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Laboratory Analysis Considerations for Beryllium in the Current Regulatory Climate

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Disclaimers

- **The contents of this presentation do not necessarily reflect the views of DOE, OSHA, SRNL, other DOE sites, or other federal agencies. The presenter does not speak for any federal agency or entity.**
- **Mention of commercial products or companies does not imply endorsement or criticism.**
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IMPORTANT:

- **This presentation is based on the *final* rule promulgated by OSHA for general industry (effective May 20, 2017), the *proposed* DOE revision to 10 CFR 850 (promulgated June 7, 2016), and the *draft* report of the European Commission's Working Party of Chemicals (based on their March 21, 2017 meeting).**
  - What is ultimately adopted by DOE and the European Union may differ.
  - The OSHA final rule for general industry could be affected by pending litigation.
  - The OSHA final rules for shipyards and construction, and the proposed changes to them, are generally not considered in this presentation but will impact those industries.

An Additional Note

- This presentation is focused on *laboratory* analysis.
- Considerations may be different for real-time monitoring. It will depend on the technologies that may be utilized and how they are utilized.
- More on real-time later (Kathy Creek presentation).

Outline

- **Where we are now versus June 2016**
- **Effects of air volume and pump rates on what the lab can detect – and why that matters**
- **Setting yourself and your lab up for success under the new paradigms**
- **Special cases:**
  - Beryllium oxide
  - Bulk sampling
  - Inhalable sampling
  - The EC's proposed Biological Guidance Value

Where We Were in June 2016

- **OSHA Proposed Rule was promulgated (80 FR 47566, August 7, 2015)**
  - Applied to general industry but not shipyards or construction
- **DOE NOPR (to revise 10 CFR 850) had just been promulgated**
- **No outward indication of activity in the European Union**

Agency	Proposed PEL ($\mu g/m^3$)	Proposed AL ($\mu g/m^3$)	Proposed STEL ($\mu g/m^3$)
OSHA	0.2	0.10	2.0
DOE	N/A	0.05	N/A
EC	N/A	N/A	N/A

Where We Are Today

- **OSHA Final Rule took effect (after delays) on May 20, 2017**
  - As originally promulgated in January, applied to general industry, construction, and shipyards
  - Changes proposed in June 2017 for construction and shipyards – public comments presumably still being considered by OSHA
  - Under litigation
- **Final rule to revise 10 CFR 850 not yet promulgated**
- **EC committees have proposed 8-hour Binding OEL and (non-binding) Biological Guidance Value**

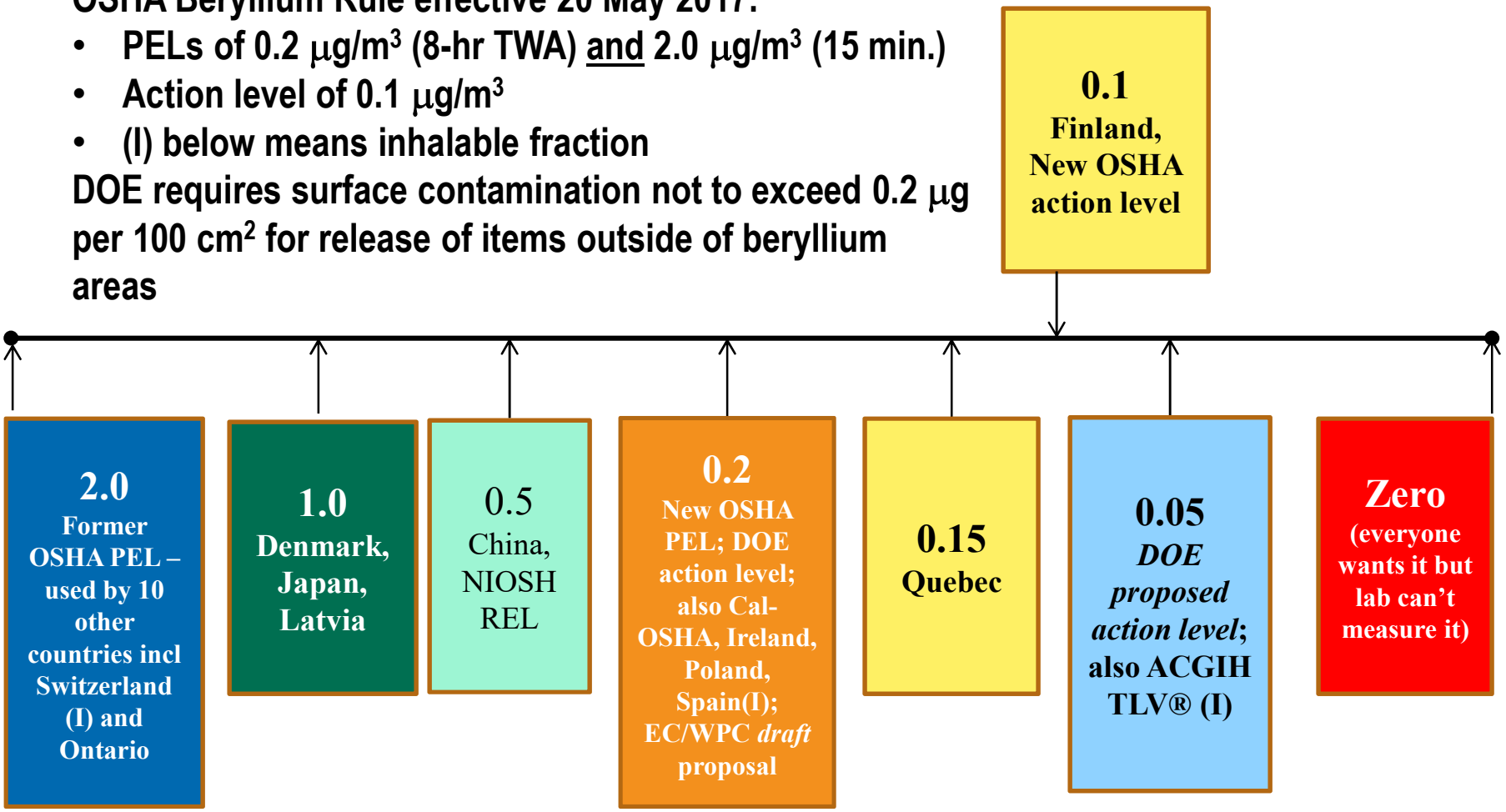
Agency	PEL (μg/m³)	AL (μg/m³)	STEL (μg/m³)	Size-Selective Fraction	BGV (μg/L)
OSHA (final)	0.2	0.10	2.0	None	N/A
DOE (NOPR)	N/A	0.05	N/A	None	N/A
European Commission (draft WPC report)	0.6 for five years, then 0.2 afterward	N/A	N/A	Inhalable	0.04

Beryllium 8-Hour OELs/Action Levels Around the World

OSHA Beryllium Rule effective 20 May 2017:

- **PELs of 0.2 μg/m³ (8-hr TWA) and 2.0 μg/m³ (15 min.)**
- **Action level of 0.1 μg/m³**
- **(I) below means inhalable fraction**

DOE requires surface contamination not to exceed 0.2 μg per 100 cm² for release of items outside of beryllium areas



(Partial source: GESTIS International Limit Value Database, IFA – Germany, as of June 2016)

Beryllium Short-Term Limits Around the World (June 2016 except as noted)

Country	STEL (μg/m³)
Australia	8.0
Belgium	10.0
Canada – Ontario	10.0
Denmark	2.0
Finland	0.4(1)
Hungary	2.0
People's Republic of China	1.0(1)
Republic of Korea	10
USA – OSHA	2(2)
USA – NIOSH Recommended	0.5(1)
SCOEL Recommendation	0.2

- **(1) – 15-minute average value**
- **(2) – As of May 20, 2017**
- **Source: GESTIS International Limit Value Database, IFA – Germany**
- **DOE does not currently have a STEL but is considering whether the OSHA STEL would be applicable.**

Effects of Air Volume and Sampling Rate on What Laboratory Can Detect

	Sampling duration (hr) and resulting volume of air drawn (cubic meters)					
Sampling Rate (L/min)	0.25 hr (15-minute STEL)	0.5 hr (30-minute excursion)	1.0 hr	2.0 hr	4.0 hr	8.0 hr (conventional TWA interval)
2.0	0.03 m^3	0.06 m^3	0.12 m^3	0.24 m^3	0.48 m^3	0.96 m^3
3.5	0.05 m^3	0.10 m^3	0.21 m^3	0.42 m^3	0.84 m^3	1.68 m^3
4.0	0.06 m^3	0.12 m^3	0.24 m^3	0.48 m^3	0.96 m^3	1.92 m^3

- **PEL and STEL are based on mass per volume of air, but lab detection is based on mass only (whatever is on the filter)**
- **Therefore, as more air is drawn through the filter, one can expect more mass to be collected and a better chance to detect something, especially when dealing with sub-microgram (or perhaps even sub-nanogram) quantities**

Laboratory Analysis Methods

- For years, ICP-ES has been "workhorse" for trace-level elemental analysis
- DOE's proposed revision to 10 CFR 850 would set an action level of 0.05 $\mu g/m^3$
- ISO 20581 requires measuring range to be at least 10% to 200% of the applicable limit value
  - In this case, 5 ng/m^3
- ICP-ES (e.g., NIOSH 7300) can't do that consistently for Be
- Methods that can:
  - ICP-MS (e.g., ASTM D7439)
  - Molecular fluorescence (e.g., NIOSH 7704)

(ICP-MS installed at SRNL radiological lab)

(Portable fluorimeter, courtesy Berylliant, Inc.)

Mass Collected Versus Laboratory Detection Limits

Criterion	Air Conc. (µg/m³)	Volume of air collected and the resulting mass collected on filter (µg)					
		0.03 m³	0.06 m³	0.25 m³	0.50 m³	1.0 m³	2.0 m³
ACGIH® TLV-TWA and Proposed DOE AL	0.05	0.0015 µg	0.003 µg	0.013 µg	0.025 µg	0.05 µg	0.1 µg
OSHA Action Level (2017 Final Rule; 8-hr TWA)	0.1	0.003 µg	0.006 µg	0.025 µg	0.05 µg	0.1 µg	0.2 µg
OSHA PEL (2017 Final Rule; 8-hr TWA)	0.2	0.006 µg	0.012 µg	0.050 µg	0.10 µg	0.2 µg	0.4 µg
OSHA STEL (2017 Final Rule; 15 min.)	2.0	0.06 µg	0.12 µg	N/A (requires sampling rate < 4 L/min)			

- MQL for ICP-AES is 0.03 µg/sample; ICP-MS 0.004, fluorescence 0.005 (all based on ASTM standards) – ICP-AES can achieve 0.01 when used with a column separation method
- Values in **red** can be met only by fluorescence; values in **blue** can also be met by ICP-MS or GF-AAS; values in **green** can also be met by ICP-AES.
- This does NOT consider reporting limits that may be higher, or samples requiring extra dilution (e.g., due to dust loading)
- Also, since water-soluble samples need less dilution volume, it may be possible to use ICP-AES or AAS successfully

Setting Yourself and Your Laboratory Up for Success

- Does the laboratory have any special requirements for how samples are collected and submitted?
- Can the laboratory meet your data quality objectives?
- What methods will the laboratory use?
- Can the laboratory handle your sample matrices?
- Is the laboratory accredited?
  - Not required by OSHA, but is required by DOE
- Is the laboratory experienced with beryllium samples?
- Can you get the results when you need them?
  - Consider transport time as well as laboratory turnaround time
  - Could your process be idled while waiting?

Special Case: Beryllium Oxide

- Some common methods (e.g., NIOSH 7300) cannot dissolve BeO
- Requires fluoride (e.g., HF or ammonium bifluoride) or sulfate (e.g., H_2SO_4)
- More Info: Oatts T.J. et al., "Preparation, certification and interlaboratory analysis of workplace air filters spiked with high-fired beryllium oxide", *J. Environ Monit* 14:391-401
- Note that the BePAT program (AIHA-PAT LLC) includes samples spiked with BeO

Special Case: Bulk Sampling

- Not required by OSHA
- May be required under 10 CFR 850 surface rules (e.g., when sampling legacy facilities for decommissioning)
- May require a greater amount of acid solution to solubilize the beryllium
- May also present more interferences for the laboratory
- Both of the above may effectively increase the minimum quantity that the laboratory can detect

Special Case: Inhalable Sampling

- **Not required by OSHA or DOE, but proposed by EC/WPC and included in ACGIH TLV® (2009)**
- **Kock et al. (2015) reported GSP/CFC ratios of 2.88 for personal samplers and 1.99 for static samplers (geometric means)**
- **Issues regarding inhalable particulate samplers:**
  - Limited number of models commercially available (IOM, GSP, Button)
    - *IOM and GSP are designed for 2 L/min; Button for 4 L/min*
  - Risk of cross-contamination (not disposable)
  - In U.S., lack of laboratory capacity to handle
- **Disposable inhalable samplers under development**
- **Universities: Iowa, Colorado State, Utah**

Special Case: Biological Guidance Value

- Proposed level is 0.04 μg/L (40 parts per quadrillion)
- At that level, ICP-MS or fluorescence will be required

For More Information

- *AIHA Laboratory Quality Assurance Manual*, Fifth Edition
- *Beryllium: Environmental Analysis and Monitoring* (RSC Publishing, 2009)
- And, once it is issued, the Practitioner's Guide

Questions or Comments?

Contact Information:

- **My email: mike.brisson@srs.gov**
- **Beryllium Health and Safety Committee:**
- **https://bhsc.llnl.gov**

THANKS FOR YOUR ATTENTION!