Fluorescence Analysis of Beryllium in Samples Contaminated by Strongly Fluorescent Impurities

Anoop Agrawal, John Cronin, Lori Adams
Akshay Agrawal and Juan Carlos Tonazzi

Berylliant Inc, 4541 E fort Lowell Road, Tucson, AZ 85712

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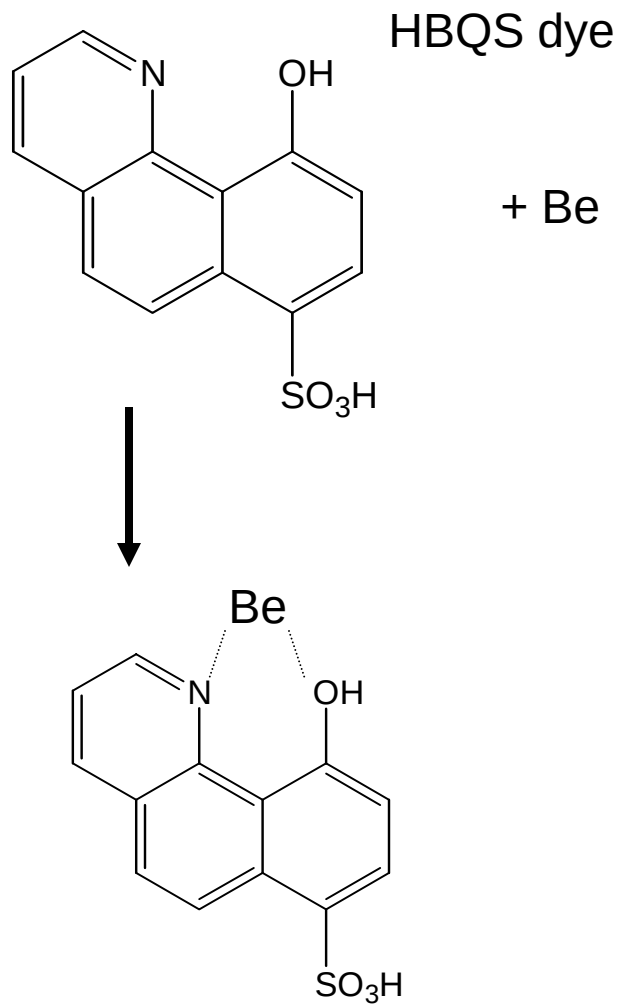
Why an Interest in Fluorescent Impurities?

- Fluorescent method is
  - Simple to use
  - Is very sensitive (detection limit to 0.002μg on media)
  - No known interferences
- What happens if an organic fluorophore is introduced in small concentrations with overlapping spectra with HBQS?



Preliminary Experiments with Activated Carbon

D&D unknown samples analyzed by Fluorescence* before and after treatment with activated carbon (Darco G-60)

Sample	[Be] (μg)* No Carbon	[Be] (μg)* With activated carbon	[Be] (μg)** With ICP-AES
Wipe (#15), 3wt% ABF	0.143	0.052	Not Known
Liquid Sample #8, 1wt% ABF	0.081	0.027	0.013
Liquid Sample #11, 1wt% ABF	0.059	0.043	0.015
Liquid Sample #13, 1wt% ABF	0.068	0.028	0.009
Liquid Sample #20, 1wt% ABF	0.115	0.06	0.038

***Excitation/Emission 365/475nm, ** Results provided by D&D group**

Method to Remove Organic Fluorescent Impurities

ABF dissolution solution **with activated carbon (1mg/ml)** is added to the sample

→

Conduct dissolution process at **elevated temperature** (80 to 90°C)

→

Cool dissolution solution and **remove activated carbon by filtration**

↓

Mix dye solution in dissolution solution

←

Filter if necessary to remove yellow color, e.g., iron

←

Measure fluorescence

Two types of activated carbons were obtained from Sigma Aldrich, (1) Darco-60, (2) HCl washed

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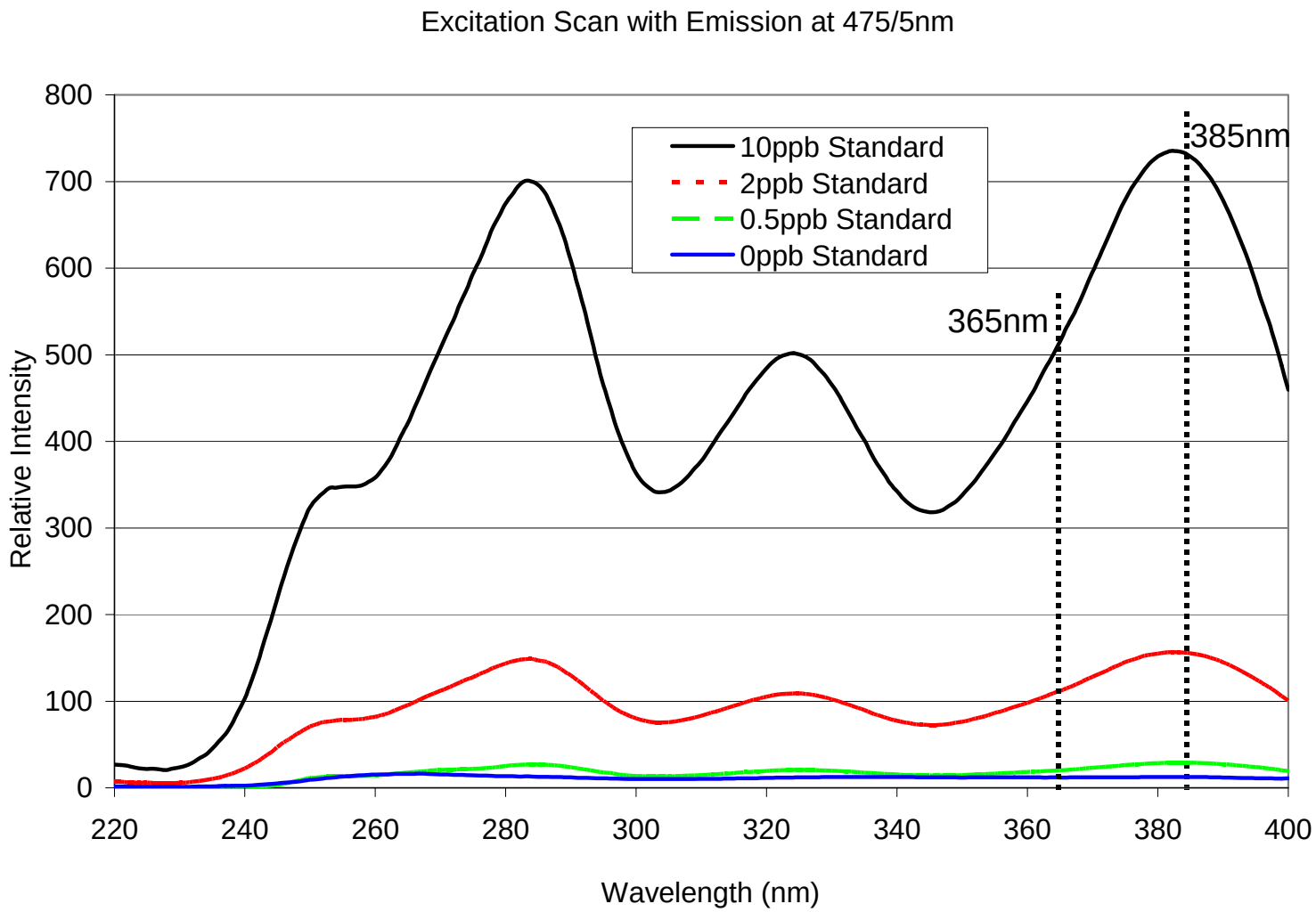
Excitation Spectra of HBQS with Beryllium



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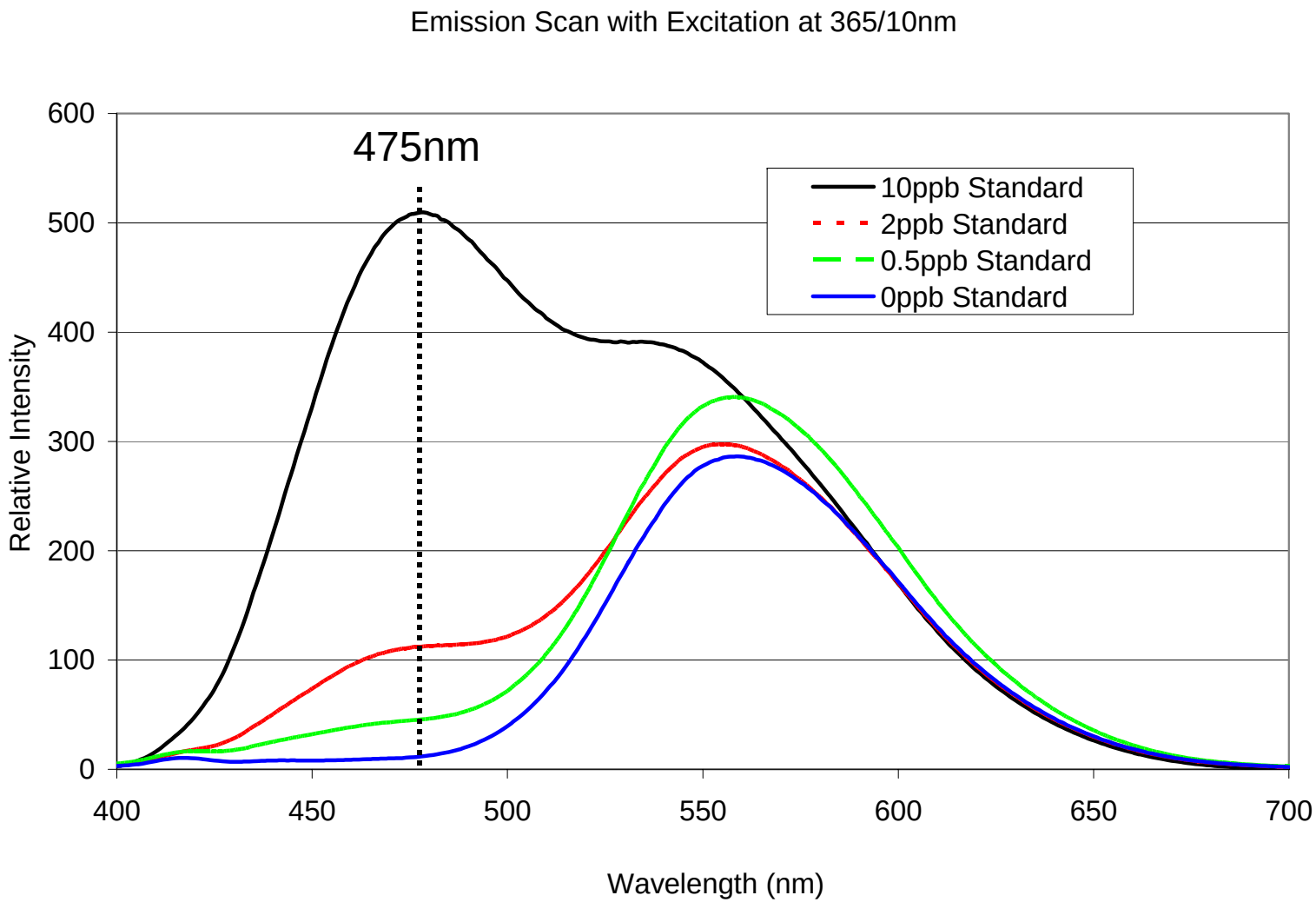
Emission spectra of HBQS with Beryllium



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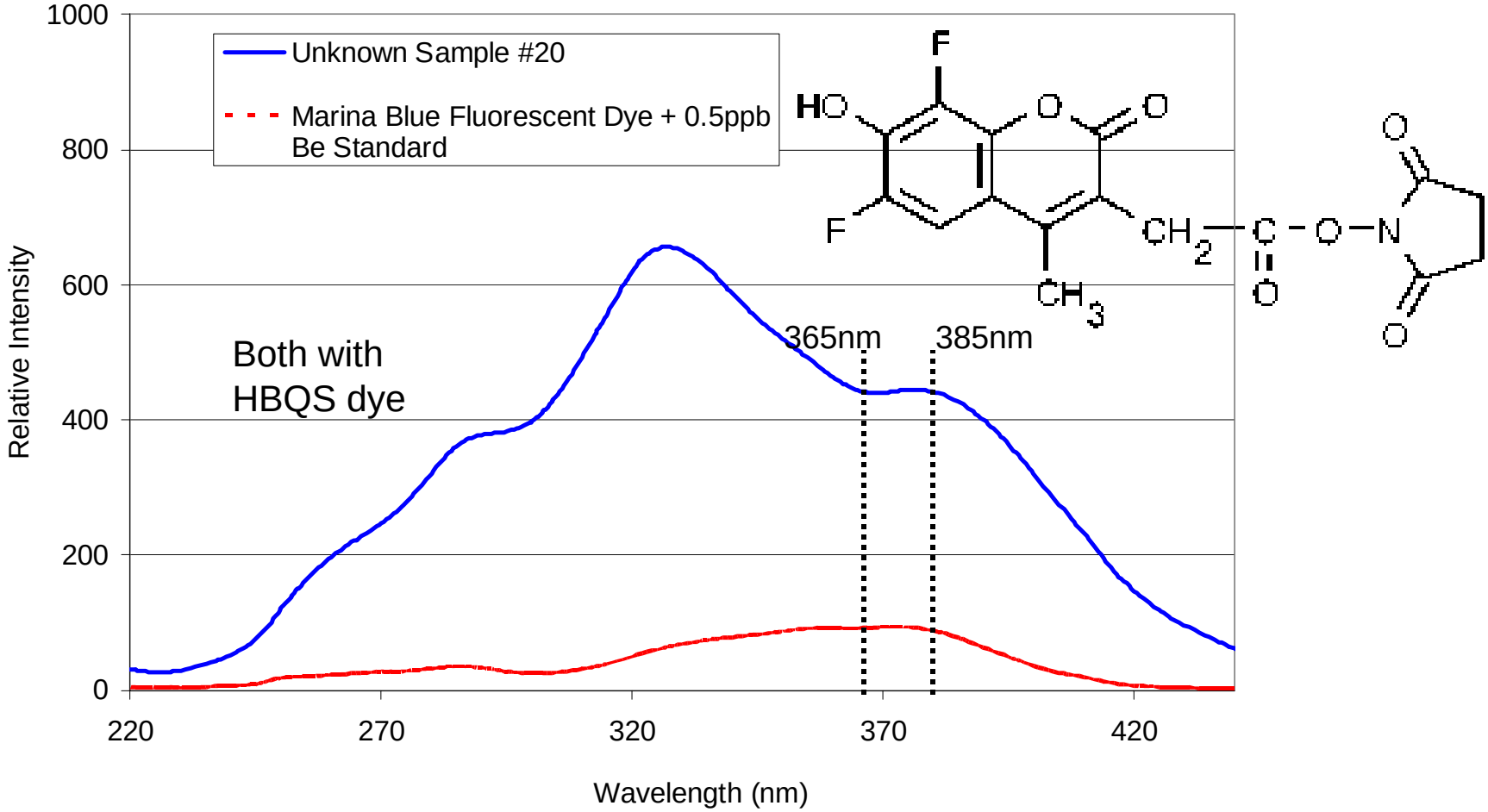
Excitation Spectrum of an Unknown Fluorescent Impurity and that of Marina Blue

Excitation Spectra with Emission set at 475/10nm



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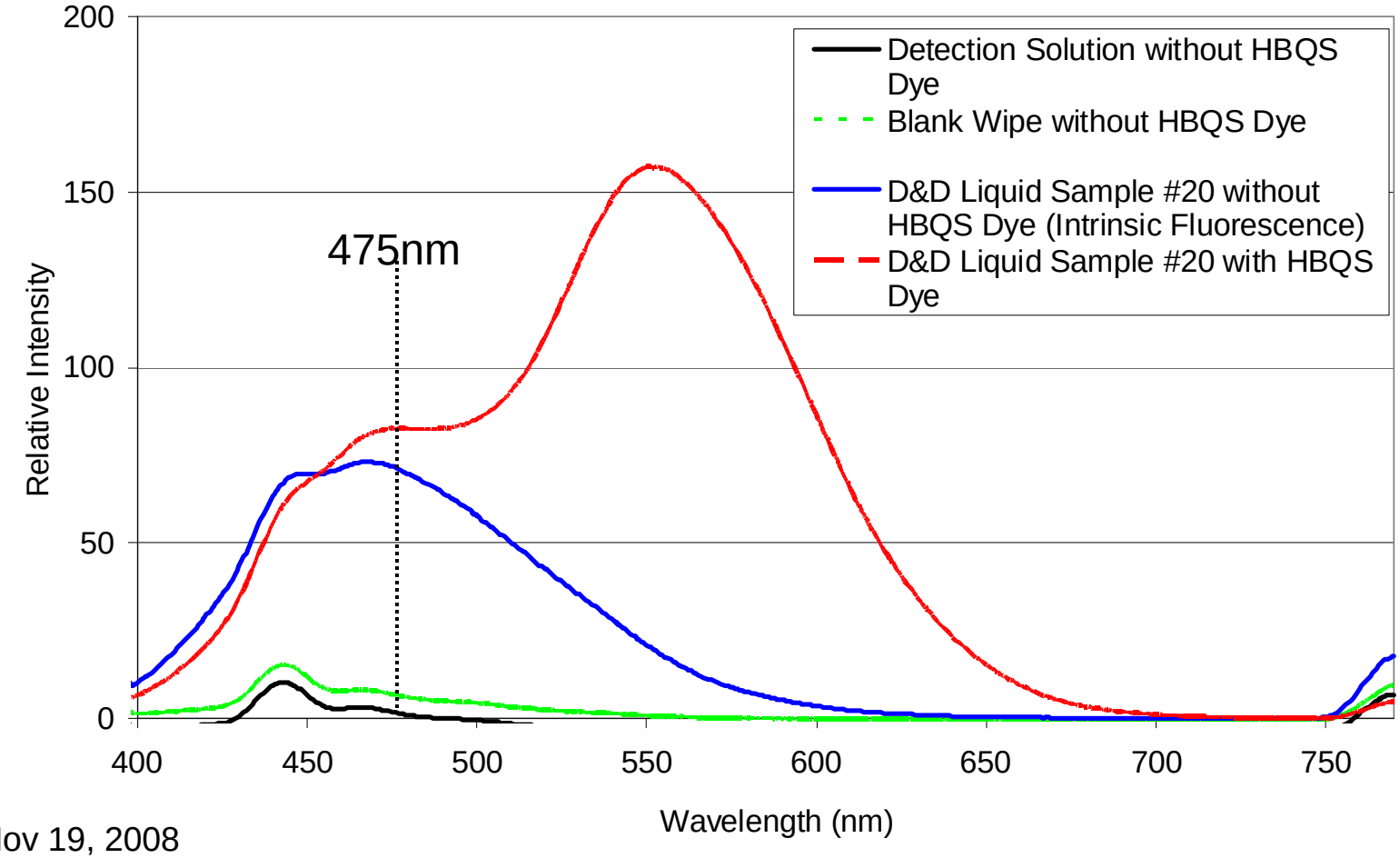
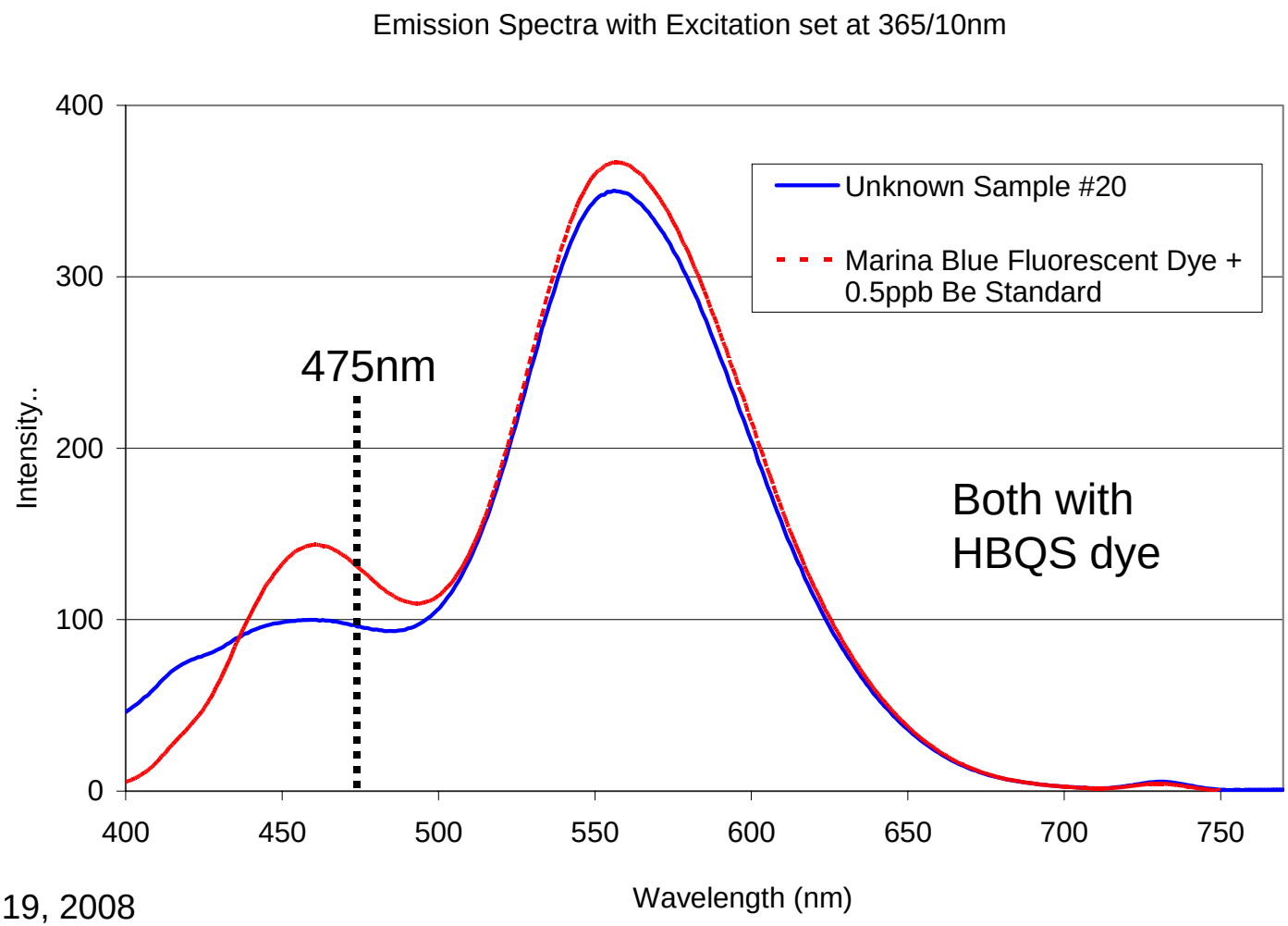
Effect of Fluorescent Impurity Interference



Emission Spectrum of an Unknown Fluorescent Impurity and that of Marina Blue



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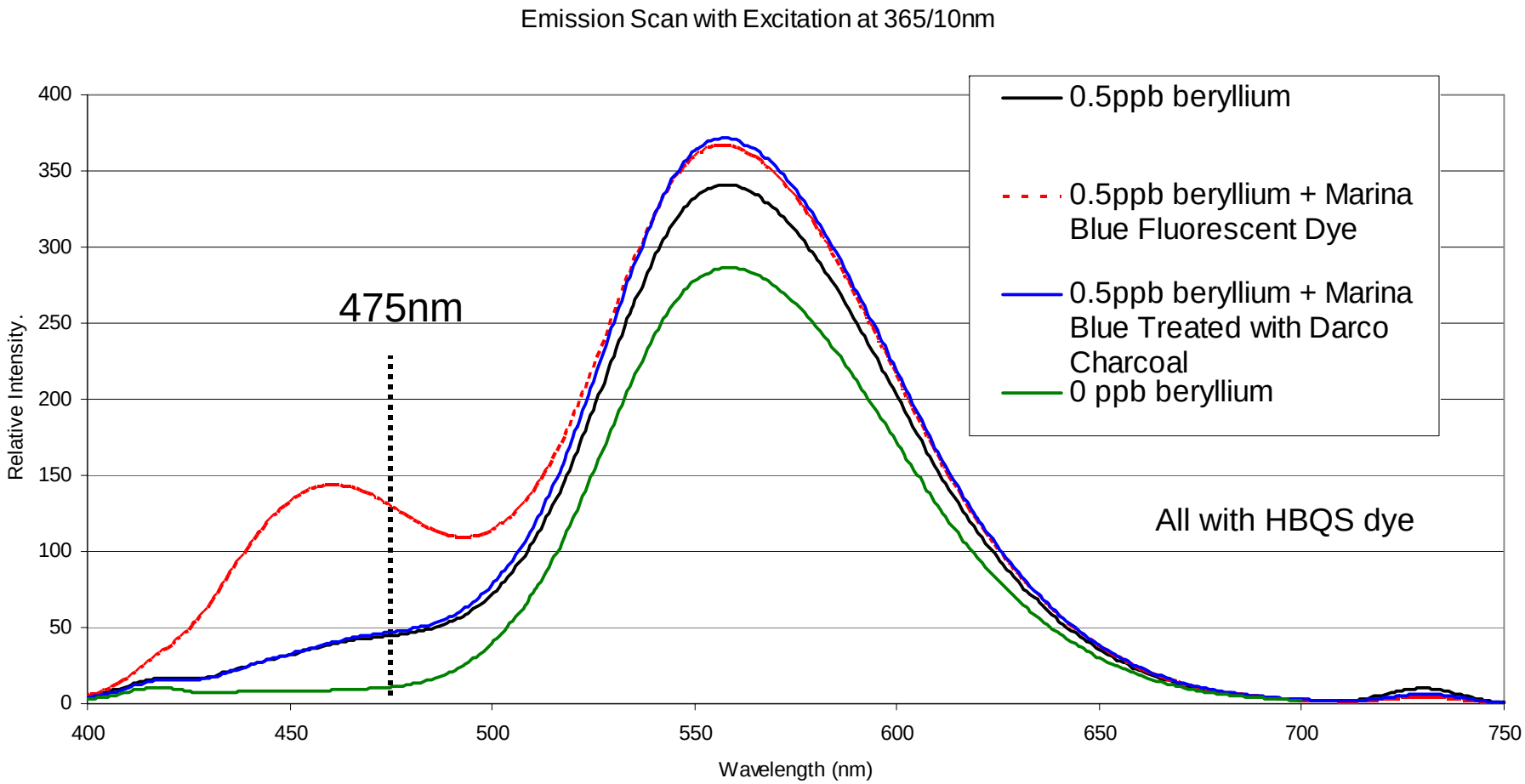
Removal Process Effectiveness



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Removal Process Effectiveness

Sample	Beryllium reading [ppb]* before heating to 90°C	Beryllium reading [ppb]* after heating to 90°C	Expected beryllium amount [ppb]*
Marina Blue	1.34**	1.35	0
Marina Blue + DARCO G-60 activated charcoal	1.34	0	0
Marina Blue + HCL washed activated charcoal	1.34	0	0

*ppb beryllium in solution (**equivalent to 0.135μg on media using 20X analysis)

All data in 1% ABF dissolution solutions. Excitation/Emission 365/475nm. Activated charcoals were added to 1%ABF solution and heat treatment was for 30 minutes at 90°C. Activated carbon amount was 1mg/ml of dissolution solution.

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Effect of Dissolution at 90°C for 40 Hours

Sample	Actual [Be] reading, ppb*	Expected [Be] reading, ppb*
0.5ppb beryllium + Marina Blue	0.98	-----
0.5ppb beryllium + Marina Blue + DARCO G-60	0.45	0.5
0.5ppb beryllium + Marina Blue + Carbon washed with HCl	0.51	0.5

***Excitation/Emission 365/475nm**

Effect of Carbon Treatment on Soil Analysis

Sample	[Be] BeFinder* Method (ppb)	[Be] Reference Values (ppb)
SRM 2702 Marine Sediment	2.5	3
SRM 2702 Marine Sediment with Darco G-60 **activated carbon**	2.5	
SRM 1944 Waterway Sediment	1.8	1.6
SRM 1944 Waterway Sediment with **activated carbon** (HCl washed)	1.6	
SRM 2702 Marine Sediment	2.8	3
SRM 2702 Marine Sediment with **activated carbon** (HCl washed)	2.7	
SRM 2710 Montana Soil	2.5	2.5
SRM 2710 Montana Soil with **activated carbon** (HCl washed)	2.3	

Excitation/Emission 365/475nm, dissolution in 3%ABF at 90°C for 40 hrs (0.5g soil, 0.5g carbon and 50ml dissolution solution)

Stability of Activated Carbon in Dissolution Solution

Dissolution solution: 1wt%ABF with activated charcoal

Sample	**Aging Period, days**	**Actual ppb* reading**	**Expected ppb* reading**
0.5ppb Standard + Marina Blue		0.95	N/a
0.5ppb Standard + Marina Blue in dissolution solution with **Darco G-60**	105	0.54	0.5
0.5ppb Standard + Marina Blue in dissolution solution with **HCl washed charcoal**	62	0.52	0.5

***Excitation/Emission 365/475nm, dissolution conditions: 90C for 30 minutes**

Conclusions

- Samples suspected of comprising organic fluorescent impurities with overlapping characteristics can be easily analyzed by fluorescence analysis.
- The presence of such materials can be checked by looking at emission characteristics of the solutions after dissolution (before the addition of dye solution)
- Procedure to remove the affects of such contamination is
  - The samples need to be dissolved using dissolution solution comprising activated carbon.
  - Dissolution processes must be carried out at elevated temperatures (80-90°C).
  - Dissolution process can be carried out in 1%or 3%ABF solution from 30 minutes to 40 hours.
  - Activated carbon must be removed by filtration after the dissolution process, before adding the HBQS dye solution.
- ABF Dissolution solutions with activated carbon do not loose their effectiveness when stored up to several months.