SAND2011-7865C

Exceptional service in the national interest

Sandia National Laboratories

Development of microfabricated thin film nitrogen-phosphorus thermionic detector

Ryan F. Hess

Microsystems-enabled Detection Department

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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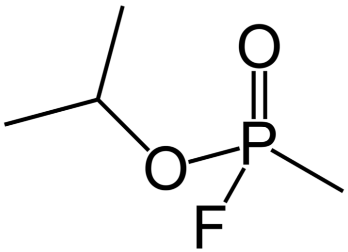
Topics

- Overview of chemical warfare agent detection – current capability
- Commercial Nitrogen-Phosphorus Detectors (NPDs)
- Sandia's Microfabricated NPD Research
  - Microhotplate fabrication
  - Sol-gel synthesis of metal silicates
  - Film characterization – XPS, Work Function, Thermionic Electron Emission Measurements (TEEM)
  - Detector performance

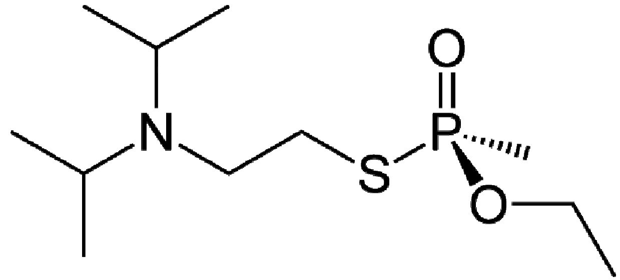
We have come along way…

Library of Congress, Prints and Photograph Division, Historic American Engineering Record: HAER COLO,1-COMCI,1-221

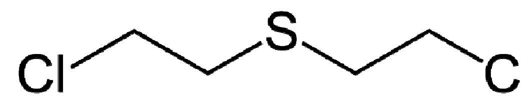
Chemical Warfare Agent Detection



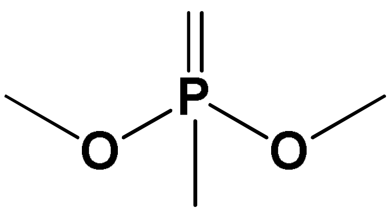
Sarin



VX

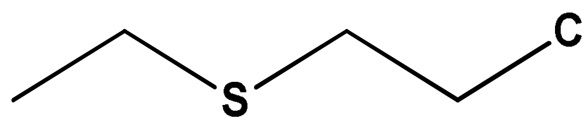


Sulfur Mustard



Dimethyl methylphosphonate

Surrogates



2-chloroethyl ethyl sulfide

The goal of our work is to develop portable hand-held detectors for use by Emergency Responders and Military Personnel

Commercial Laboratory-scale NPDs

Evolution of the concept used in Alkali Flame Ionization Detectors (AFID) developed in mid-1960s

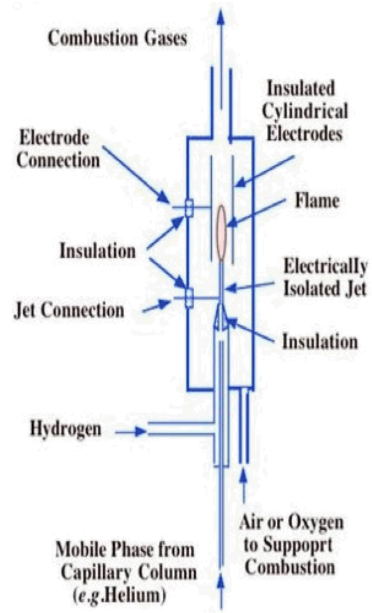
AFIDs:

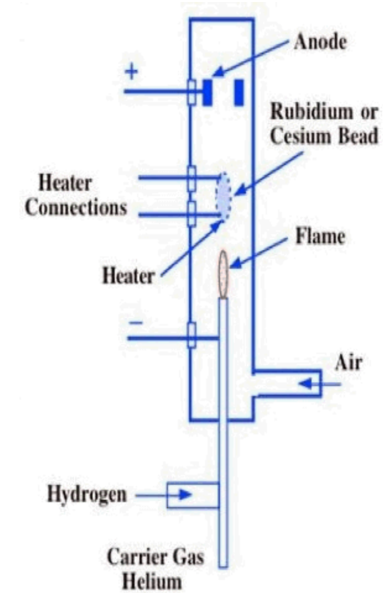
used volatile alkali metal salts and a hydrogen gas flame

difficult to operate and short lifetimes

Kolb and Bischoff's NPD (mid-1970s):

used alkali metal (often Rb) silicate glass bead on a Pt wire with a low flow of hydrogen gas





Why NPDs?

They are highly selective for N and P containing analytes (P:C ratio of 10^4)

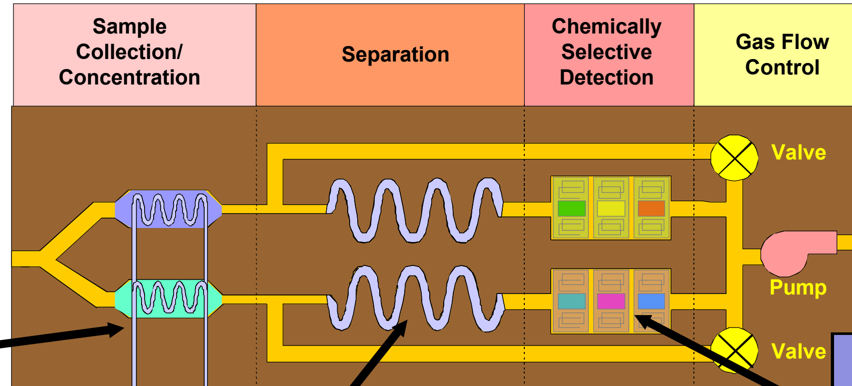
Despite 40 years of use the detection mechanism is still poorly understood

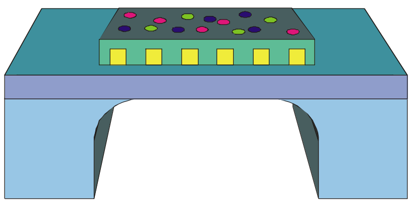
Patterson, Paul; Chemical analysis: a series of monographs on analytical chemistry and its applications, Chapter 7; 1992

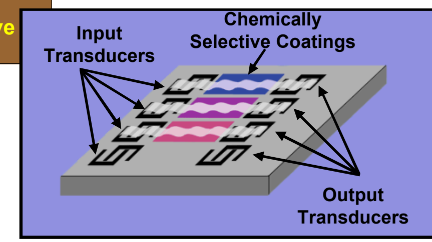
DETector Engineering and Technology, inc currently produces thermionic ionization detectors

Micro Chem Lab Technology

A hand-held chemical analysis system that uses three microfabricated analysis stages



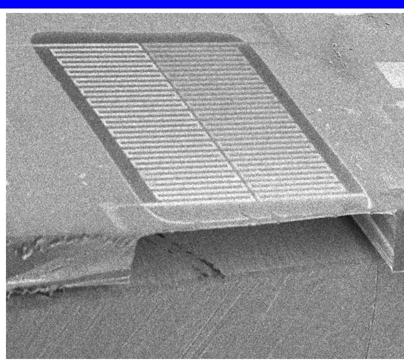


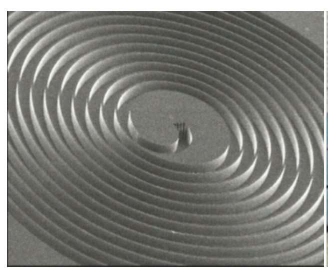


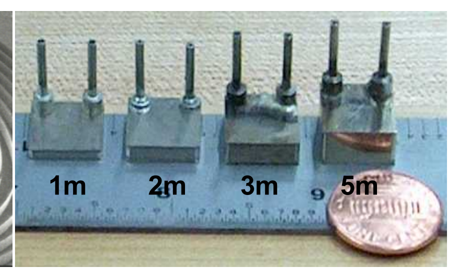
Preconcentrator accumulates species of interest

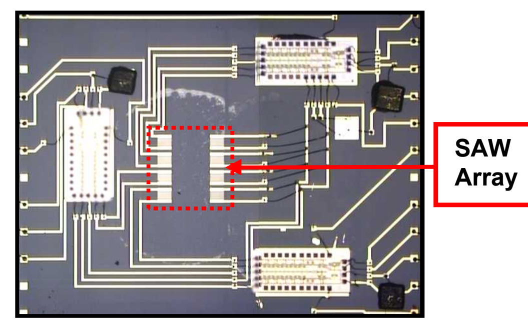
Gas Chromatography separates species in time

Acoustic Sensors provide sensitive detection



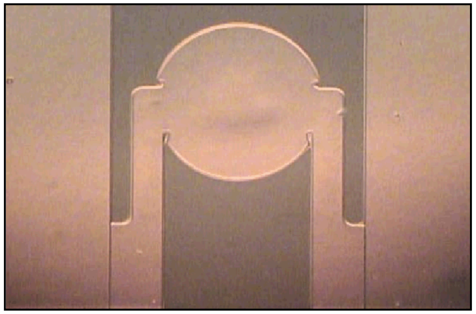






µNPD Project Overview

Front End – Preconcentrator/ GC Column



Front End – Electrometer

Microhotplate design and fabrication

Sol-gel silicate film chemistry

Device performance

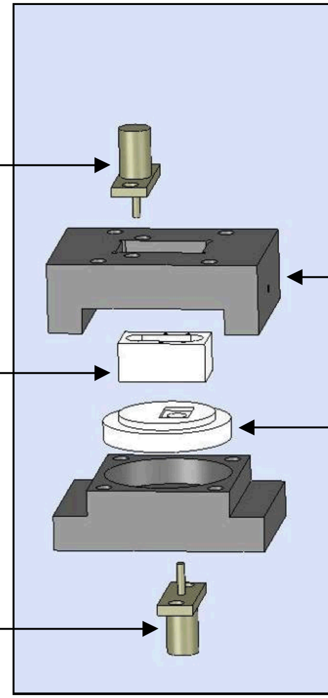
Newly designed NPD testing fixture

Sandia National Laboratories

SMA Connector for low noise current measurement from collector electrode.

Macor insert for pogo pins and collector electrode.

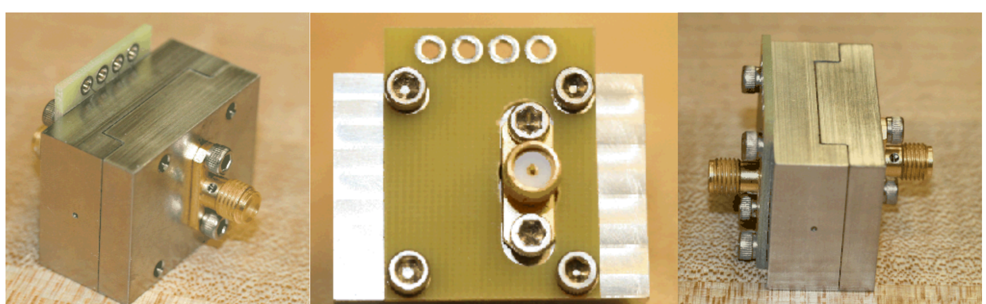
SMA Connector for bias electrode.



Stainless steel clamshell fixture for uniform heating and shielding.

Macor insert for microhotplate (fits both silicon nitride and silicon designs) and bias electrode.

- Fixture can be directly connected to GC exhaust using capillary tubing.
- Interfaces with custom circuit board to allow easy input of microhotplate bias voltages.

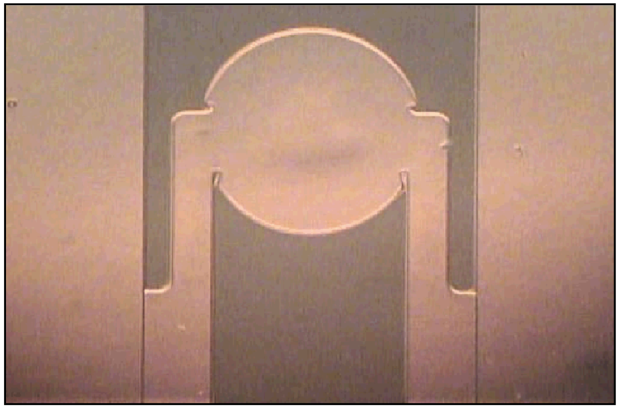


Devices: New “All-Silicon” Design

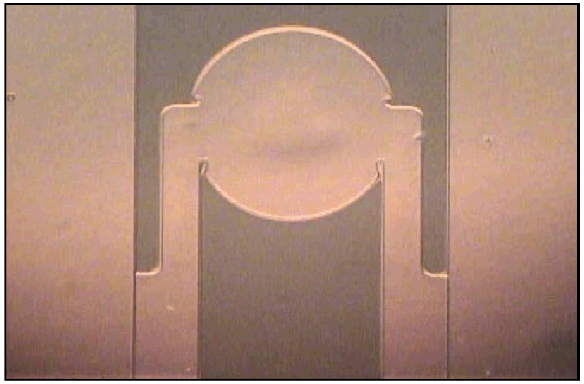
New silicon microhotplate designs featuring conductive silicon lines enable high temperature (> 600 C) operation ***in air***.

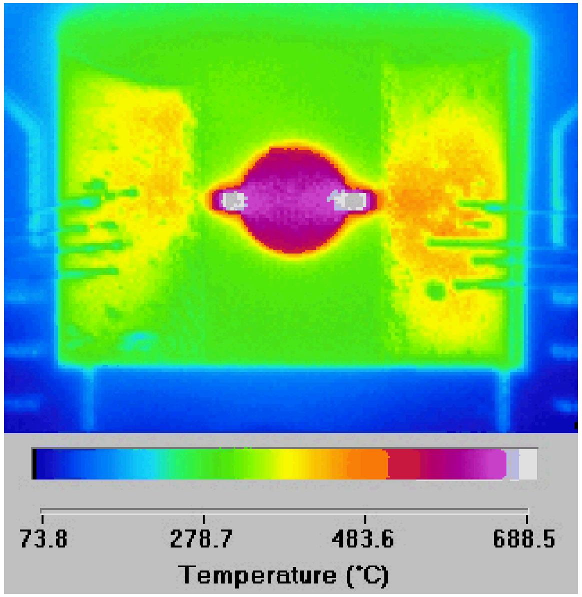
Current problems with these devices:

- Thermally conductive silicon requires relatively high power to maintain an elevated temperature.
- The temperature coefficient of resistance (TCR) is nonlinear for silicon, making it difficult to determine the device temperature.



Microhotplate Temperature Profile



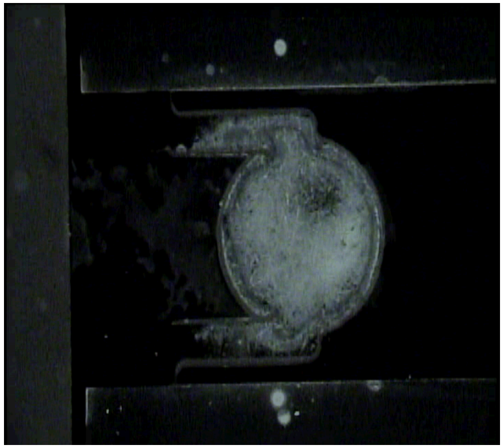


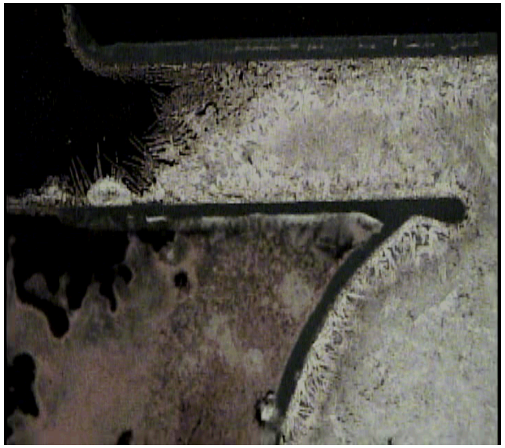
IR camera unable to record temperatures above 700 C.

- Current-limited resistive heating was used to increase T of devices to onset of "intrinsic runaway" in flowing carrier gas, where thermal carrier concentration exceeds doping level.
- Devices survived multiple T cycles
- Mechanical warping is observed due to stress annealing
- We suspect underetching of the SOI substrate BOX layer

Exploring Novel NPD Materials

- We have formed thin films of Cs-doped silicates on microhotplates by sol-gel condensation of TEOS + Cs salts, targeting the $Cs_6Si_2O_7$ crystalline phase





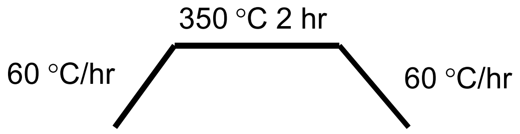
- Alkaline earth metals such as Ba^{2+} and Sr^{2+} can accept more elections within a silicate-film NPD, potentially decreasing volatility and increasing device lifetime. Effects on sensitivity and selectivity must be tested.

Commercially available Barium Precursors
- barium hydroxide 0.05M
- barium isopropoxide ~ 95%
- barium peroxide ~ 95%,
-barium *tert*-butoxide ~ 85%

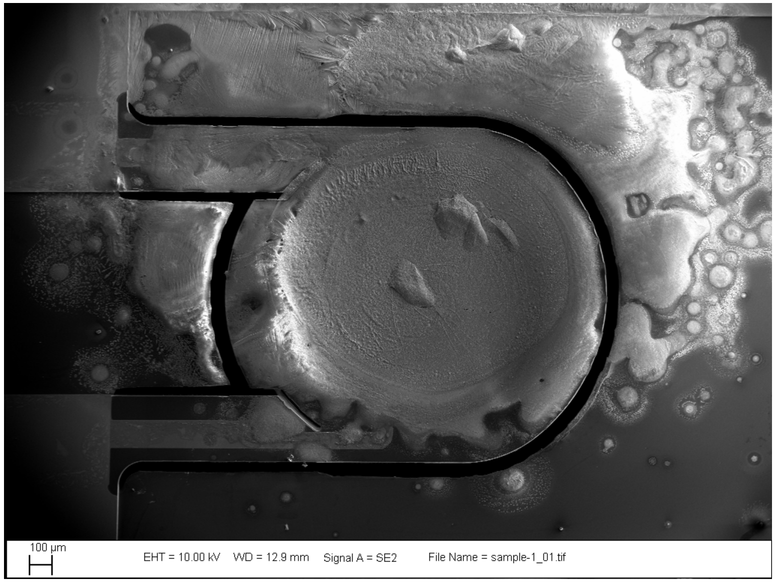
Due to the sparse selection and low solubilities of possible Ba film precursors, we have developed novel candidates.

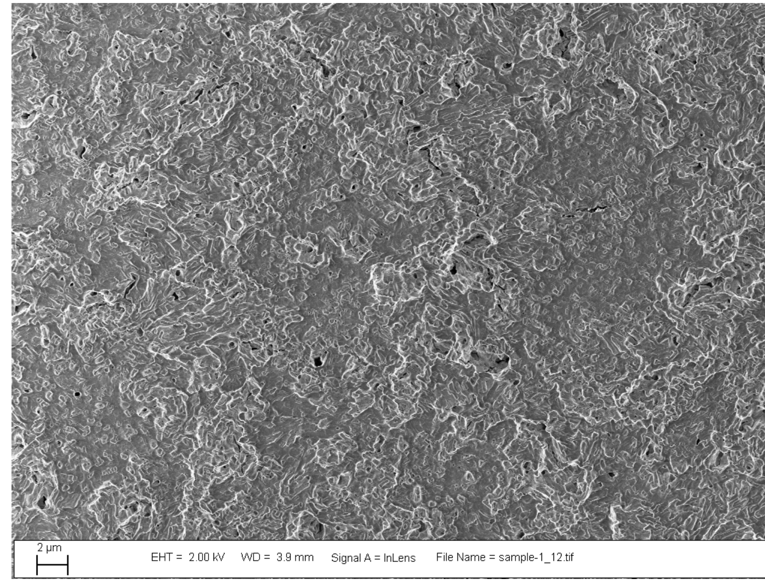
Example Synthesis

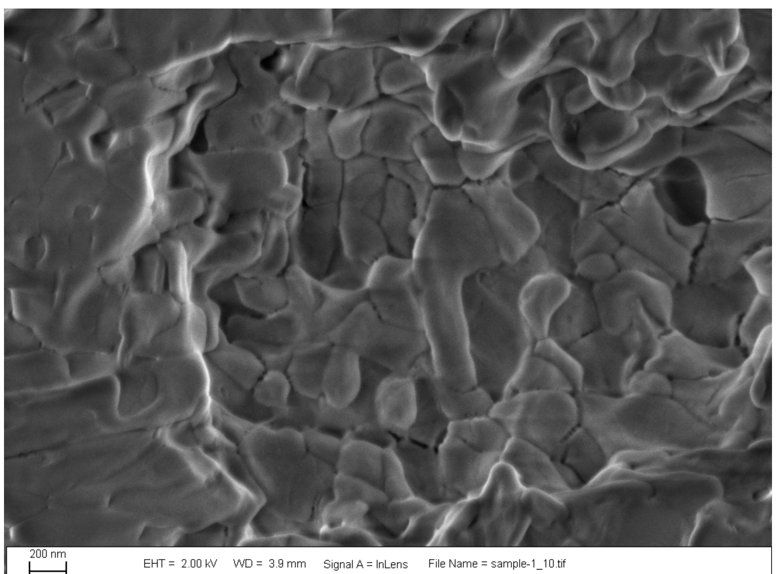
- Target – $Cs_6Si_2O_7$ (a known crystalline phase)
- Sol-gel preparation:
  - Dissolve $CsOH\bullet H_20$ in 10 mL deionized water
  - Add enough tetraethyl orthosilicate (TEOS) to reach a Cs:Si ratio of 3:1
  - Stir until initial two phase mixture becomes monophasic (3-4 hours)
    - The OH- from CsOH $\bullet H_20$ catalyzes a condensation reaction forming an amorphous network of SiO_4 tetrahedra
- Film deposition – ultrasonic spray coating (Sono-Tek)
  - Substrate holder is heated 80 – 100 °C
  - Flow rates 10 – 40 ml/hr, number of passes 30 – 60
- Film calcination
  - Heat coated devices to 350 °C for two hours under flowing nitrogen

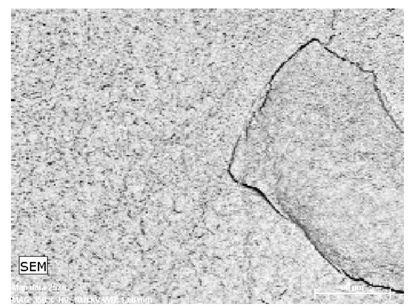


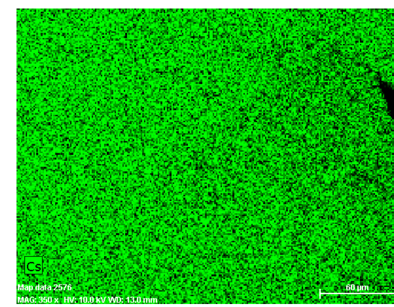
SEM/EDS of a Cs-Si-O Film Targeting $Cs_6Si_2O_7$











EDS indicates relatively uniform distribution of Cs

Work Function Measurements

Work Function – the amount of energy needed to remove an electron from a a solid to a point just outside the surface

this is usually considered as moving an electron from the Fermi level to vacuum

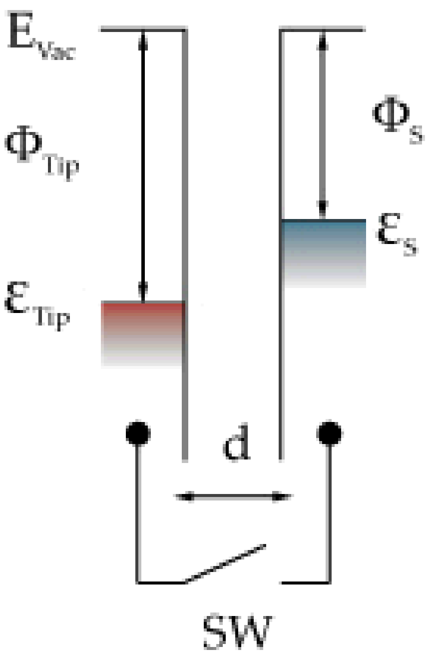
Thermionic Emission – the energy comes from heat and is governed by the Richardson-Dushman Equation

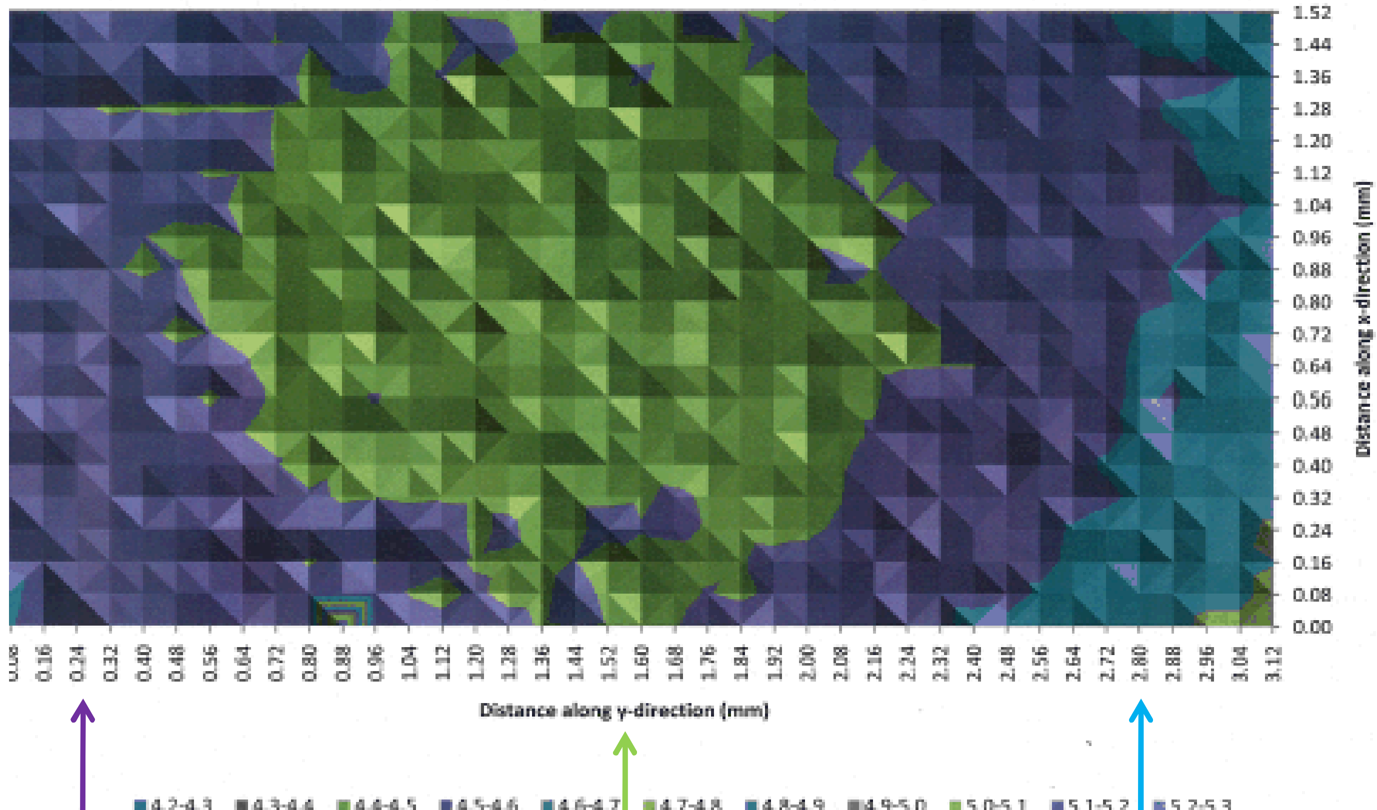
$$J = AT^2 e^{-\phi/kT}$$

We measured work function primarily using the SKP5050 from KP Technology though we did some measurements using Thermionic Electron Emission Measurements

- Our films have work functions from 2.9 – 5.2 eV
- Work function is highly sensitive to small surface impurities
- Films that should have the same work function often vary by up to 0.5 eV

Work Functions of Silicate Thin Films





4.5 – 4.6 eV

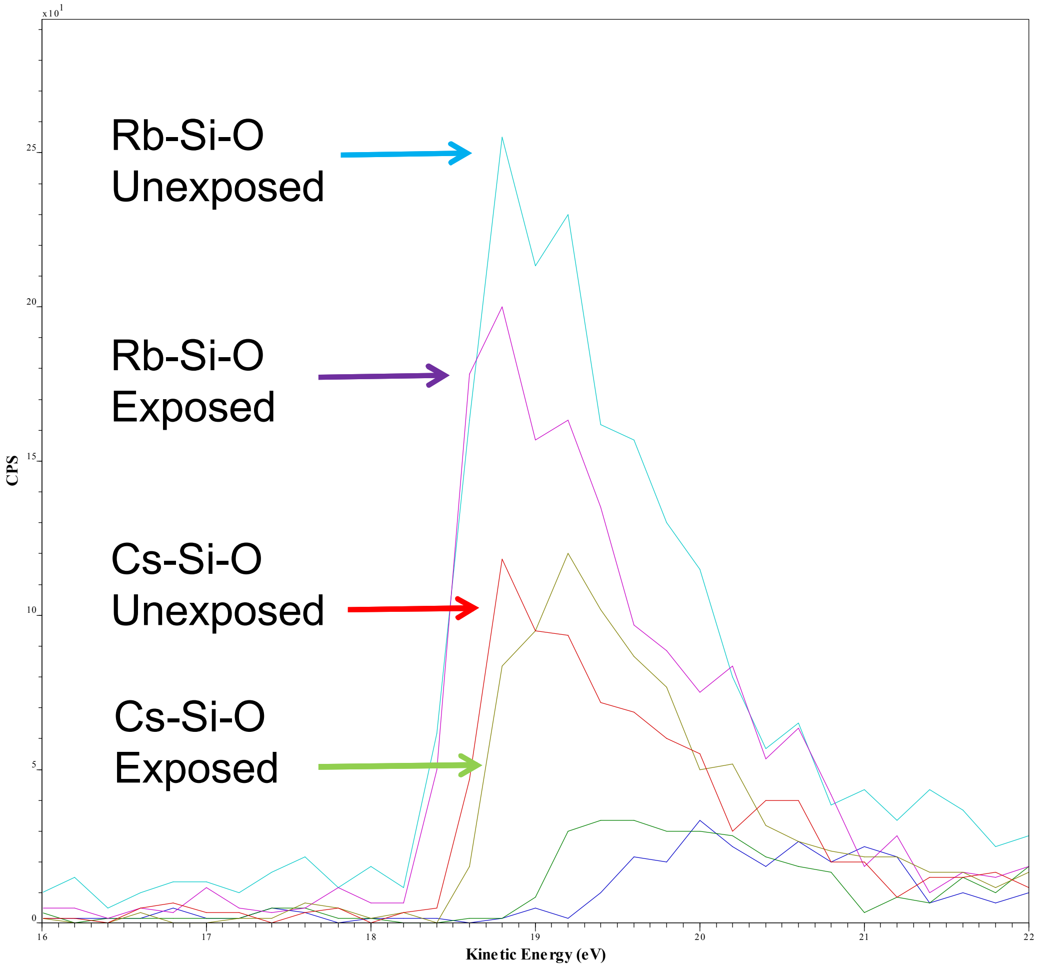
4.4 – 4.5 eV

4.6 – 4.7 eV

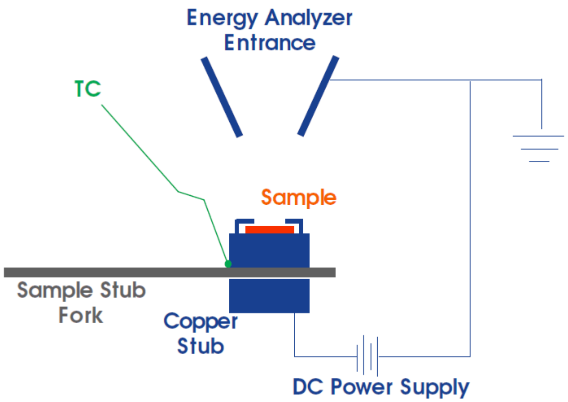
http://www.kelvinprobe.info/technique-theory.htm

Thermionic Electron Emission Measurements

Method development by Hong Piao and Vance Robinson at GE-GRC



Kratos Axis Ultra DLD
Operated in UPS mode , -15V bias

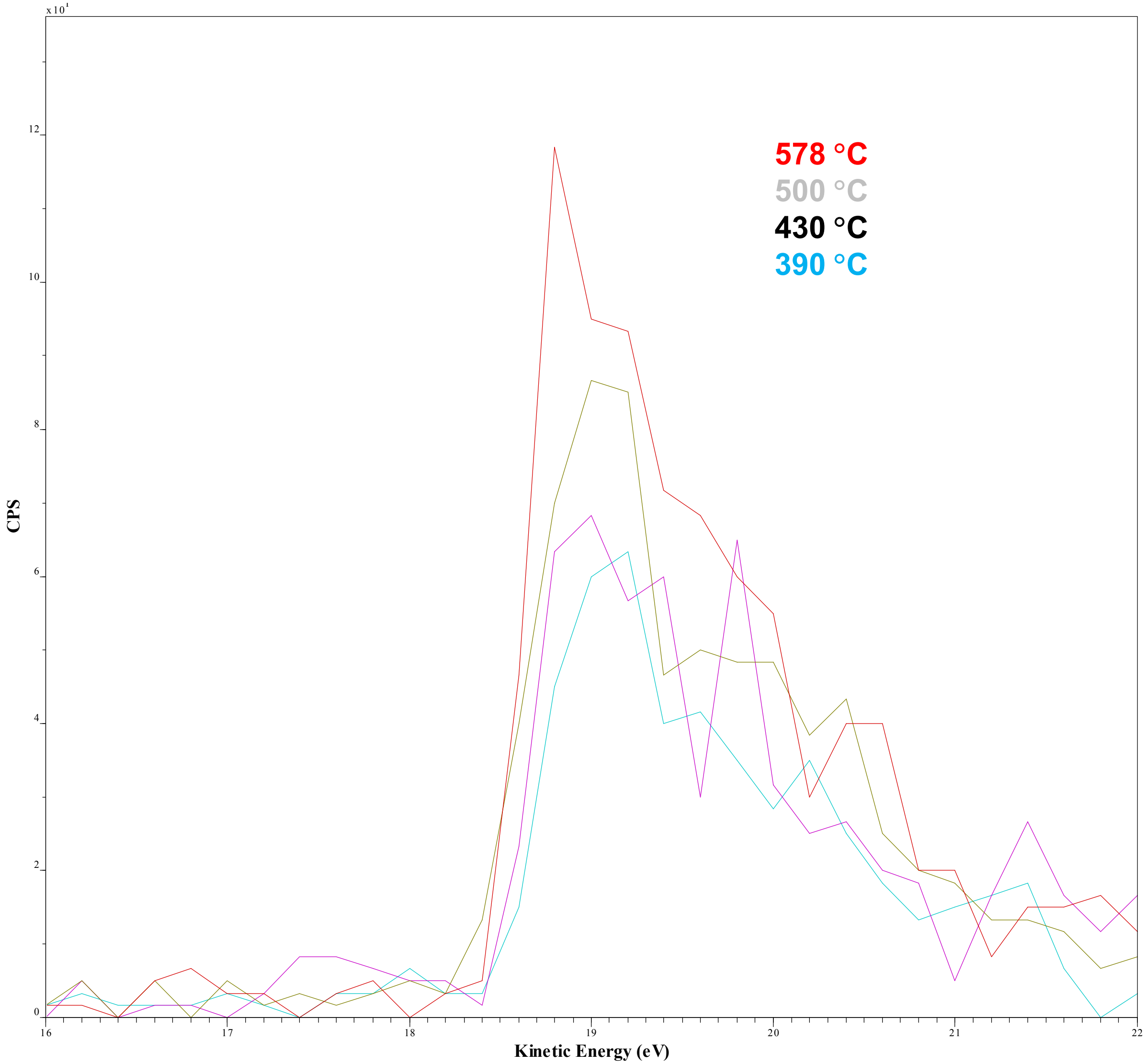


Work Function Results
From TEEM

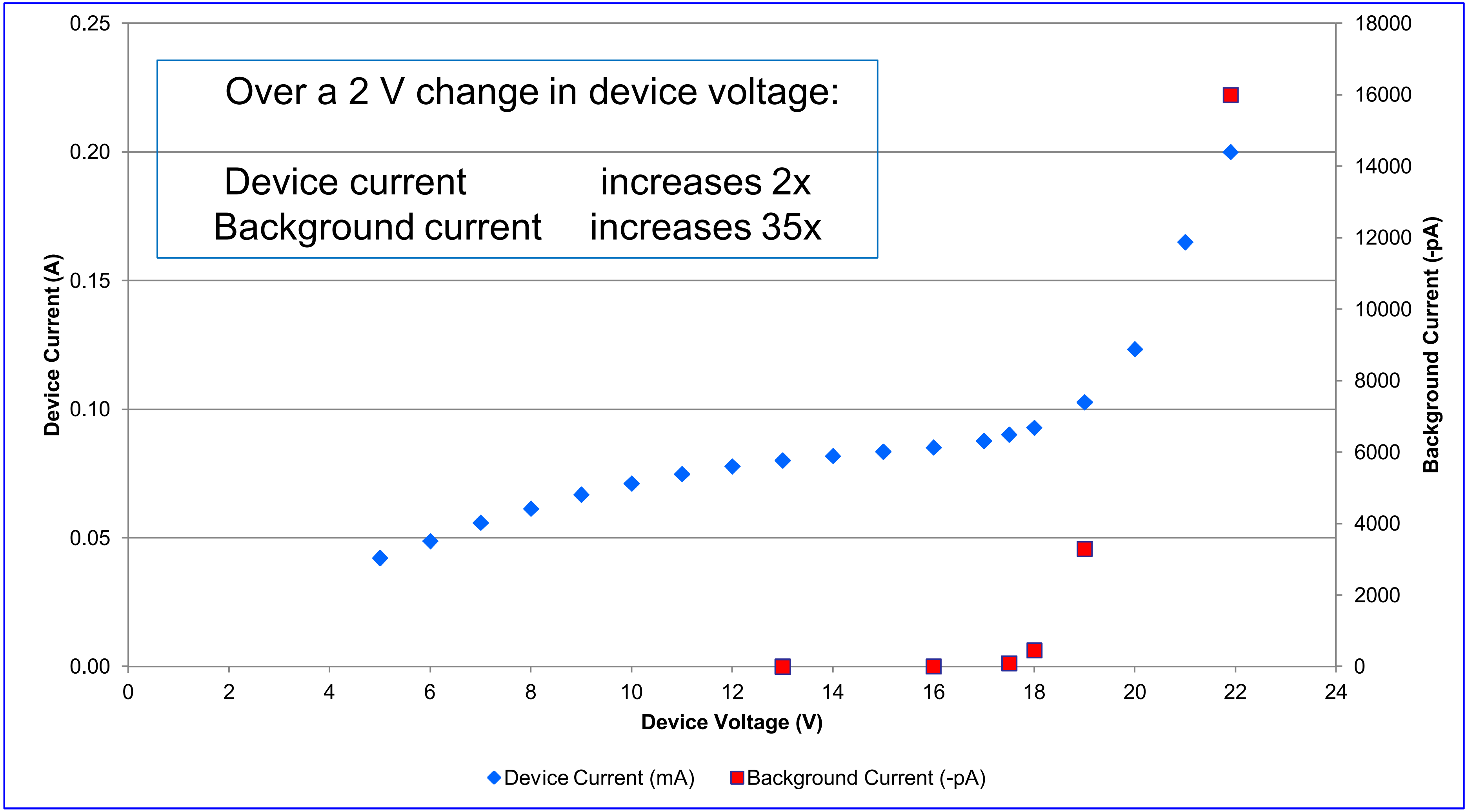
3.53 eV	Rb-Si-O	Unexposed/Exposed
3.65 eV	Cs-Si-O	Unexposed
3.72 eV	Cs-Si-O	Exposed
4.12 eV	Silicon	
4.64 eV	Gold	

The big question…..
Will a material with an intense, sharp TEEM peak and a low work function have the highest selectivity for N and P analytes?

Effect of Temperature on Thermionic Emission of a Cs-Si-O Film



Effect of Temperature on Detector Response

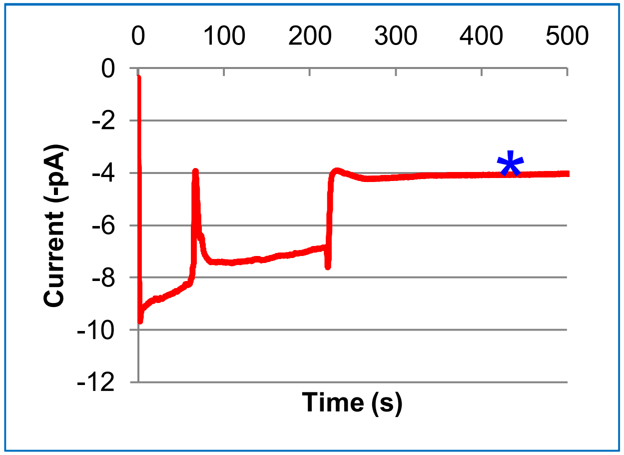


GC Conditions

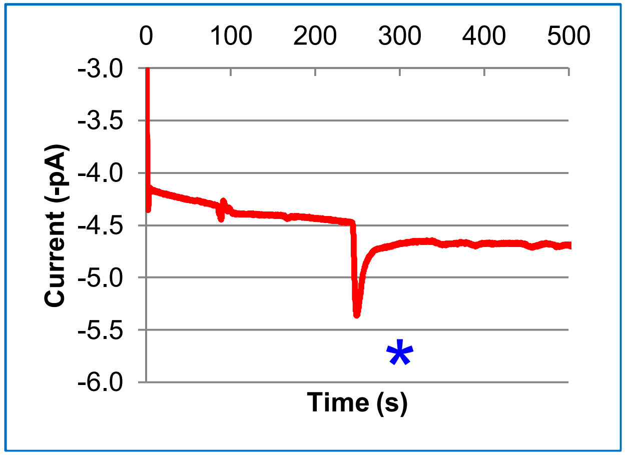
- Injection volume = 0.5 µL
- Analyte concentration was 10 µL/ml in hexane solvent
- Injector temperature = 250 °C
- Column temperature = 55 °C
- 9.5 meter RTX-1 column
- µ NPD Device fixture outside temperature = 55 °C
- Nitrogen carrier gas at flow rate = 50 ml/min
  - Split ratio = 7:1
- µ NPD film temperatures 500 – 800 °C range

Tantalum Silicate Film (ϕ = 4.7 eV)

17.0 V
91 mA



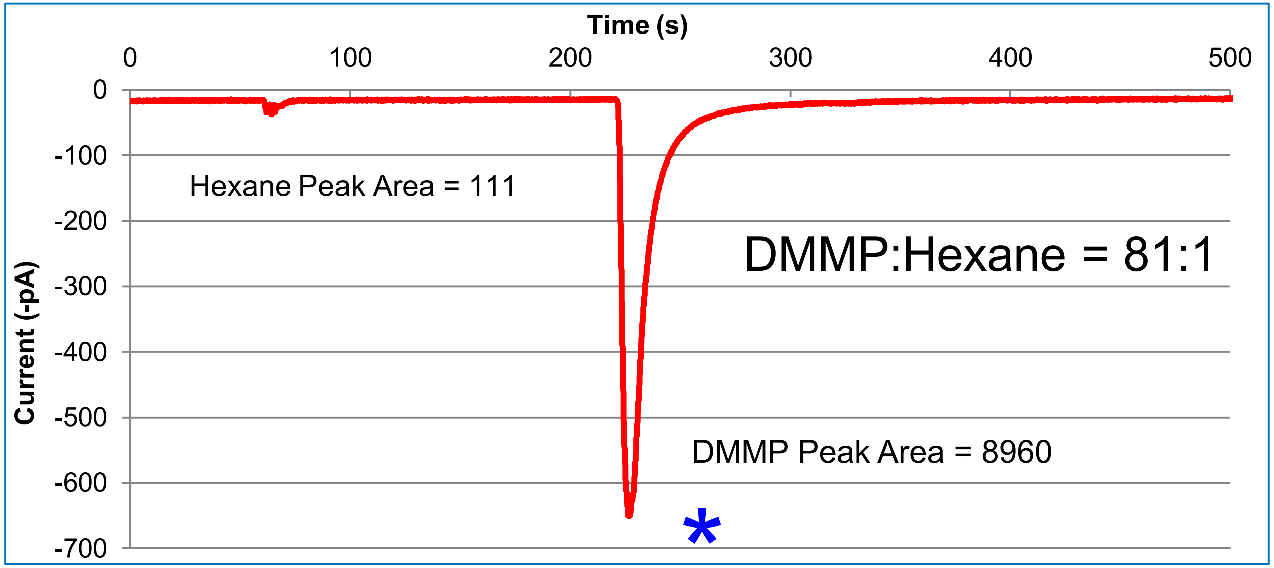
17.7 V
101 mA



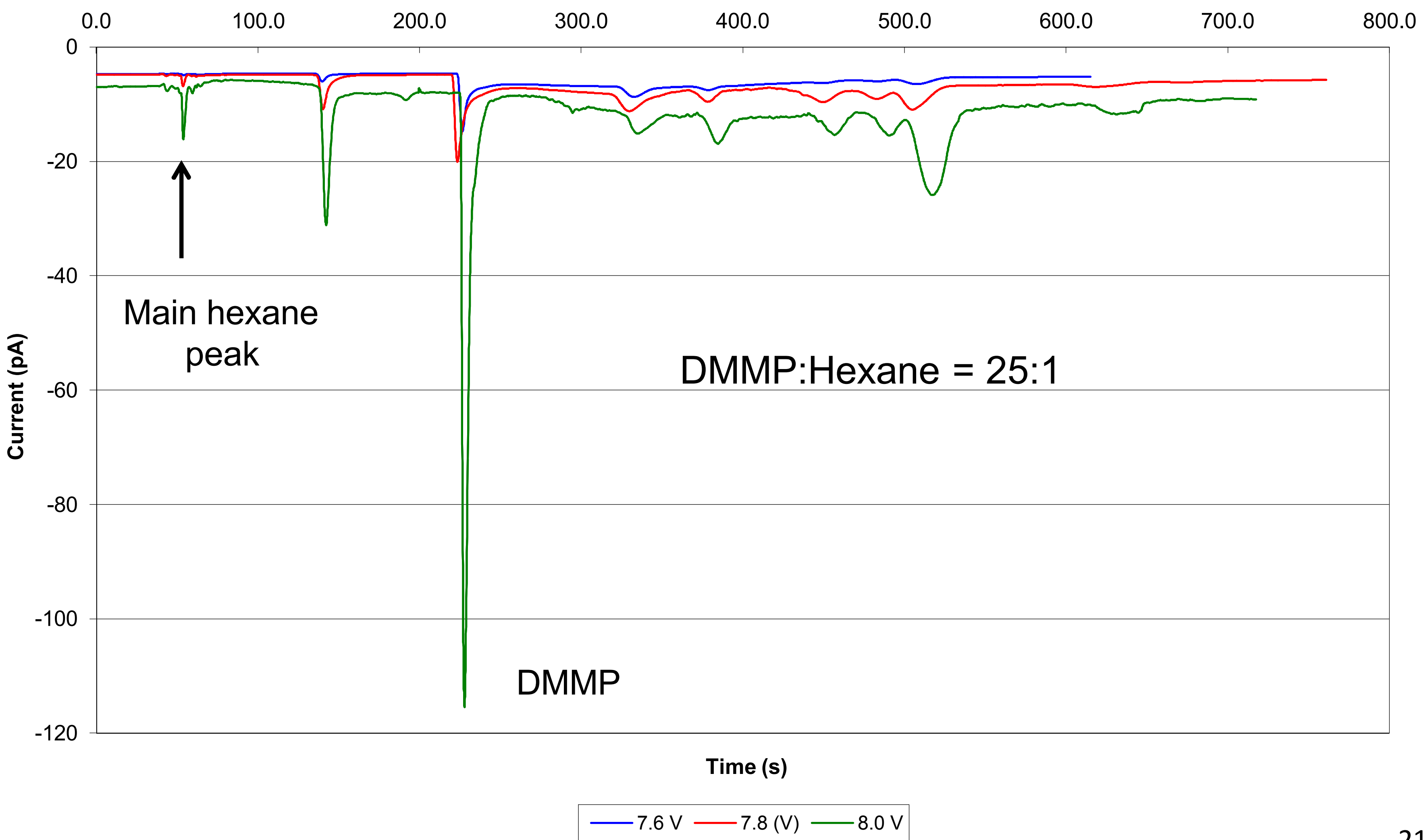
10 ul/ml DMMP
In hexane solvent

We observe both a change in peak polarity and amplitude over a very small voltage range

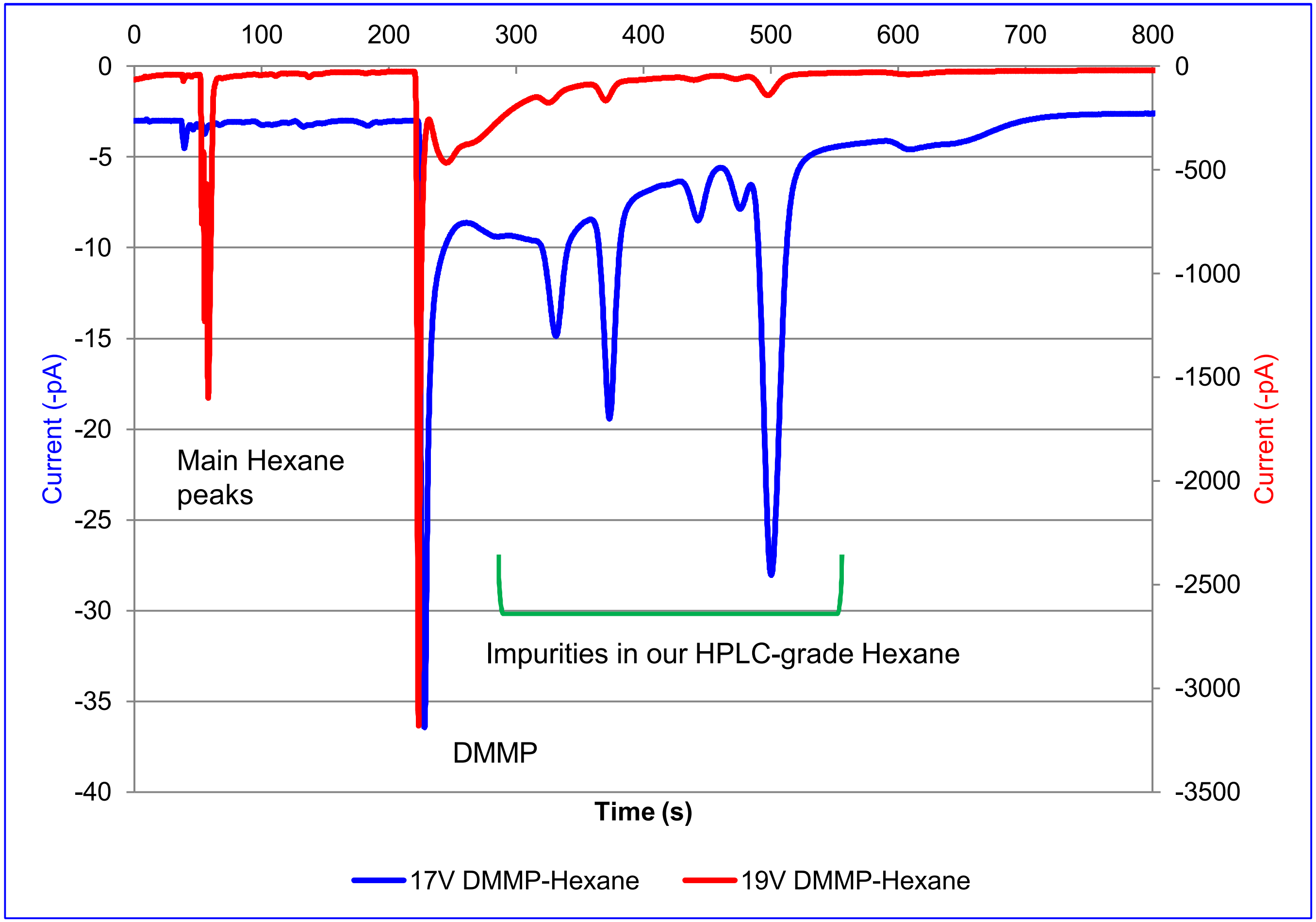
16.5 V
200 mA



Rubidium Silicate Film (ϕ = 3.4 eV)



Cesium Silicate Film (ϕ = 4.1 eV)

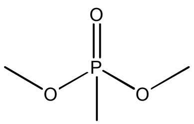


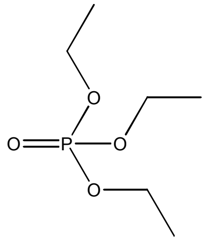
Long retention time impurities:

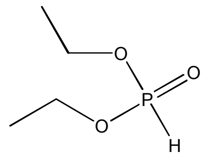
Very weak in an FID compared to main hexane peak (10's pA compared to 50,000 pA)

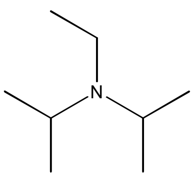
These peaks are significantly more intense in our NPD

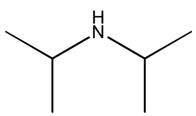
Detection of N-containing Analytes

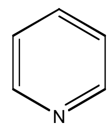

DMMP

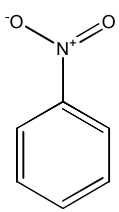

Triethyl Phosphate

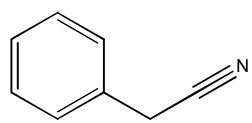

Diethyl Phosphite

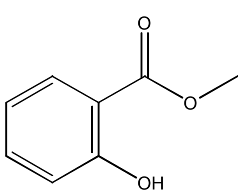

Diisopropylethylamine

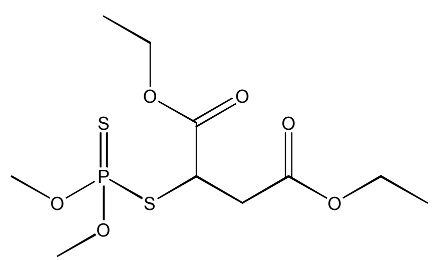

Diisopropylamine


Pyridine


Nitrobenzene


Benzyl cyanide


Methyl salicylate


Malathion

For the films tested so far we have seen the following trend in selectivity of N-analyte versus hexane solvent:

Selectivity ↑

DIPEA

DIPA
Nitrobenzene and Malathion

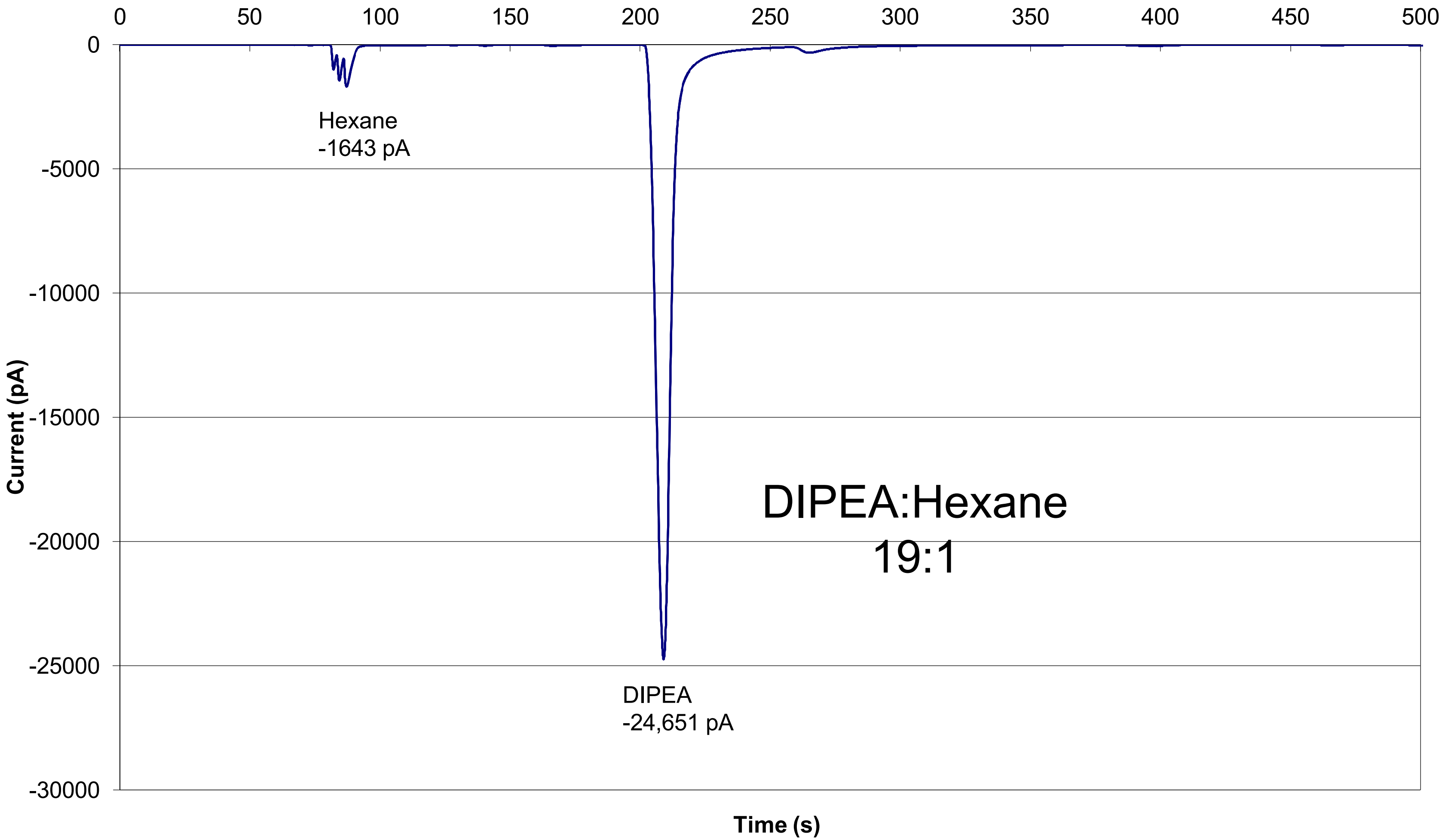
Pyridine and Benzyl cyanide

Quinoline

Is pKa a driving factor??

Response to Nitrogen Containing Analytes

0.5 ul injection of a 10 ul/ml DIPEA in Hexane sample



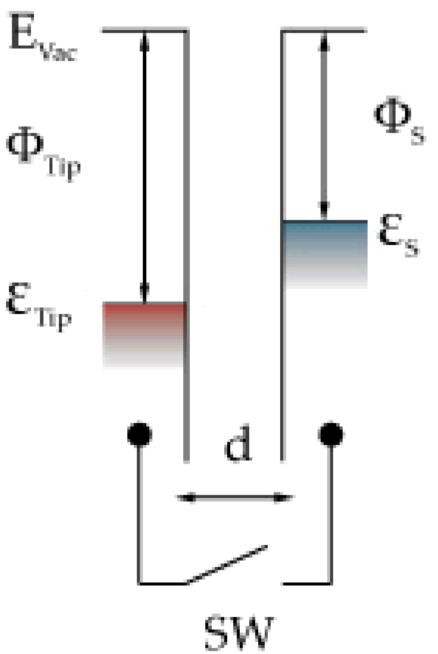
Summary

- We have demonstrated the selective detection of N and P containing analytes in a thermionic detector that does not involve the use of a hydrogen flame
  - However – more research needs to be done to increase our limit of detection and selectivity
- The exact microheater current plays a key role in the detector performance – we see a significant change in response to DMMP before and after thermionic emission ramps up
- Our early hypothesis is that the absolute work function of the film is not as important a parameter as its ability to be lowered by exposure to N and P analytes

Acknowledgements

- Principal Investigator – Robert J. Simonson
- Metal Alkoxide Synthesis
  - Tim Boyle, Leigh Anna Ottley, Alia Saad, and Chelsea Lockhart
- XPS and XANES Characterization
  - Michael Brumbach
- Work Function Measurements
  - Ana Trujillo
- Microheater Design and Fabrication
  - Mattew Moorman
- Brainstorming on detection mechanism and new materials
  - David Wheeler
- Funding
  - Sandia Laboratory Directed Research and Development

Backup



$$J = AT^2 e^{-\phi/kT}$$

A = Richardson's Constant = $1.20173 \times 10^6\ Am^{-2}K^{-2}$

http://www.kelvinprobe.info/technique-theory.htm

Background Physical Data on CW agents

	LCt_{50} Inhalation mg·min/m³	LD_{50} Skin mg/individual
Tabun	200	4000
Sarin	100	1700
Soman	100	300
VX	50	10

Property	Tabun	Sarin	Soman	GF	VX
Molecular weight	162.1	140.1	182.2	180.2	267.4
Density g/cm³ at 25 °C	1.073	1.089	1.022	1.120	1.008
Boiling-point °C	247	147	167	92 at 10 mm Hg	300
Melting-point °C	-50	-56	-42	<-30	-39
Vapour pres. mm Hg at 25 °C	0.07	2.9	0.3	0.06	0.0007
Volatility mg/m³ at 25 °C	600	17,000	3,900	600	10
Solubility in water % at 25 °C	10	∞	2	~2	3 (∞ < 9.5 °C)