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Title: Near Real-Time Fluorescence Detection of Beryllium

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Los Alamos
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Abstract
We report on a fluorescent test for beryllium designed for analyzing swipes. The detection is rapid, quantitative and deployable in the field with $5,000 portable fluorimeter. Swipes are placed in a vial and a dilution solution is added. The vials are then rotated for 30 minutes and then syringe filtered. An aliquot of 100 μL is added to a detector solution and fluorescence measured with a portable ocean optics unit. We can readily detect down to 0.02 μg on a filter paper. Interference studies have been carried out with various metals including Al, Fe, Pb, U, Ca, W, Ni, Co and Cu. The technique has proven to be successful under various conditions including a variety of surfaces both in the lab and in field. It is a user-friendly, cost effective method.

Beryllium detection

- Although it is being regulated much like a radioactive material there is no Geiger counter for beryllium
  - Currently inductively coupled plasma-atomic emission is the method for the detection of beryllium
  - Requires a minimum of 1 day for analysis usually >2days
- A new visible spot test has been developed
  - Detection limit of 2.0 $\mu g/100\ cm^2$
  - Several metals such as iron can give false positives
- Fluorescence assay that can be done on-site with a "fast" turnaround time is needed
  - improves the detection limit
  - it is more selective for Be
- Potential impact on several programs is significant

Near Real-Time Fluorescence Detection of Beryllium

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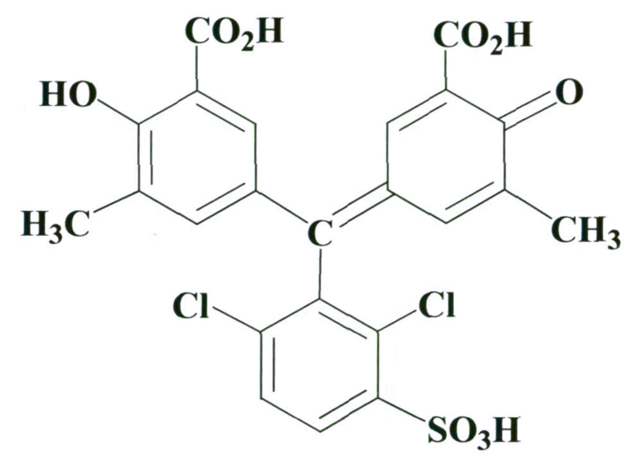
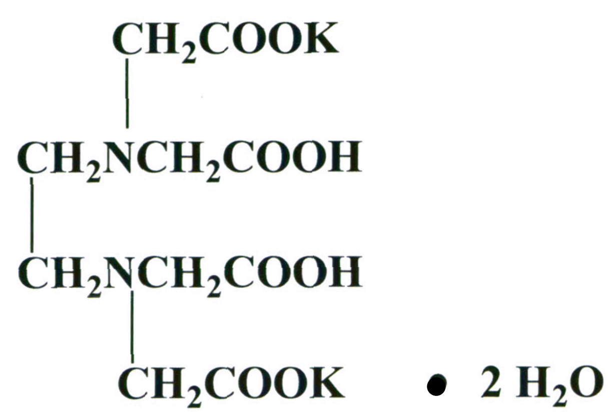
Colorimetric detection of Be

- Chrome Azurol S (Mordberg and Filkova, 1974)

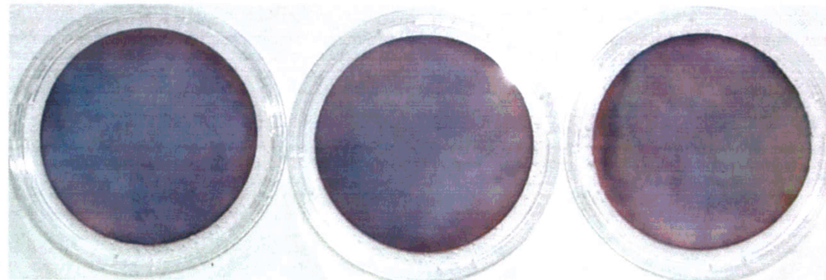


- EDTA (dipotassium salt dihydrate)

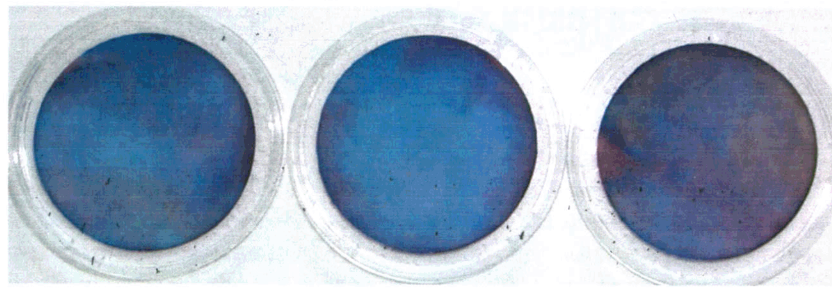


Detection with visible color requires 2 μg

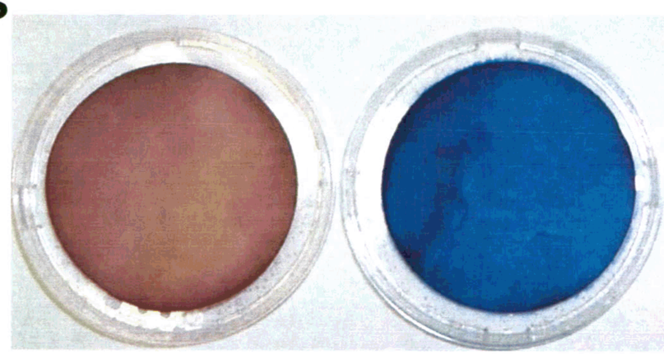
- **Positive Be detection occurs when 2 μg of Be is collected on a filter.**
- **Qualitative results only**
- **Can tolerate many potential interferences at low levels**



1 μg Be on filter



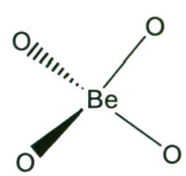
2 μg Be on filter



Left:	Right:
Pb: 100 μg	Pb: 100 μg
Fe: 40 μg	Fe: 40 μg
Cd: 30 μg	Cd: 30 μg
Zn: 30 μg	Zn: 30 μg
Mn: 20 μg	Mn: 20 μg
	Be: 10 μg

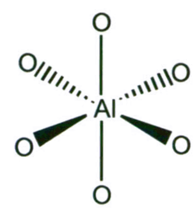
Be vs. Al binding

- Be only binds in a tetrahedral geometry
- Many metals that might interfere such as iron and aluminum bind in an octahedral fashion
- Although the O-O distance preferred by Be and Al is nearly identical it may be possible to design fluorescent ligands that only permit tetrahedral coordination



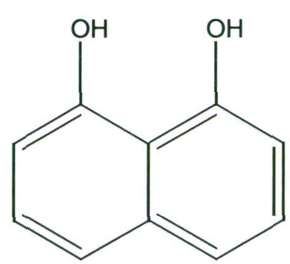
Be-O distance 1.57 Angstroms

O-O distance 2.556 Angstroms



Al-O distance 1.82 Anstroms

O-O distance 2.574 Angstroms



O-O distance 2.43 Angstroms

A complete detection system is needed

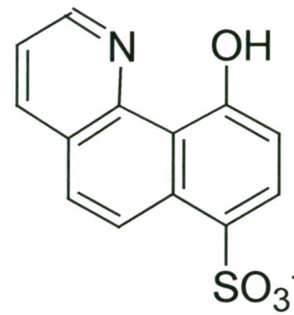
- **Dissolution – This is an important problem especially for Be metal and BeO. Most digestion techniques for ICP involve microwave digestion in acidic media and are not practical in the field.**
- **pH adjustment – pH must be neutralized at some point if dissolution is done in an acidic environment. This will involve some type of dilution of the sample.**
- **Addition of fluorescent indicator and EDTA - Typically EDTA is required to enhance selectivity.**
- **Indicator characteristics**
  - **Selective**
  - **Stable**
  - **Low detection limit**

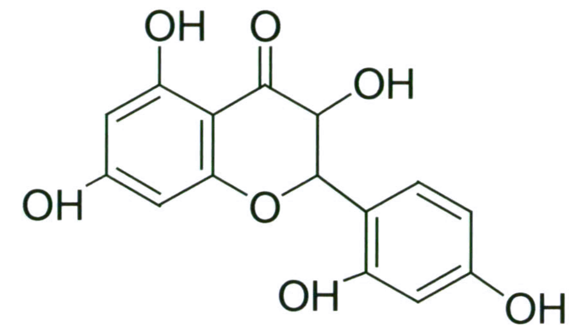
Dissolution

- Sulfuric acid at 5% dissolves Be metal in 15 minutes (10 mg metal used in a 100mL solution), but does not dissolve BeO.
- NaF at 1 or 5% does not dissolve the metal or the oxide at 30 minutes.
- A solution of 1% ammonium bifluoride at pH 4 dissolves Be metal quantitatively in 5 minutes, and dissolves 70% of the oxide in 30 minutes with just small amounts of shaking by hand.
- The ammonium bifluoride solution does not dissolve the filter paper commonly used for swipes.

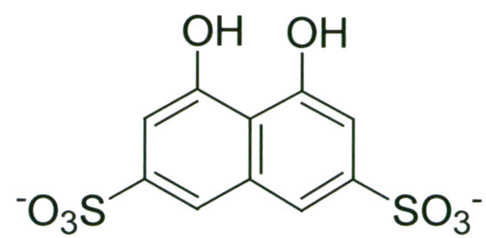
Developing a luminescent detection system

- We are in the process of testing several potential luminescent indicators
- Beryllium binds phenolate groups very strongly
- A six member chelate ring provides almost the ideal O-O or O-N distance
- All of the indicators are pH dependent
- Claims in literature suggests high interference tolerance at high pH

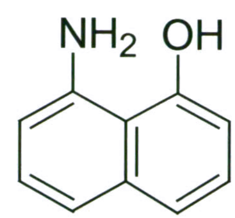


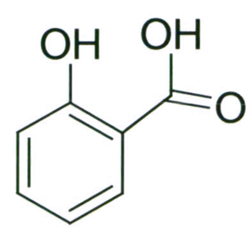


Morin

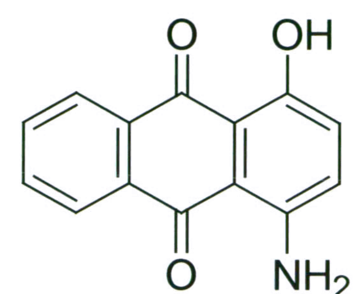


Chromotropic acid



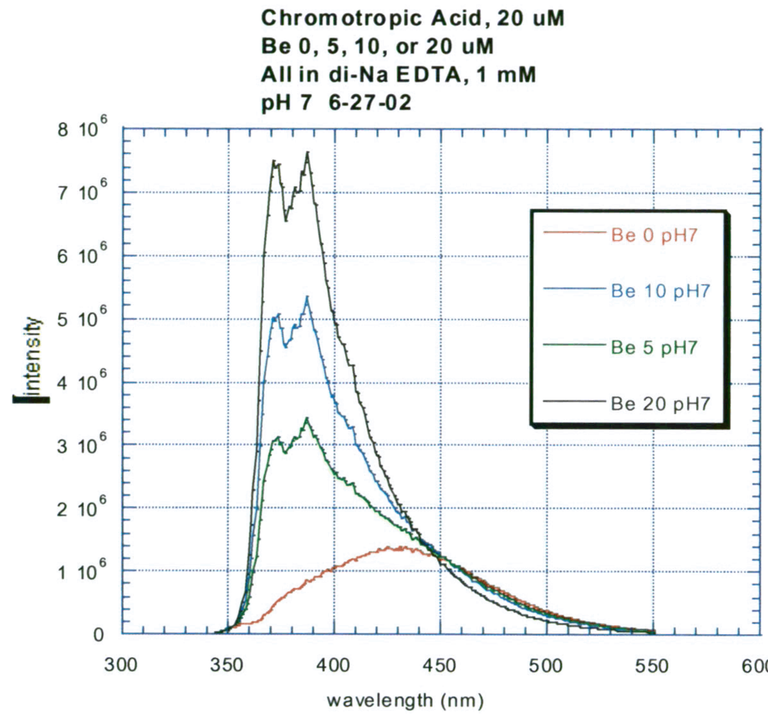


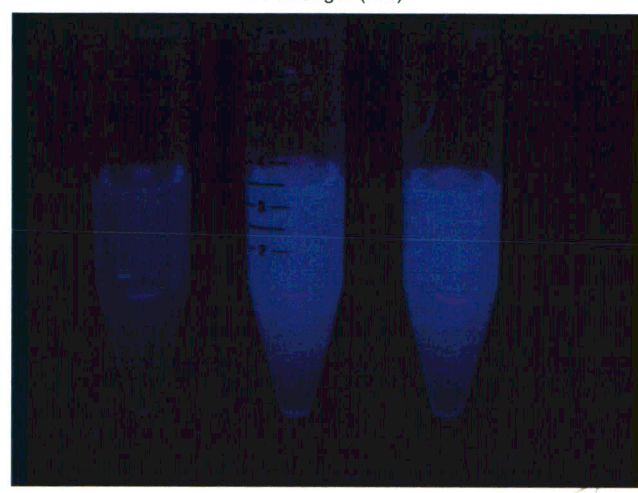
Salicylic acid



Chromotropic acid results

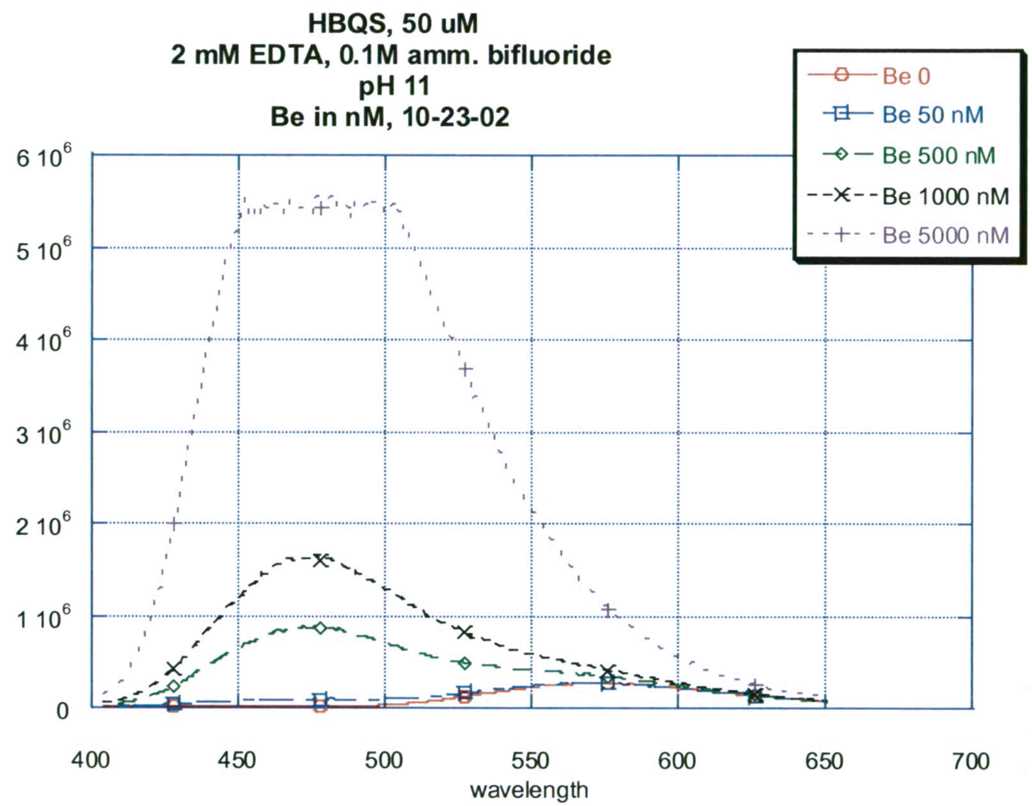
- Chromotropic acid can detect beryllium at 1 μM in solution at pH 7
- Detection is quantitative down to 9 ng/mL
- Detection can also be qualitative at > 45 ng/mL
- Severe fluoride interference





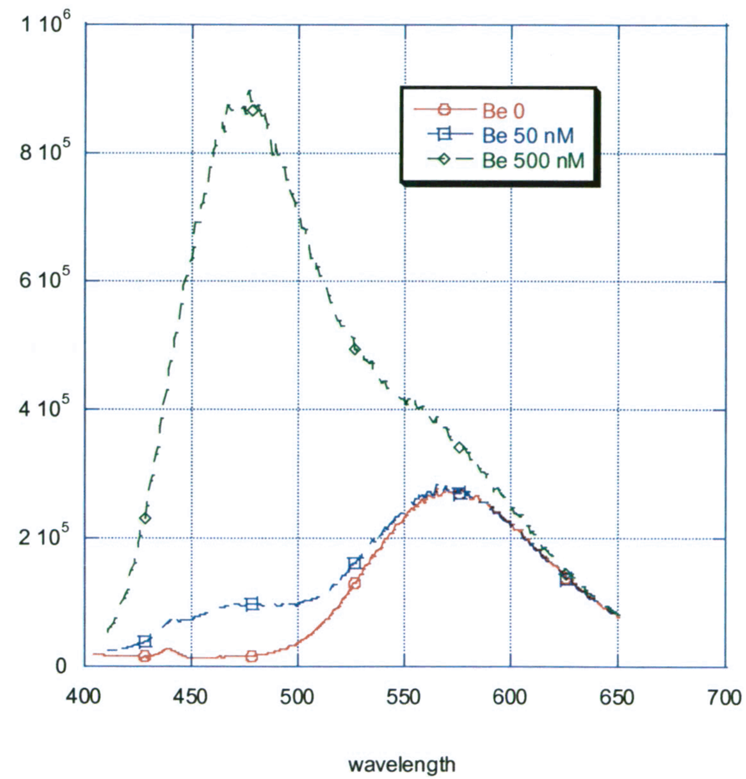
Results with hydroxy benzoquinoline

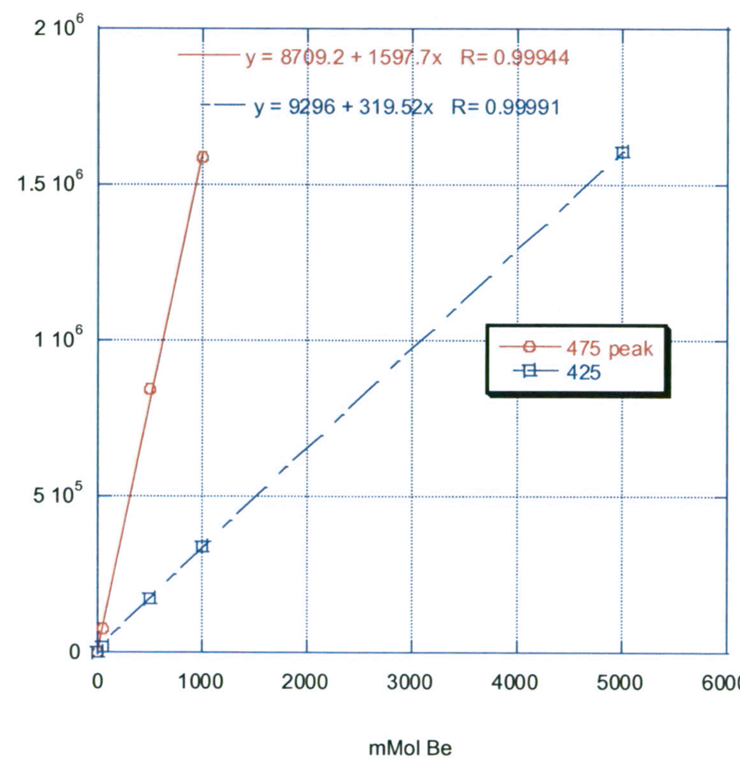
- Must be synthesized
- Detection is quantitative down to 90 pg/mL
- Detection can also be qualitative at > 900 pg/mL
- Literature reports high tolerance to interferences such as iron (20,000 to 200,000) and fluoride (20,000,000)
- We have looked at interferences from uranium and other metals



HBQS detection

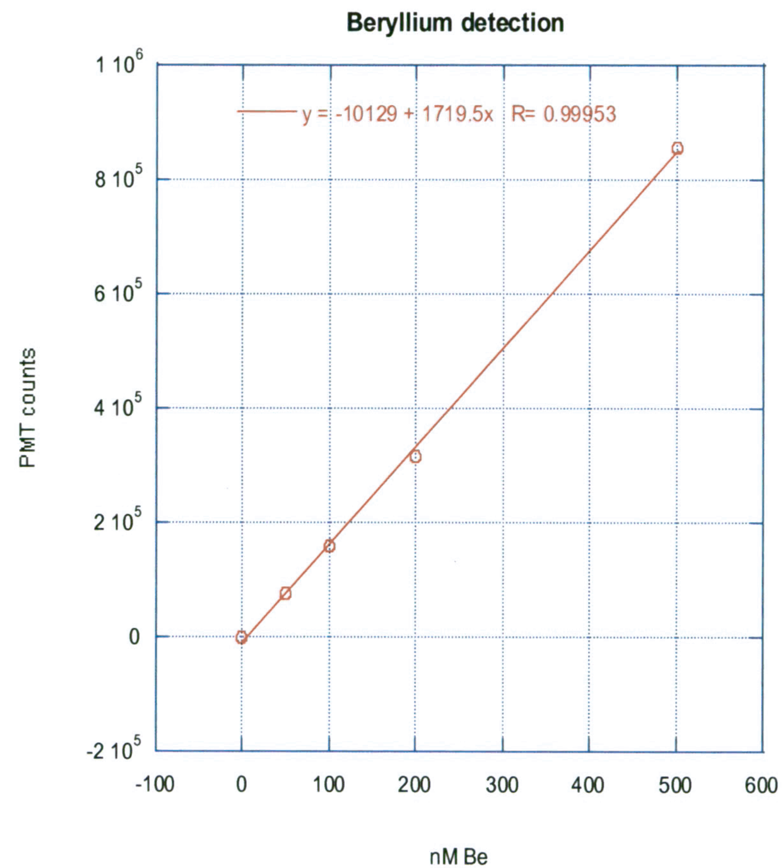
Readily detects beryllium at 10 nM
Linear response past 5000 nM





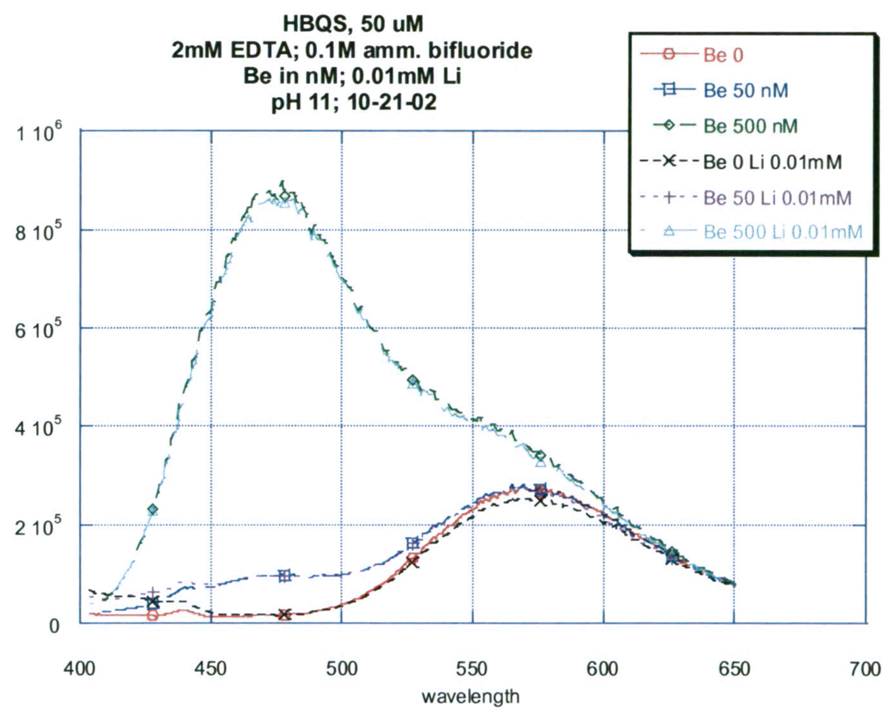
What does 50 nM detection mean?

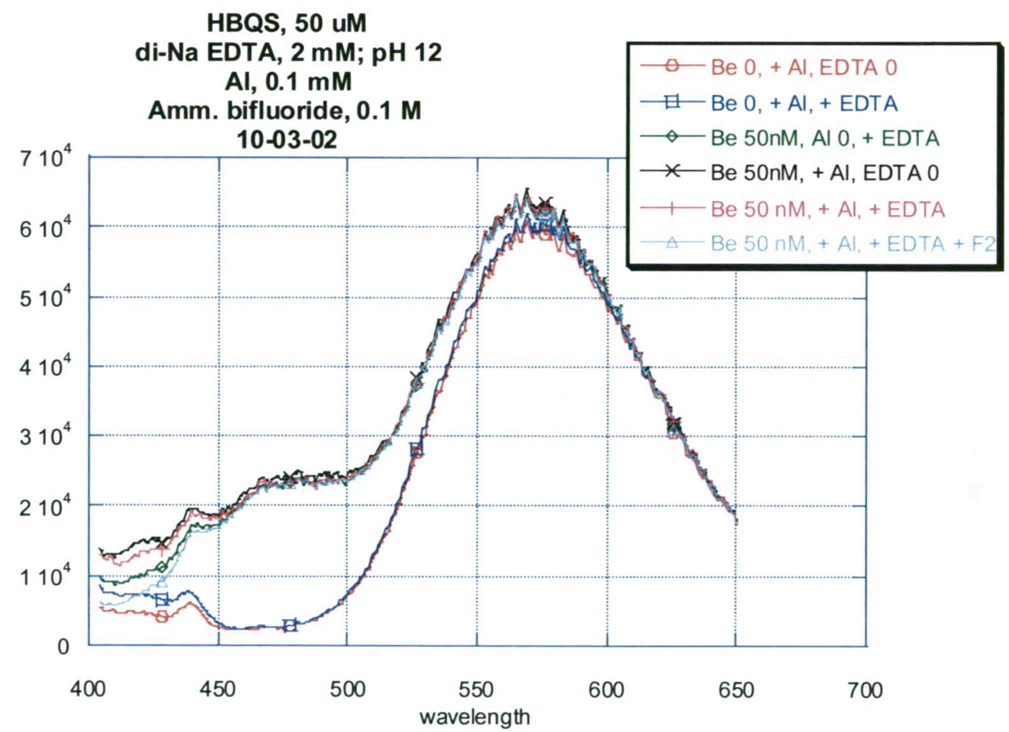
- 50 nM is 450 pg/mL
- Assume that we swipe a 100 cm^2 -area with a filter paper
- Dissolve filter paper in approximately 5 mL of solution and do a 1 to 4 dilution in order to adjust the pH
- We can see 9 ng on a filter paper.
- This is over an order of magnitude below the 200 $ng/100cm^2$ called out in the regulations



Interferences?

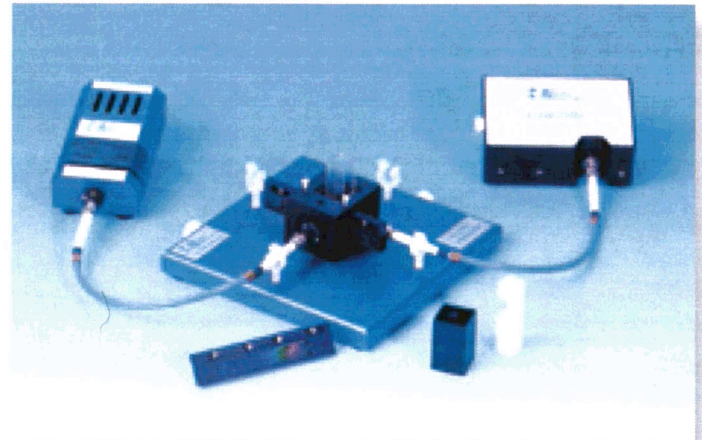
No interferences observed from a suite of metals Including Al, Li, Ca, U, Zn, Pb, …

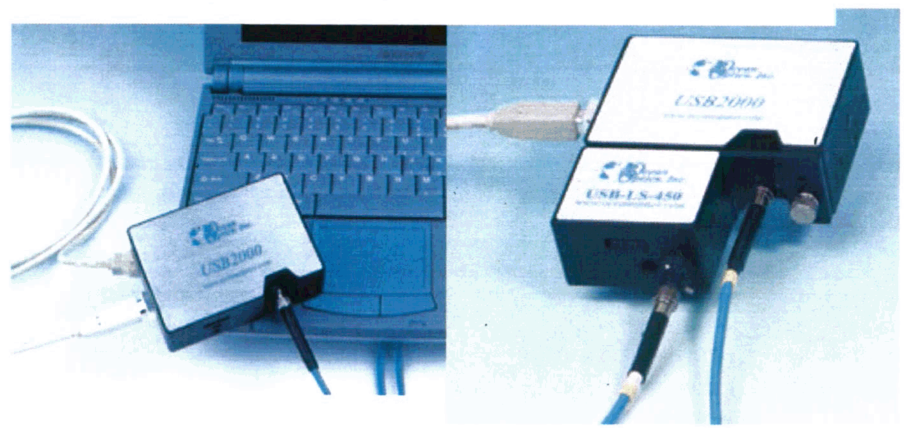




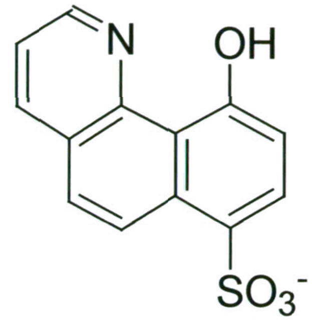
Field unit

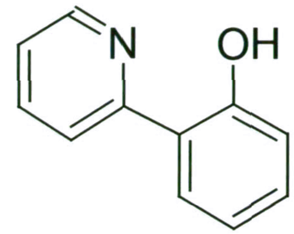
- We have tested the system with a portable ocean optics field unit and HBQS.
- Detection limit is 50 nm or 9 ng per filter paper based on dissolving in 5 mL followed by a 1:4 dilution
- We are now in the process of testing field swipes.





Alternative indicator





- Both HBQS (left) and HPP (right) have been studied as potential OLED materials
- HBQS emission is based on excited state proton transfer when protonated
  - internal standard from low energy emission
  - works at pH 12 with no fluoride interference
- HPP has a rotational energy coupled to the emission that quenches all fluorescence when freely rotating
  - no fluorescence background
  - works at pH 8-10 (higher detection limit and some fluoride interference)

Comparison of indicators

HPP

Advantages

•No background fluorescence from the ligand

•Easy to synthesize

Disadvantages

•Absorption at 360 nm instead of 380 nm (no 360 nm LED)

•Higher detection limit

•Some fluoride interference

HBQS

Advantages

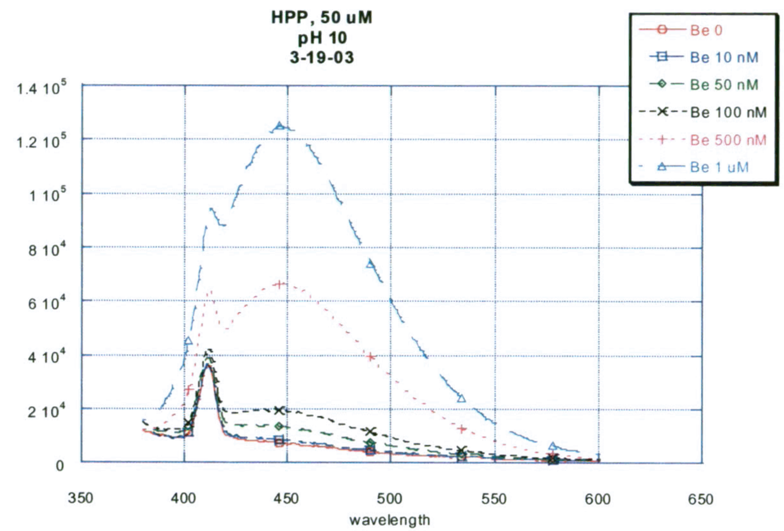
•Triplet emission can be used as an internal standard

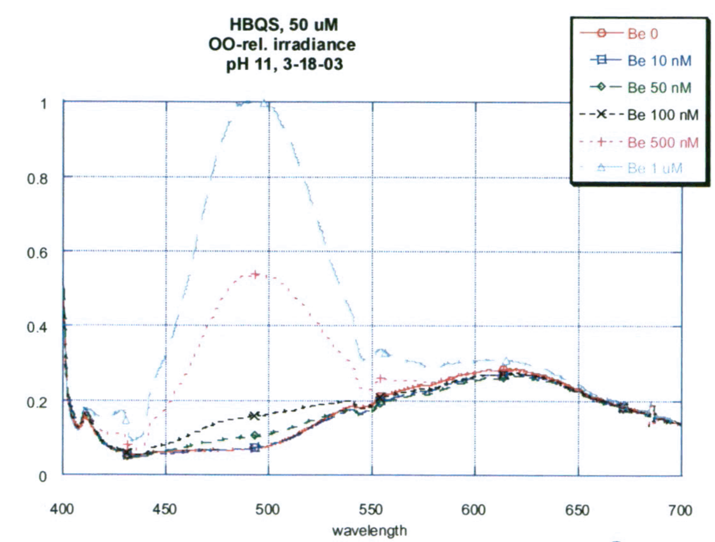
•Amazing tolerance to interferences

•Very low detection limit

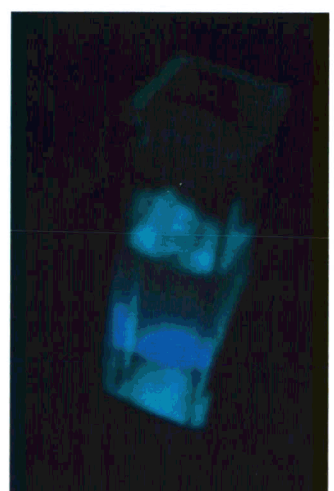
Disadvantages

•Difficult to synthesize

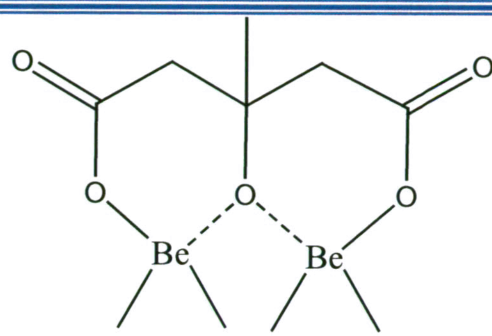




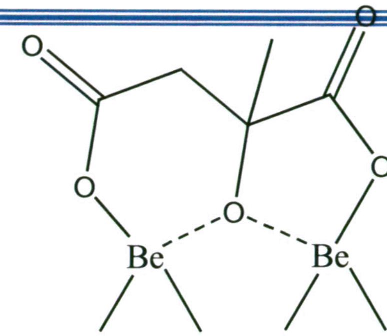

LANL



Be-O-Be Binding Motif



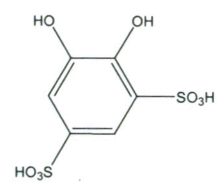
HMGA



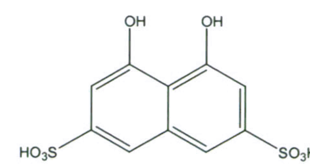
CMA

- Two COOH and OH are necessary for good binding
- The best binding occurs with one 5- and one 6-member ring
- We have studied new ligands based on this motif that have high affinity for beryllium

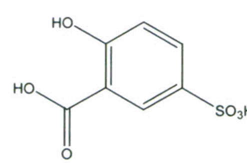
Ligand	K_1
DHBA	18.3
DCHB	17.5
ChA	16.2
Tiron	12.2
SSA	11.2



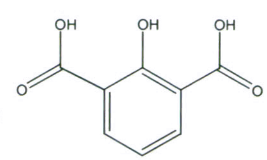
Tiron



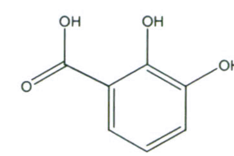
Chromotrophic Acid
(ChA)



5-SulfoSalicylic Acid
(SSA)

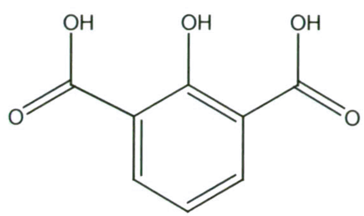


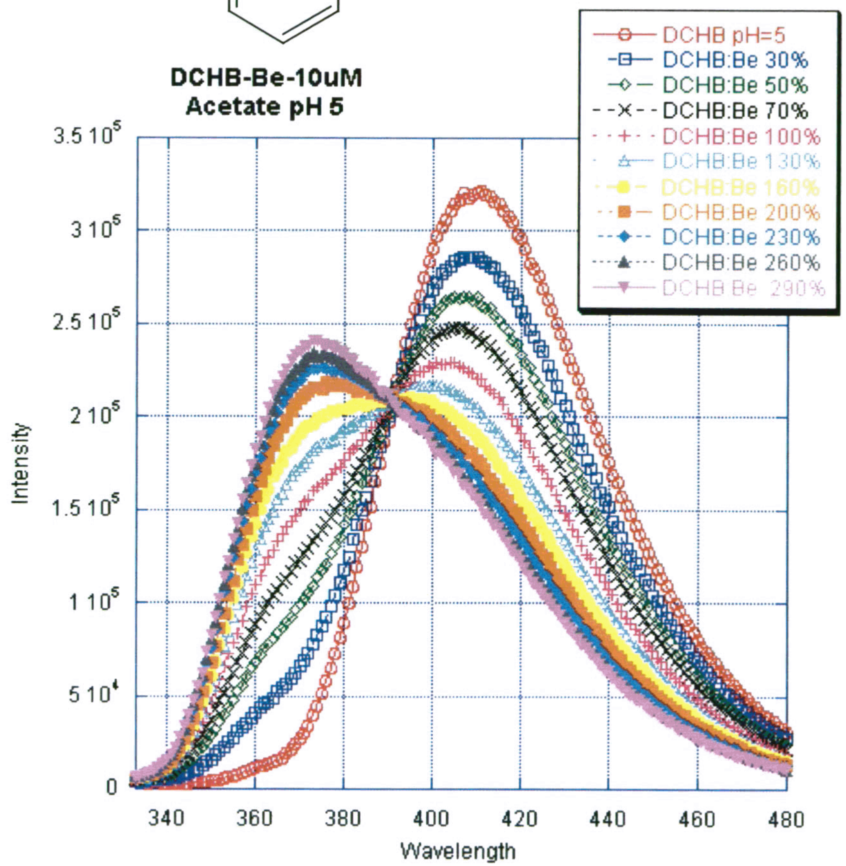
2-Hydroxy-isophthalic acid
(DCHB)

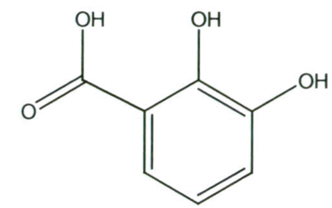


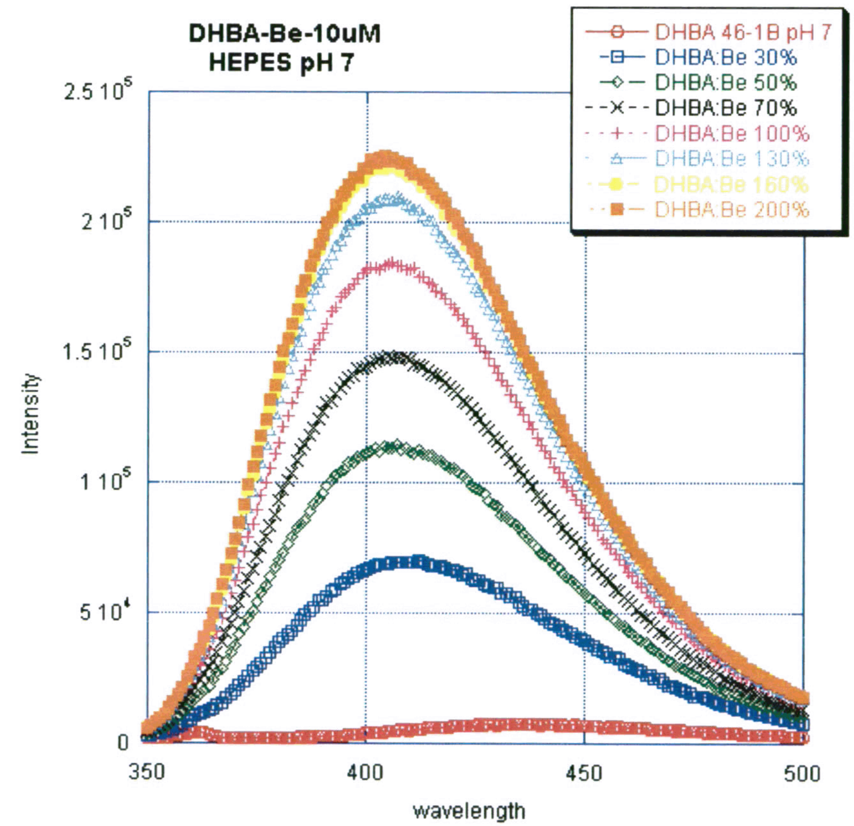
2,3-Dihydroxybenzonic acid
(DHBA)

Fluorescence Indicators



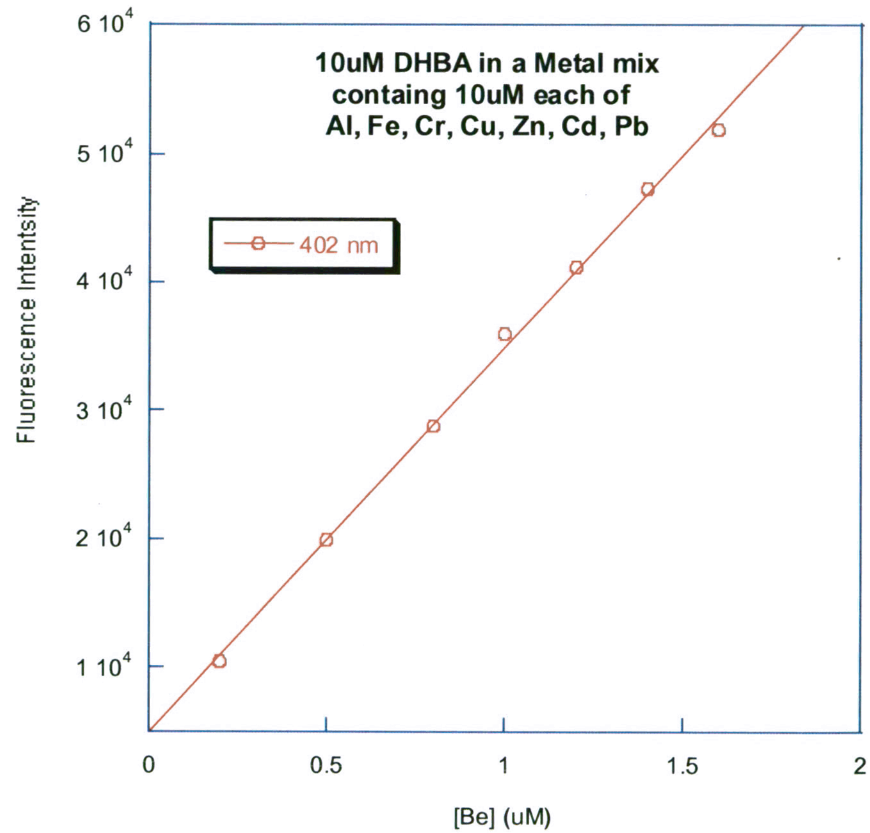






Selectivity

- DHBA can be used to detect beryllium down to 50 nm or 4.5 pg/mL at pH 7
- All other fluorescent techniques for Be are non-selective and require the addition of EDTA to mask other metals
- DHBA is highly selective and can readily detect Be down to 200 nm (1.8 ng/mL) in a solution that containing 7 other metals at 50 fold excess each. Metals tested were Al, Fe, Cr, Cu, Zn, Cd and Pb



Importance of a chemistry team

- Deb Ehler
- Edel Minogue
- Gavin Collis
- Anthony Burrell
- Kevin John

•We have a team that incorporates spectroscopists, inorganic chemists and organic chemists.

•This has lead to a complete system that will be field tested in less than two years including:

Portable fluorescent spectrometer

Details of dissolution

Synthetic route to HBQ

Paid for by AHF and the Materials Control programs


LOS ALAMOS