Comparison of Beryllium Determinations by High Throughput Fluorescence and ICP Emission Spectroscopy: Data from the Oak Ridge Y-12 National Security Complex

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Current Y-12 ICP-OES Method

1. Filter or smear samples prepared using open-vessel microwave digestion using H_2SO_4 + H_2O_2 + HNO_3.
2. Digested samples brought to 10-mL or 30-mL final volume (matrix is 6% H_2SO_4 + 10% HNO_3).
3. ICP instruments are Thermo Jarrell Ash model 61E simultaneous systems.
4. Primary emission interferents monitored: Cr 267.7 nm, Fe 273.9, Mo 204.5, Nb 316.3, Th 401.9, Ti 337.2, U 367.0, V 292.4, and Zr 339.1. (prominent in spectral interference and presence on detector array).
5. Follow a quality control analysis program consistent with AIHA and EPA protocols.

Y-12 beryllium determinations by ICP- OES

- Currently running 25,000 – 50,000 samples/year. (Does NOT include calibration and QC samples!)
- ICP's utilize autosamplers, however process is sequential, one sample at a time.
- Long batches (40-50) take 4-5 hours to complete. (difficult to interrupt for rush samples)
- Short batches of rush samples (5-10) interrupt lab efficiency planning. (difficult to handle large loads of samples in efficient manner)

Sample Loads

Fiscal Year	# of Samples	# Batches
2006	26648	1045
2007	40078	1471
2008	33871	1244
2009	26112 (proj.)	1116 (proj.)

Problems and concerns

- Sample turnaround times – always too long.
- Best case ICP turnaround: 4 hours *(too often considered default!)*
- Average case ICP TAT: 24-36 hours
- Desired TAT: 15 minutes before sampling!
- Lab ergonomic problems: current method creates many potential repetitive stress injuries. (lab pipette example)
- New instrument costs ($75K- $100K)

ICP digestates often contain:

- Chromium (up to 5 mg/L)
- Iron (up to 35 mg/L, often over 500 mg/L)
- Thorium (up to 10 mg/L)
- Titanium (up to 10 mg/L, often over 50 mg/L)
- Uranium (up to 17 mg/L, isotopic issues with ICP)
- Vanadium, zirconium, molybdenum, yttrium, and scandium have all been difficult-to-accommodate interferents.

ICP interference correction

- Utilize software corrections from IEC factors.
- IEC approach requires batch checking and maintenance.
- IEC approach does not easily work for analytes not on simultaneous detector array. (Er example)
- Isotopic issues with uranium.
- Direct overlap issues with some analytes (V example)

Fluorescence complications

- Manual preparation of microplate samples is NOT practical!
- Reagent mixing
- Dilution
- Pipetting
- Contamination
- pH buffer capacity of CH-2 reagent

Sample results comparison

Sample ID	ICP result (µg)	**Fluorescence mean (µg)**	**Fluorescence Std. Dev. (µg)**	**Fluorescence RSD (%)**
LCS	1.0	0.95	0.012	1.2
152	0.159	0.16	0.003	1.8
153	0.244	0.25	0.009	3.8
154	0.429	0.44	0.003	0.6
155	0.687	0.69	0.008	1.2
16	1.76	1.81	0.026	1.4
17	0.365	0.39	0.003	0.7
18	2.2	2.29	0.017	0.8
24	0.331	0.36	0.008	2.1

Fluorescence advantages

- Instrument costs significantly lower.
- Method much less detailed and complicated.
- Easier to automate (especially ABF prep)
- Plate reader fluorimeter significantly faster than ICP (3 minutes v. 5 hours for 80 samples)
- Fewer sample manipulations – fewer sources of RSI problems.
- Increased capacity using automated approach.
- Decreased turnaround times using automated approach.
- Decreased overall cost/analysis.
- Capable of lowering RL's to accommodate future data needs.

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