Std #7	Well left empty									
E	Blank	Blank	Method blank#1									Method blank#2
F	Std #4	Std #8	LCS-1									LCS-2
G	Std #5	Std #9										CCB
H	Blank	Blank										CCV

Comparison of Methods from Y12

	ICP-AES	HT Fluorescence
Batch size	45 samples	70 samples
Sample digestion time	63 minutes	140 minutes
Sample analysis time (for all)	180 minutes	2 minutes
Total sample digestion and analysis time	243 minutes	147 minutes
Time/sample	5.4 minutes	2.1 minutes

This comparison does not include labor time

Preliminary System/Analysis Cost

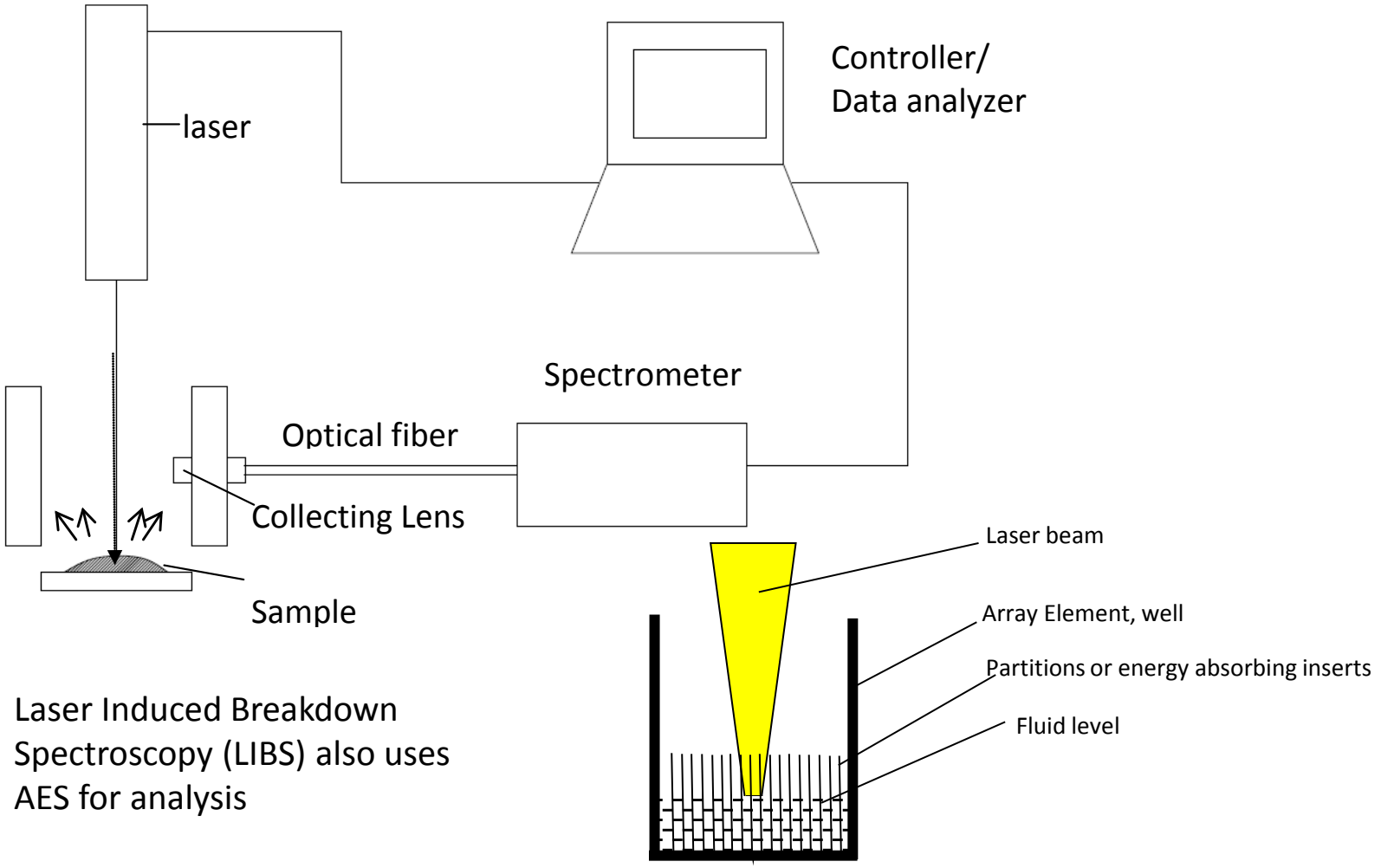
- Cost /test (all consumables+chemicals+labor)
  - $15/test to down to $7/test depending on the volume.
  - Includes labor cost (at peak instrument throughput ~ $1-2/test).
- Throughput with 4 tip robotic Instrument ~200 samples/shift/person
- Time to read one 96 well plate ~2 minutes.

Current cost at DOE labs is estimated to be $60/sample
Average current throughput ~45 samples/shift/person

Can HT Systems be Used for Other Materials and Analytical Methods?

- We need to separate sample prep from sample analysis.
  - Sample prep consumes most of the labor and the output could be plates (typical for optical methods) or separate vials for other analytical techniques.
- One needs to rethink if analytical methods could be adapted for plate format, e.g. atomic emission spectroscopy (AES).

Can AES be Adopted for a Plate Format?



Laser Induced Breakdown Spectroscopy (LIBS) also uses AES for analysis

Conclusions

- HT methods can be used for preparation and analysis of environmental and industrial hygiene samples.
- These methods have the potential to significantly lower analytical costs and increase lab safety.
  - Reduction in labor, materials, equipment and facility costs
- Optical techniques lend well to analyzing samples in an array format, however, other methods could also be adapted.