SANDIA REPORT

SAND2012-7778

Unlimited Release

September 2012

Microfabricated Nitrogen-Phosphorus Detector: Chemically Mediated Thermionic Emission

Robert J. Simonson

Ryan F. Hess

Matthew Moorman

Timothy Boyle

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: <http://www.osti.gov/bridge>

Available to the public from

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: <http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online>

Microfabricated Nitrogen-Phosphorus Detector: Chemically Mediated Thermionic Emission

Robert J. Simonson, Ryan F. Hess, Matthew Moorman
Microsystems-enabled Detection Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS0892

Timothy Boyle
Ceramic Processing and Inorganic Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS1349

Abstract

Many chemical warfare agents and toxic industrial chemicals contain nitrogen and phosphorus atoms. Commercially available benchtop Nitrogen-Phosphorus Detectors (NPDs) for gas chromatographs are highly selective for nitrogen and phosphorus compared to carbon. However, the detection mechanism for these thermionic detectors is poorly understood despite 60 years of use. In addition these detectors require the use of flammable gas and operate at high power. We developed a microfabricated NPD (μ NPD) with similar selectivity that does not require the use of flammable gas and uses relatively low power. Our μ NPD consists of an alkali metal silicate thin film spray coated onto a microhotplate. The silicate thin film is responsible for providing the thermionic emission necessary for analyte detection. We conducted a series of experiments designed to better elucidate the detection mechanism. Our results indicate that surface catalyzed ionization of nitrogen and phosphorus containing analytes is the most likely mechanism.

ACKNOWLEDGMENTS

The authors acknowledge the following people for their contributions to this work:

Alkoxide Pre-cursor Synthesis and Characterization

Leigh Anna Steele

Alia Saad

Chelsea Lockhart

Daniel Yonemoto

X-ray Photoelectron Spectroscopy and Thermionic Electron Energy Distribution Work

Michael Brumbach

Microhotplate Development and Production

John Anderson

Ron Manginell

μ NPD Data Collection

Terisse Brocato

Douglas Read

Alan W. Staton

Detection Mechanism Discussions

David R. Wheeler

CONTENTS

1.0 Introduction.....	7
2.0 Microhotplate Development	11
3.0 μ NPD Fixture Development	15
4.0 Thin Film Synthesis	17
4.1 Cesium and Rubidium Silicates Targeting the $\text{Cs}_6\text{Si}_2\text{O}_7$ Composition	17
4.2 Metal Alkoxide Silicates.....	17
4.3 Spray Coating Procedure	18
5.0 Materials Characterization	19
6.0 New Crystal Structures	25
7.0 Detection of Amines and the Role of Nitrogen Atom Environment	27
8.0 Performance of Metal Alkoxide-based Silicate Devices	35
9.0 Insight into μ NPD Detection Mechanism.....	43
10.0 Recommended Future Work	45
11.0 References	47
12.0 Distribution	49

FIGURES

Figure 1.1. Schematic of a representative benchtop NPD design.....	8
Figure 2.1. Microhotplate fabrication steps.	11
Figure 2.2. Images of the oxidation of a W wire	12
Figure 2.3. Plot of the average device temperature as a function of the input power.....	13
Figure 3.1. Exploded view of the testing fixture	15
Figure 3.2. Schematic of the electrical connections used in the testing setup	16
Figure 3.3 Cartoon depicting how the fixture fits in with sample gas flow.....	16
Figure 5.1 SEM Images and EDS maps of a Cs silicate film coated onto a Si microhotplate	20
Figure 5.2. TEED set-up and measurement of Rb and Cs silicate devices.....	22
Figure 5.3. Work function maps uncoated and coated devices.....	24
Figure 6.1. New sodium alkoxide crystal structures.....	25
Figure 6.2. New rubidium alkoxide crystal structure	26
Figure 7.1: Chromatograms of substituted anilines acquired using a Rb-doped silicate μ NPD .	28
Figure 7.2. Chromatograms showing FID responses to substituted anilines	29
Figure 7.3: μ NPD detector current vs. pKa for a series of anilines	31
Figure 7.4: Plot of NPD/FID peak area response vs. heating bias voltage for series of amines .	31
Figure 8.1. Chromatograms showing effect of different alkali metals on DMMP peak polarity .	38
Figure 8.2. Chromatograms showing effect of different alkali metals on DMMP peak polarity .	39
Figure 8.3 Effect of the alkali metal on power requirements for DMMP detection	40
Figure 8.3. Current-Voltage behavior of an uncoated p-doped Si microhotplate.....	41
Figure 8.4. Effect of temperature on DMMP selectivity and sensitivity	41

TABLES

Table 5.1 Elemental composition of Cs silicate films of varying thickness from XPS.....	21
Table 7.1: Estimate mass of substituted anilines injected for chromatograms	28
Table 8.1. Gas Chromatography Parameters for A(DMP) Experiments	35
Table 8.2. Effect of the alkali metal on the silicate film work function	36
Table 8.3. Data showing the polarity of the DMMP peak in hexane solvent as a function of the alkali metal.....	36
Table 8.4. Data showing the polarity of the DIPEA peak in hexane solvent as a function of the alkali metal.....	37

1.0 INTRODUCTION

The chemical structures of many chemical warfare agents and toxic industrial chemicals (TICs) contain nitrogen (N) or phosphorus (P) atoms. Detection of these compounds is of great importance to the defense, homeland security, and emergency response communities. Commercially available benchtop thermionic nitrogen phosphorus detectors (NPDs) are capable of phosphorus over carbon molar selectivities of 10^5 which make them particularly attractive for use in GC-based detection systems. In these laboratory instruments thermionic electron emission is provided by a resistively heated glass or ceramic bead suspended above a hydrogen-air flame. Despite nearly 60 years of laboratory use the detailed detection mechanism is poorly understood. A goal of this project was to further our understanding of why these thermionic detectors are highly selective for P and N containing compounds.

A review of the NPD literature shows that most commercially available NPDs contain a bead of glass or ceramic material consisting of a proprietary mixture of alkali metals – most often cesium (Cs) or rubidium (Rb) – in a glass or ceramic matrix.¹ The work functions of Cs (2.14 eV) and Rb (2.26 eV) are among the lowest in the periodic table. The advantage of using low work function materials is apparent when one looks at the Richardson-Dushman equation (1).

$$J_{the} = A_R T^2 e^{-\left(\frac{\phi}{kT}\right)} \quad (1)$$

Where J is the current density, A_R is the Richardson constant, T is temperature, ϕ is work function, and k is Boltzman's constant. One can see that a material with a higher work function will require operation at a higher temperature to get the same thermionic emission output compared to a material with a lower work function. It is thought that the NPD beads made of low work function materials will operate at lower temperature and have a longer lifetime than beads made from high work function materials.

Paul Patterson from DETector Engineering and Technology, Inc. has written a number of papers describing the operation of various NPD designs.² His company supplies NPD's that can fit many modern benchtop GC instruments. An example of one NPD geometry described in a Patterson paper is shown in Figure 1.1.^{2a}

Figure 1.1. Schematic of a representative benchtop NPD design.^{2a}

Patterson's NPD's have the following major components¹:

- Sample inlet
- Thermionic ionization source
- Heating current
- Polarization voltage
- Ion collector
- Electrometer

After separation on a GC column the sample is mixed with hydrogen gas (low flow rates of 2 – 6 mL/min) which flows into the NPD chamber containing air carrier gas (high flow rates of 60 – 200 mL/min). The sample/gas mixture flows past an electrically heated glass or ceramic bead containing alkali metals. The sample interacts with the heated region around the bead and generates negatively charged ions which are collected on positively charged metal shield. The current collected on shield – the ion collector – is connected to an electrometer for measurement.

Two mechanisms have been promoted over the years to explain why NPDs are highly selective for P and N containing compounds, gas phase ionization or surface mediated ionization. A key goal of our project was to (1) further develop the community's understanding of selectivity in NPD instruments and (2) develop a microfabricated NPD that did not require the use of flammable gas.

We have devised a microfabricated thermionic NPD (μ NPD) which does not require the use of hydrogen gas and uses relatively low power. In place of the glass or ceramic bead found in benchtop NPDs, we developed a series of alkali and alkaline earth thin films to function as the thermionic electron emission source using sol-gel chemistry. Sandia has successfully used ultrasonically sprayed sol-gel materials in the past for coating surface acoustic wave (SAW)

detectors and preconcentrators for the MicroChemLab project. The metal silicate film is deposited on a microfabricated hot plate which can be rapidly heated using relatively low power.

In our search for low work function silicate films we investigated the use of the following metals: Li, Na, K, Rb, Cs, Sr, Ba, La, Hf, Ta, and W. These thermionic emitter films were made using either hydroxide or alkoxide precursors depending on the metal. We examined how thermionic cathode films made of these metal silicates performed in the selective detection of dimethylmethylphosphonate (DMMP) – a surrogate for CW agents – and a series of N containing amines.

2.0 MICROHOTPLATE DEVELOPMENT

The microfabricated platform for the thermionic emitter material was a newly designed microhotplate. This design is different from previous Sandia microhotplates because it is fabricated using heavily doped silicon as the basis for its resistive heating elements and structural material.³ The silicon on insulator (SOI) wafers used to create these hotplates have a 10 μm thick, P-type device layer with a resistivity of 0.005-0.020 $\Omega\text{-cm}$ and a handle thickness of 400 μm . Electrical conduction through patterned device-layer silicon provides the joule heating that brings the microhotplate to temperature. Temperatures in excess of 700 $^{\circ}\text{C}$ have been recorded using IR thermography on these devices, with the areas of highest temperature being the cantilever struts. The microhotplate's cantilever structure is designed to minimize the thermal-mechanical stresses that arise when the structure is under a thermal load. Compared to metal wiring, the heavily-doped silicon provides a current conduction path whose resistance is stable over many thermal cycles, in part due to the resistance of the silicon conduction path to oxidation.

Figure 2.1. Microhotplate fabrication steps. A-D) The four-step fabrication process flow for the silicon microhotplate, with E) topside and F) bottom side SEM images of the completed device.

The fabrication of the silicon microhotplate is completed in four basic fabrication steps, as shown in Figure 2.1. The first step, shown in Figure 2.1(A), is the sputter deposition of aluminum with 1% silicon to a thickness of 1 μm onto the device layer to form the contact pads. Following deposition, a 450 $^{\circ}\text{C}$ forming gas annealing step is performed to assure intimate contact between the pads and the silicon device layer. In Figure 2.1(B), a plasma etch forms the topside mechanical/electrical structure after the device layer is patterned via lithography and the etch is stopped on the buried oxide layer. Lithography and a backside plasma etch define the “cup” structure and the device’s thermal isolation features in Figure 2.1(C). The final fabrication step, in Figure 2.1(D), shows the oxide removal that is performed via plasma etching to completely release the cantilever from the remaining buried oxide.

While the highly doped silicon was demonstrated to be a robust heater material, it suffered from the disadvantage of possessing a non-linear temperature coefficient of resistance (TCR) and a relatively high electrical resistance. The first meant that determining the device’s temperature using a direct measurement of resistance was difficult. The second meant that we had a limited ability to create a uniform thermal hotspot at the device’s center. To correct for both of these

deficiencies, we sought to deposit a metal heater line to act as the thermal element onto the device.

We knew from previous experience that platinum thin film heaters were insufficiently robust at the desired operational temperatures for the thermionic emitter materials, and so we experimented with applying both W and Pt-ZnO films to the devices. Blanket sputter deposition and patterning via SF₆ plasma etching was used to define the W film. During operation, the film demonstrated the ability to heat the silicon device to high temperatures, however it also readily

Figure 2.2. Images of the oxidation of a W wire on the microhotplate device after testing in air with the A) device topside and B) a detail of the oxidized wire shown.

oxidized in ambient air during long term testing. Figure 2.2 shows SEM images of the oxidized wiring, clearly showing delamination and cracking due to oxidation. Attempts were made to deposit dielectric overcoats to the wiring to seal against oxygen exposure, however at the high device operational temperatures the dielectric coating would fracture and fail. This failure was believed to be caused by thermal stress and localized annealing in the dielectric films.

The next material system tried was the replacement of the traditional Ti or Cr adhesion layer for Pt with a ZnO adhesion layer. This work represents the first demonstration of this material system for MEMS thin film heating applications, and is a Sandia National Laboratories developed material system. The ZnO material forms a superior adhesion layer that encourages the growth and stabilization of grain boundaries within the Pt metal. This prevents the delamination of the thin film, but it also greatly increases the resistance of the Pt to agglomeration, which is a classic failure mechanism of thin films at high temperature. The ZnO layer was deposited via sputter deposition and patterned using photoresist lift-off.

The Pt-ZnO material system performed well in its microhotplate wiring application. It possessed a linear TCR and the capability to locally heat the device center to extremely high temperatures. Figure 2.3 shows a chart of the TCR-derived microhotplate temperature as a function of microhotplate power. This shows that the average temperature of the device can now be driven to over 1000 °C. To determine more precisely the hotspot temperature in the center of the device, small amounts of various metals were deposited on the microhotplate and observed as the input power was increased. When the metal melted, this would give an accurate estimate of the hotspot temperature. The SEM image in Figure 2.3 shows 99.9% pure Cu melted on the microhotplate hotspot. In this case the average microhotplate temperature, as derived by the TCR, was approximately 850 °C, though the melting point of pure Cu is 1085 °C. This process

showed that the hotspot temperature is higher than the device's average temperature by as much as several hundred degrees Celsius.

Figure 2.3. Plot of the average device temperature as a function of the input power to a microhotplate with the Pt-ZnO material system as the heater wiring. The inset shows pure Cu melted in the device's hotspot. An arrow shows the average microhotplate temperature when the material melted, indicating a hotspot temperature offset.

While the Pt-ZnO wiring performed well electrically and thermally, there were noted problems with the material delaminating from the silicon substrate in the presence of the thermionic emitter materials. The delamination of the wiring occurred with irregularity, though problems were noted over multiple devices. The cause of this issue is unknown, though hypothesized mechanisms could be the stress of the emitter material after sintering or a chemical attack of the sol-gel material against the ZnO adhesion layer. Future work will likely address this issue by applying the thermionic emitter material to the backside of the device in the material holding cup.

3.0 μ NPD FIXTURE DEVELOPMENT

A fixture, composed primarily of stainless steel with Macor inserts, was developed to provide a testing interface for the coated microhotplates. The fixture integrated all of the electrical and gas flow connections into a single setup, and featured SMA connections to the collector electrodes and pogo pin connections to the microhotplate. The fixture features heavy stainless steel walls to provide excellent electrical shielding of the device and the collector electrodes, as well as mechanical robustness against the high thermal loads from prolonged microhotplate testing. Macor inserts were used to hold the microhotplate and the electrical connections, in order to keep them from shorting to the metal walls. The initial design featured electrical connections to the microhotplate that positioned the topside of the device in the gas flow channel, while the second design iteration positioned the backside of the microhotplate in the gas flow channel, and thus allowed material deposition into the backside cup. Figure 3.1 shows an exploded image of the fixture and its electrode connections.

Figure 3.1. Exploded view of the testing fixture showing the inner Macor inserts, and the SMA connections to the collection electrodes.

A system of several external power supplies are used to apply the proper biases to the test fixture, microhotplate, and collector electrode, while a picoammeter reads the charge collected from the sensor. Figure 3.2 shows a schematic view of the electrical connections in this setup. The picoammeter is biased to a positive potential, using an external power supply, relative to the fixture walls which are held at system ground. The microhotplate is biased negatively to the fixture and the collector electrode using an additional power supply. This creates a large voltage within the fixture that drives negative charge from the emitter film on the microhotplate to the collector electrode above it. Figure 3.3 cartoon showing how the device fixture fits in with the sample gas flow.

Figure 3.2. Schematic of the electrical connections used in the testing setup.

Figure 3.3 Cartoon depicting how the fixture fits in with sample gas flow.

4.0 THIN FILM SYNTHESIS

4.1 Cesium and Rubidium Silicates Targeting the $\text{Cs}_6\text{Si}_2\text{O}_7$ Composition

In a fume hood, cesium hydroxide hydrate or rubidium hydroxide (50 wt% solution) was mixed with water and tetraethylorthosilicate (TEOS). An alkali metal:silicon ratio of 3:1 was used for majority of the hydroxide based materials in this report. The sol-gel was then stirred until the two phase solution (the organic TEOS on top of the aqueous metal ion solution) became monophasic. This most often took between two to five hours depending on reaction scale. Once monophasic the solution was loaded into a syringe, placed in an automated syringe pump and spray coated onto the NPD devices using an ultrasonic spray coater.

4.2 Metal Alkoxide Silicates

All the alkoxide-based materials described below were handled with rigorous exclusion of air and water using standard Schlenk line and glove box techniques. Metals alkoxide precursors prepared for this project included Li, Na, K, Rb, Cs, Sr, and Ba DMP, DIP, and DBP compounds. All solvents were used as received (Aldrich) in Sure/SealTM bottles and stored under argon, including pyridine (py) and tetrahydrofuran (THF). The following chemicals were used as received (Aldrich) and stored under argon: Sr^0 , Ba^0 , H-DMP, H-DIP, H-DBP. ' $\text{Sr}(\text{ONep})_2$ ' and ' $\text{Ba}(\text{ONep})_2$ ' were synthesized according to literature routes.

All of the metal alkoxide precursors were prepared in a glovebox under an inert atmosphere. For Sr and Ba compounds – $\text{AE}(\text{OR})_2$ – 2.5 equivalents of the appropriate HOAr were added to the desired AE^0 in pyridine. The reaction mixture was then transferred to a Schlenk line, heated to reflux conditions for 72 h, and then allowed to cool to room temperature. The volatile portion was removed *in vacuo* and the reaction transferred back to an argon filled glovebox. Pyridine was added to the dark orange powder and the reaction mixture was filtered (medium frit) to remove any insoluble material and remaining metal fragments. X-ray quality crystals were grown by slow evaporation of the filtrate or by cooling to -35°C . Yields were not optimized.

The Na alkoxides were prepared by adding the appropriate alcohol to a stirring solution of $[\text{Na}(\text{NR}_2)]$ in the solvent of choice (THF, or py), in a 20 mL vial. Most reactions turned a pale yellow or brown color upon addition and the reaction was left to stir for 12 h. If a precipitate formed, the reaction was warmed slightly until the solid dissolved and then set aside until crystals formed. Otherwise, the cap was removed from the vial and the volatile portion of the reaction mixture was allowed to evaporate until crystals formed.

The Rb alkoxides were prepared by adding the appropriate alcohol to Rb^0 in a 1:1 toluene/pyridine mixture, in a 20 mL vial. Most reactions slowly turned a dark color after stirring for 12 h. If a precipitate formed, the reaction was warmed slightly until the solid dissolved and then set aside until crystals formed. Otherwise, the cap was removed from the vial and the volatile portion of the reaction mixture was allowed to evaporate until crystals formed. Yields reported are from the first batch isolated and were not optimized.

4.3 Spray Coating Procedure

Spray coating NPD devices was conducted using an ultrasonic spray coater produced by Sono-Tek Corporation. For aqueous solution the ultrasonic nozzle power was set at 2.5 W while for THF solutions the power was set at 1.2 W. Most devices were coated using a flow rate from 10 – 30 mL/hr and between 30 – 120 passes.

After coating the devices were placed in a tube furnace and heated under flowing nitrogen gas to 350 °C for two hours. The ramp up and down rate was set at 60 °C/hr. This heating set is thought to increase rate of the cross-linking reaction and burn off excess solvent. After the devices are removed from the furnace they are ready for use in the NPD fixture.

5.0 MATERIALS CHARACTERIZATION

Alkoxide precursor materials were characterized by infrared spectroscopy, NMR spectroscopy, elemental analysis, and single crystal x-ray diffraction. FTIR data were obtained on a Nicolet 6700 FTIR Instrument using KBr pellets under an atmosphere of flowing nitrogen. Elemental analyses were performed on a Perkin-Elmer 2400 CHN-S/O Elemental Analyzer. All NMR samples were prepared at as high as concentration as possible using crystalline material handled under an argon atmosphere. Spectra were collected on a Bruker Avance 500 NMR spectrometer under standard experimental conditions: ^1H analysis was performed with a 4-second recycle delay at 16 scans; spectra were referenced to the residual protons in pyridine- d_5 at δ 8.71 ppm; ^{13}C analysis was performed with a 10-second recycle delay at a minimum of 64 scans, and spectra were referenced to the carbons of the pyridine- d_5 peak at δ 149.9 ppm.

Single crystals were mounted onto a glass fiber from a pool of Fluorolube™ and immediately placed in a cold N_2 vapor stream, on a Bruker AXS diffractometer employing an incident-beam graphite monochromator, $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) and a SMART APEX CCD detector. Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINTPLUS Version 6.01 software and corrected for absorption using the SADABS program within the SAINT software package. Structures were solved by direct methods that yielded the heavy atoms, along with a number of the lighter atoms or by using the PATTERSON method, which yielded the heavy atoms. Subsequent Fourier syntheses yielded the remaining light-atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined using SHELX software. The final refinement of each compound included anisotropic thermal parameters for all non-hydrogen atoms. Table 1 lists the unit cell parameters for the structurally characterized compounds **1** - **5**. All final CIF files were checked using the CheckCIF program (<http://www.iucr.org/>). Additional information concerning the data collection and final structural solutions can be found in the supplemental information or by accessing CIF files through the Cambridge Crystallographic Data Base. Additional information concerning the data collection and final structural solutions can be found in the CCDC database.

Spray coated NPD devices were characterized by SEM/EDS, XPS, Thermionic Electron Energy Distribution (TEED) analysis, and Scanning Kelvin Probe (SKP) work function analysis. In most cases our spray coated films were rough in texture and varied in porosity and thickness. Figure 5.1 contains SEM micrographs and EDS maps of a typical Cs silicate film sprayed on a Si microhotplate.

(A)

(D)

(B)

(E)

(C)

Figure 5.1 SEM Images and EDS maps of a Cs silicate film coated onto a Si microhotplate.

XPS was performed using a Kratos Axis Ultra DLD instrument with a monochromatic Al K α (1486.6 eV) source. Full survey spectra were collected with an analyzer pass energy of 160 eV and a step size of 1 eV. High resolution spectra were collected with an analyzer pass energy of 20 eV and step sizes of 0.1 eV. The analyzer was used in Hybrid mode with a large spot size of 300 microns by 700 microns elliptically. UPS was obtained using an Omicron VUV source HIS13 lamp producing He I (21.2 eV) illumination. The analyzer was operated in UPS mode with a pass energy of 5 eV. A -7 V bias was applied to samples for UPS measurements. Base pressures were less than 5×10^{-9} Torr. All spectra were analyzed using CasaXPS software. For

XPS and UPS spectra, the spectra were referenced to the E_F for pure, sputter cleaned gold. E_F was determined by applying a Heaviside step function to the edge of emission.⁴ E_F was taken as the kinetic energy of the center of the Gaussian step function and was set to 0 eV (BE) for the corresponding spectra. Quantifications were obtained from CasaXPS using the built in relative sensitivity factors. Peaks were fit using a Shirley background and a Gaussian (70%)/Lorentzian (30%) lineshape.

XPS analysis of our silicate thin films was difficult due to significant sample charging. While we were clearly able to discern which elements were present in our films a more rigorous analysis of chemical bonding environments was not possible. XPS analysis was used to determine if film thickness played a role in composition and in how our devices performed in N and P detection. One key experiment involved spray coating different thicknesses of Cs silicate sol-gel using CsOH precursor onto Si devices. We coated sets of three devices using 30, 60, and 120 passes. Table 5.1 contains the elemental composition of the Cs silicate films from XPS analysis.

Table 5.1 Elemental composition of Cs silicate films of varying thickness from XPS.

	Cs (at%)	Si (at%)	O (at%)	C (at%)
30 Passes	9	38	33	20
60 Passes	9	38	28	25
120 Passes	11	37	33	19

To help us better understand how film composition effects thermionic emission (the magnitude of emission and the energy at which it begins to ramp up) we developed the capability to conduct TEED measurements at Sandia. This technique is relatively new and has not been conducted by many researchers to date based on our review of the literature. This is the first time this technique has been used at Sandia. TEED data were recorded with no light source. All window ports on the chamber were covered with aluminum foil. The sample was heated using the heating controller on the Kratos sample stage. Samples were heated for 2 hours or more at >550 °C to ensure equilibration of the stage with the sample. For analysis, the heater was decabled from the stage such that no current could influence the measured electron emission from the sample. A -15 V bias was applied to the sample.

The leading edge of this TEED emission curve – shown in Figure 5.2 – corresponds to the work function of the film. Work function values obtained by this method were close to those obtained by the SKP method described below. Using TEED we were also able to determine that for at least these Rb and Cs silicate samples, having the devices be exposed to DMMP through repeated GC injections did not significantly change the film's work function.

Figure 5.2. (A) TEED set-up and (B) measurements of Rb and Cs silicate devices before and after exposure to DMMP. The Cs silicate experiment used the same device for the unexposed and exposed measurements (CsOH-3) while the Rb silicate experiment used different devices for the unexposed (RbOH-8) and exposed (RbOH-5) measurements. Rb silicate films both unexposed and exposed have a 3.53 eV work function. The unexposed Cs silicate has a 3.65 eV work function that changes to 3.72 eV after exposure to DMMP. For reference silicon and gold have work functions of 4.12 eV and 4.64 eV, respectively.

A KP Technologies SKP5050 was used to make ambient temperature and atmosphere work function measurements of our coated devices. Measurements were made using gold alloy tips with a 2 mm diameter. For most measurements the following settings were used: tip vibrating frequency = 79.5 Hz, amplitude = 70, backing voltage = 5V, and a gradient = 300. Based on our experience using this instrument and given the roughness of our film surface we believe the accuracy of our SKP measurements to be +/- 0.2 eV. We found that the work function of films spray coated onto microhotplates varied greatly between samples. This made it difficult to determine the effect of compositional changes on absolute work function values difficult. Based on our experience using the SKP5050 instrument to measure work functions on our very rough and unevenly coated films the best accuracy we can expect is plus or minus 0.2 eV. Most of our blank, uncoated microhotplates had work functions between 4.0 – 5.5 eV. Our silicate films had work functions in the range of 2.5 – 5.5 eV with the most common values around 3.5 – 4.0 eV.

As shown in Figure 5.3 the act of spray coating the microhotplate device clearly lowered their work functions. In fact, detection experiments using uncoated microhotplates never showed detection of any solvent or analyte. Clearly, the film sprayed onto the devices is necessary for N and P detection. Thermionic emission simply from heating the uncoated devices is not enough to detect any of the solvents or analytes we tested.

(A)

(B)

Figure 5.3. Work function maps uncoated and coated devices. The region in the center of the x- and y- direction corresponds to the “hot spot” of the device. The map in (A) is of an uncoated p-doped Si microhotplate while the map in (B) is of p-doped Si microhotplate coated with a Cs silicate thin film. The only region that contains the film in (B) is the “hot spot” of the device.

6.0 NEW CRYSTAL STRUCTURES

A number of new crystal structures were obtained during the course of this project using a range of different metals and alkoxide ligands. Three of these compounds played a key role in one set of experiments discussed in this report. These compounds include:

- $[\text{Na}(\mu_3\text{-DMP})(\text{THF})]_4$ and $[\text{Na}(\mu_3\text{-DMP})(\text{py})]_4$ shown in Figure 6.1
- $[\text{Rb}_7(\eta^x, \mu\text{-DMP})_7(\text{py})_2]_n$ shown in Figure 6.2

These compounds were used in an experiment where a series of alkali metal dimethylphenol compounds were used as sol-gel precursors to make alkali metal silicate thin films using Li, Na, K, Rb, and Cs. These films were all prepared with the same alkali metal to silicon ratio so that we could test the effect of changing the alkali metal on DMMP and DIPEA selectivity.

Figure 6.1. New sodium alkoxide crystal structures. (A) Structure plot of $[\text{Na}(\mu_3\text{-DMP})(\text{THF})]_4$. (B) Structure plot of $[\text{Na}(\mu_3\text{-DMP})(\text{py})]_4$. Thermal ellipsoids are drawn at 30 % level.

Figure 6.2. New rubidium alkoxide crystal structure. Structure plot of $[\text{Rb}_7(\eta^x, \mu\text{-DMP})_7(\text{py})_2]_n$. Thermal ellipsoids are drawn at 30 % level. Hydrogen atoms have been removed for clarity.

7.0 DETECTION OF AMINES AND THE ROLE OF NITROGEN ATOM ENVIRONMENT

A key hypothesis in this work is that the energy barrier to charge transfer between the emitter cathode and the analyte molecule is a significant factor in the rate of ionization of the analyte, and therefore determines the selectivity of the NPD. The thermodynamic energy difference between a negative charge carrier in the emitter film and a free electron emitted from the surface defines the work function. However, the ionization of an organic molecule could proceed either by a stepwise mechanism (emission of a free electron followed by collisional ionization) or a concerted mechanism wherein a charge carrier is transferred directly from the emitter film to an adsorbed molecule or molecular fragment. In the latter case, the proximity of the adsorbed molecule to the emitter surface could allow for the possibility of partial charge donation into or out of the surface upon adsorption, prior to the ionization reaction. Qualitatively, electron donation into the surface could effectively function as “doping”, increasing the occupation of allowed but normally unfilled electron energy states at the surface of the emitter film. Such doping would then increase the availability of mobile negative charge carriers in the near-surface region, indirectly lowering the energy barrier to a notional concerted charge transfer mechanism. Under this scenario organic adsorbates with strong electron-donating functional groups might be expected to be more readily ionized than electrophilic molecules.

In order to test this idea we measured the micro NPD response to a series of amines. These nitrogen-containing molecules exhibit varying electron donating character (Lewis basicity) depending on the details of their molecular orbital structure, often qualitatively described as availability of the electron lone pair at the nitrogen atom. In order to try to minimize possible variations in detector response due to, for example, the presence of multiple rather than single heteroatoms in the molecular structure, we selected candidate molecules as members of several homologous series. The goal was to search for correlation of the NPD response to the Lewis basicity of the molecules. Specifically, we measured the response of a microfabricated NPD to a series of substituted anilines, where electron density donated to or withdrawn from the aromatic ring by the substituent(s) would be expected to affect the availability of electron density at the amine nitrogen atom. In addition, we investigated the response of a micro NPD to a series of aromatic and aliphatic compounds with 6-membered ring structures: Pyridine, an aromatic secondary amine; piperidine, an aliphatic secondary amine; and aniline, an aromatic primary amine. We also investigated responses of the micro NPD to a series of primary, secondary, and tertiary aliphatic amines having no ring structures, although the effect of degree of substitution upon Lewis basicity of aliphatic amines is expected to be weak.⁵

Figure 7.1 displays a series of gas chromatograms acquired for a series of aniline derivatives, acquired using a microfabricated NPD as the detector. These data were acquired with a Rb-doped silicate solgel thin film as the emitter cathode layer on a Si microfabricated NPD device, using a 22V DC heater bias to achieve an operating temperature in the 650 C range. The silicate films were deposited by spraycoating a RbOH/TEOS sol having a Rb:Si molar ratio of 3:1, for a target silicate stoichiometry in the solid (gel) phase of $\text{Rb}_6\text{Si}_2\text{O}_7$. The analytes were dissolved at 0.1M concentration in acetonitrile solvent. An Agilent autoinjector was used with 0.2 μL injection volume and a 5:1 inlet split flow ratio. Calculated sample masses injected are summarized in Table 7.1. The amplitudes of the chromatograms displayed in Figure 7.1 have

been normalized for the variation in injected sample mass, and therefore exhibit changes in response amplitude for the different analytes due to negative ion formation efficiency at the detector rather than differences in injected sample mass. The chromatograms were acquired using nitrogen carrier gas under isothermal conditions.

Figure 7.1: Chromatograms of substituted anilines acquired using a Rb-doped silicate μ NPD. Peak amplitudes have been normalized for variation in injected sample mass.

The normalized peak intensity data displayed in Figure 7.1 provide an example of the extremely high chemical functional group selectivity of the μ NPD, even when operated in nominally unreactive carrier gas conditions. Note that this selectivity is dependent upon analyte molecular structure and not only on the presence of the group 5 heteroatom: Although the solvent contains a nitrogen atom and is present at 25-40X the mass of the injected analyte, the solvent peak amplitudes are on the same order of magnitude as the analyte peaks. This selectivity of the detector is in marked contrast to the relatively nonselective response of the standard, commercially available Flame Ionization Detector (FID).

Table 7.1: Estimate mass of substituted anilines injected for chromatograms displayed in Figure 7.1.

Analyte	M.W. (g/mol)	Mass injected (μ g)	Amplitude normalization
aniline	93.13	3.7252	1
p-fluoroaniline	111.2	4.448	0.838
2,6-diethylaniline	149.23	5.9692	0.624
p-methoxyaniline	123.15	4.926	0.756
p-hydroxyaniline	109.13	4.3652	0.853
MeCN (solvent)	41.05	~150	na

Responses of the FID to substituted anilines under nominal injection and chromatographic conditions identical to those used in Figure 7.1 are displayed in Figures 7.2 (a-c). Note that while the FID exhibits excellent signal to noise and dynamic range, the relative response to different nitrogen containing functional groups (-CN vs. amines) is effectively negligible compared to that of the μ NPD.

This selectivity is a key result for the eventual usefulness of the μ NPD as a detector deployed in portable GC instrumentation. Engineering constraints on portable GC equipment typically include limitations on carrier gas type, flow rate, and column temperature programming, which limit the chromatographic separation performance of portable instruments. If separation between a major interferent and a low-concentration target analyte is incomplete, then detector selectivity is required for avoidance of false alarms due to coeluting species. Further, the use of a flammable fuel gas (typically hydrogen) capable of supporting the flame required for an FID may be impossible in portable instruments due to logistical constraints. Thus, the development of a selective detector that does not require maintaining a flame for ionization of analytes may expand the application space for portable GC instruments.

Figure 7.2. Chromatograms showing FID responses to substituted anilines. a) Linear axis showing full scale response to the solvent. Aniline responses are $\sim 100\times$ less than solvent response. b) Expanded linear axis. Note that FID relative response factors within the homologous series of anilines are different from those of the μ NPD. c) Logarithmic axis, showing relative response to solvent vs. analytes.

As discussed in the beginning of this section, a possible explanation for the variation in μ NPD response to different analytes could be provided by the concept of electron donation from the adsorbed analyte into the emitter cathode surface, providing an effective “doping” that would lower the barrier to charge transfer between the surface and the analyte molecule. In order to test this hypothesis we attempted to correlate the selectivity of the μ NPD with the basicity (electron

donating ability) of the substituted anilines as measured by their calculated pKa values. pKa is defined as the negative base 10 logarithm of the dissociation equilibrium constant for a weak acid in aqueous solution, i.e., for the equilibrium $\text{HA} = \text{H}^+ + \text{A}^-$, where A^- represents the conjugate base. The equilibrium constant $K = [\text{H}^+][\text{A}^-]/[\text{HA}]$ increases as the acid strength increases. Thus $\log K$ increases, and pKa decreases, as acid strength increases. An increasing value of pKa is thus a measure of increasing basicity of the conjugate base. Using pKa values as a measure of basicity correlated with μNPD measurements is at best a compromise, since the pKa is actually defined in terms of an equilibrium constant in solution. Solvation and solution entropy effects could be expected to significantly affect pKa values, independent of the measure of actual interest here – the electron donation available at the amine nitrogen site in a molecule adsorbed at the surface of the μNPD emitter. Thus the correlation might be expected to be qualitative at best. Alternative estimates of thermodynamic values for gas phase basicity are available for a range of amines, with the reviews by Lias et al. (1984) and Hunter and Lias (1998) perhaps the most comprehensive.⁶ However, not all of the substituted anilines used herein are addressed in these reviews, and other literature on amine basicity relies on results from a range of molecular orbital calculation methods using a variety of basis sets. Because such calculations can often predict relative trends in molecular properties but have difficulty in achieving accurate absolute values, we decided not to attempt to compare values derived across a range of different calculational methods. In the future, it would be valuable to conduct set of molecular orbital calculations specifically addressing the set of amines tested herein, so that a consistent set of estimates of electron donation at the μNPD surface could be generated. In the absence of such a set of calculations, in the immediate case we have obtained a consistent set of molecular orbital calculations of pKa for the various analytes, using online resources available from the Chemical Abstracts Surface SciFinder® literature search program.⁷

Figure 7.3 displays a plot of the amplitude of the μNPD response vs. the calculated pKa values for the homologous series of substituted anilines tested. Duplicate measurements are plotted for each of the amines used. Some positive trend in μNPD response with increasing pKa is apparent but it is unfortunately not conclusive. The data are sparse and the response for p-hydroxyaniline plainly does not follow this trend. It is not immediately obvious why this should be the case, although it is worthwhile to note that the hydroxyl group hydrogen of hydroxyaniline might be expected to be reactive in a protic solvent (water) used in the estimate of the equilibrium dissociation used to calculate pKa value. However, facile deprotonation of the molecule at the μNPD surface might in turn be expected to provide a lowered activation energy barrier (alternative kinetic pathway) for formation of the $\text{NH}_2\text{-C}_6\text{H}_4\text{-O}^-$ anion, thus increasing the NPD response relative to the other anilines. In short, it appears that a direct correlation of the detector response with a simple measure of basicity is unreliable as a predictor of μNPD sensitivity.

Figure 7.3: μ NPD detector current vs. pKa for a series of anilines.

The effect of basicity as measured by pKa is unambiguously not a good predictor on μ NPD response *selectivity* across a non-homologous series of amines. An example of this is summarized by the data displayed in Figure 7.4. Note that these data were acquired on a different device, which utilized a Cs-doped, rather than Rb-doped, emitter film. Rather than displaying the full chromatograms for the FID and μ NPD responses as in Figures 7.1-3, we have displayed the ratio of the NPD response peak areas to the corresponding FID peak areas for the same analytes. The response ratios are plotted against heater bias voltage, which affects the temperature (and therefore amplitude) of the μ NPD but has no effect on the FID response. These measurements were made using headspace injections of vapor-phase analytes into the gas chromatograph used to deliver analyte vapors to the detectors. The temperature of the sample injection vial was adjusted to give a constant headspace vapor pressure of ~ 50 torr for each of the analytes used. Thus, the total mass of analyte injected is approximately constant across the range of analytes.

Figure 7.4: Plot of NPD/FID peak area response vs. heating bias voltage (temperature) for a series of amines. The μ NPD device used for these measurements was spraycoated with a Cs-doped silicate thin film. pKa values are calculated (ACD Labs 2012).

There are several significant observations that can be made regarding the data summarized in Figure 7.4. The first is that the FID response to these three molecules is approximately constant (not shown) while the NPD/FID ratio changes dramatically. The change is primarily due to the magnitude of the NPD response, since the FID is effectively a “carbon counter”: The FID response is approximately proportional to the number of carbon atoms in the detected molecule. All three molecules are six-membered rings, with piperidine an aliphatic C6 ring and aniline an aromatic C6 ring, while pyridine is an aromatic C5N ring. The maxima in the NPD/FID response ratios occur at the same bias voltage (substrate temperature) for each of the analytes. A key observation is that the response ratio is *not* monotonic with temperature, but passes through a maximum. We note that this behavior is consistent with a surface catalyzed ionization mechanism rather than a gas-phase ionization mechanism.⁸ Briefly, if the charge transfer mechanism requires the adsorption of an analyte molecule at the emitter surface, the rate of catalytic ionization should increase with temperature up to the point where desorption of the reactant molecule becomes rapid as compared to the rate limiting step of the ionization reaction. Above that temperature the NPD response will begin to drop off, even though more total (thermal) energy is available for the transport of charge carriers across the surface reaction barrier. Thus, the observation of a maximum NPD response vs. temperature supports a surface-adsorbed reaction intermediate.

The second key observation from the data of Figure 7.4 is that the response ratio is not correlated with overall analyte basicity as measured by calculated pKa values. According to those values the aliphatic ring compound, piperidine, should be 5-6 orders of magnitude more basic than either of the aromatic amines, yet the NPD/FID response ratio is intermediate between that of the two aromatic molecules. Thus, again, the electron-donating ability of the nitrogen heteroatom does not appear to be the dominant factor in the rate of ionization of the molecule at the μ NPD emitter surface.

Perhaps the most striking result displayed Figure 7.4 is the wide disparity of response ratios between these analytes. The peak response ratio for aniline is 20X that observed for piperidine and more than 800X that for pyridine. The accommodation of negative charge by the delocalization of electron density around the aromatic ring could be invoked as a possible means of decreasing the energetic cost of ionization for the case of aniline vs. piperidine.⁵ However, this simple picture is inadequate to explain the details of negative ion formation, since the pyridine ring is also aromatic. The difference in pyridine vs. aniline NPD response is therefore considerably more complex and cannot be explained even qualitatively on the simple basis of aromaticity versus non-aromaticity. More detailed molecular orbital calculations for the candidate negative ions would be required to lend insight to these results.

Finally, it is worth noting that the complexity of the NPD/FID analyte response extends beyond the selected amine species displayed in Figure 7.4. Briefly, we conducted analogous measurements for a range of both aromatic and aliphatic amines using the headspace injection technique described above. Consistent with the assumption of a surface-catalyzed ionization mechanism, the relative response of the μ NPD to different amines changes as a function of surface temperature. For the Cs-doped silicate devices tested as in Figure 7.4, at low substrate

temperatures (bias voltage < 19.5 V) the observed order of selectivity (NPD/FID response) ratios was:

Aniline>diisopropyl ethyl amine>piperidine>diisopropyl amine>triethyl amine>butylamine>pyridine ~ tripropyl amine.

At higher substrate temperature (bias voltage >19.5V) the observed order of selectivity was:

Aniline>piperidine>tripropyl amine>triethyl amine>pyridine.

We did not note any systematic correlation between the NPD/FID response ratio and the degree of substitution (primary vs. secondary vs. tertiary) for the aliphatic amines. However, it is worthwhile to note that the response ratios for aniline and substituted anilines are consistently higher.

8.0 PERFORMANCE OF METAL ALKOXIDE-BASED SILICATE DEVICES

In order to better understand the role work function plays in the performance of our uNPD devices we examined a series of silicate thin films containing different alkali metals but kept the source of the metal and its ratio to silicon constant. We studied devices with Li, Na, K, Rb, and Cs in a 1:1 ratio with silicon. Alkali metal dimethylphenol – A(DMP) – compounds were used as precursors for the thin film silicates used as thermionic emission sources in these experiments. Two of the precursors the Na and Rb versions, had not be characterized before our work. The crystal structures of these compounds are shown in Figures 6.1 and 6.2.

To determine how well these films function as thermionic emission sources we spray coated them on our Si-based microhotplates and tested them in our GC set up. Each device was tested against dimethyl methylphosphonate (DMMP) and diisopropylethylamine (DIPEA) at different power levels. Analyte concentrations varied between from 1 – 10 $\mu\text{L}/\text{mL}$ in hexane solvent. The key performance metric chosen for these devices was comparing the peak areas between DMMP or DIPEA versus hexane. It is important to note that DMMP contains only one P atom and DIPEA contains only one N atom compared to six C atoms in hexane. Table 8.1. contains information regarding the gas chromatography parameters used in most of these experiments.

Table 8.1. Gas Chromatography Parameters for A(DMP) Experiments

GC Column Type	RTX-1, 0.53 mm i.d.
GC Column Length	9.3 m
GC Oven Temperature	55 °C for 0.3 mins Ramp 50 °C/min until 100 °C Hold at 100 °C for remaining run time
Flow Gas Type	Nitrogen
Flow Gas Rate and Pressure	143 mL/min, split ratio 5:1, 5 psi
Sample Injection Volume	0.2 μL

The ambient temperature work function of the A(DMP) coated silicon-based microhotplates was measured using the SKP5050 Kelvin Probe. We expected that the heavier alkali metal silicates would have lower work functions then the lighter ones based on our review of the literature and the trend found in the work functions of the metallic elements themselves. However, with in the error of our measurements we found no significant variation in work function across our A(DMP) silicate series as shown in Table 8.2.

Table 8.2. Effect of the alkali metal on the silicate film work function. In the devices below the alkali metal to Si ratio was constant at 1:1.

Alkali Metal	Device Number	Film Work Function (eV)	Metallic Element Work Function (eV)
Li	Li(DMP)-TC-0305-2	4.840±0.2	2.93
Na	Na(DMP)-TC-122-3	4.279±0.2	2.36
K	K(DMP)-TC-118-2	4.469±0.2	2.29
Rb	Rb(DMP)-TC-112-5	4.597±0.2	2.26
Cs	Cs(DMP)-TC-928-2	4.581±0.2	2.14
Cs	Cs(DMP)-TC-928-1		
Cs	Cs(DMP)-TC-1031-1		

At the beginning of the project we expected that the devices with lower work functions would perform better – be more selective for N and P at lower temperatures – than ones with higher work functions. We expected that changing the alkali metal from Cs to Li would increase the work function and decrease the selectivity of the devices but that the overall response of the device to DMMP would not change. As shown by the data in Table 8.3 and Figures 8.1 and 8.2 the polarity of the DMMP changes depending on which alkali metal is used in the film. This result was not expected and to date we do not have a good explanation for this behavior. Though the work function of our Li → Cs silicate films did not vary significantly, we did observe the power level required to first observe a DMMP peak decreased from Na → Cs as shown in Figure 8.3. The Li data was poor enough in quality that it was difficult to make this measurement.

Table 8.3. Data showing the polarity of the DMMP peak in hexane solvent as a function of alkali metal. The values shown for DMMP selectivity were the highest found for the given device at the optimum power setting for each device.

Alkali Metal	Device Number	Maximum DMMP Selectivity Over Hexane	DMMP Peak Polarity
Li	Li(DMP)-TC-0305-2	NR	Negative
Na	Na(DMP)-TC-122-3	189	Negative
K	K(DMP)-TC-118-2	1072	Positive
Rb	Rb(DMP)-TC-112-5	15,563	Negative
Cs	Cs(DMP)-TC-928-2	101	Positive
Cs	Cs(DMP)-TC-928-1	407	Positive
Cs	Cs(DMP)-TC-1031-1	3457	Negative/Positive

In most of the Cs silicate devices we tested that used the dimethyphenol precursor we saw a positive peak for DMMP. Because our system is set up to detect negative ions or electrons that means that for a given thermionic emission background current when the devices is exposed to DMMP we see a decrease in negative ions or electron emission. For the Rb, Na, and Li devices we see the opposite behavior, the thermionic emission current increase – so an increase in negative ions or electrons upon exposure to DMMP. One possible explanation for this change in

behavior may be related to a change in work function when DMMP temporarily adsorbs to the film surface. If the interaction of DMMP on the silicate film surface lowers its work function then we expect to see an increase in thermionic emission current density as long as the temperature is constant based on the Richardson-Dushman equation. This should generate a negative polarity peak in our system. The opposite is true that if DMMP causes the silicate film work function to increase then we should see a decrease in negative ion or electron emission and a positive polarity peak.

Interestingly, in all of our experiments conducted to date on the N containing analyte DIPEA we see negative polarity peaks as shown in Table 6.4. Whatever attribute of DMMP that causes the peak polarity to be sensitive to the specific alkali metal used does not appear to be present in DIPEA.

In order to better understand how the work function changes when a silicate film is exposed to DMMP or DIPEA we have begun building an apparatus to measure work function changes at high temperature in situ. Unfortunately, we have not finished this work and believe it should be a high priority for future efforts.

Table 8.4. Data showing the polarity of the DIPEA peak in hexane solvent as a function of the type of alkali metal. It is important to note that the selectivity values for DIPEA do not represent maximized values. The devices tested had the power controlled to optimize DMMP detection.

Alkali Metal	Device Number	DIPEA Selectivity Over Hexane	DIPEA Peak Polarity
Li	Li(DMP)-TC-0305-2	NR	Negative
Na	Na(DMP)-TC-122-3	14	Negative
K	K(DMP)-TC-118-2	47	Negative
Rb	Rb(DMP)-TC-112-5	22	Negative
Cs	Cs(DMP)-TC-928-2	70	Negative
Cs	Cs(DMP)-TC-928-1	3	Negative

(A)

(B)

Figure 8.1. Chromatograms showing the effect of different alkali metals on DMMP peak polarity.
(A) Cs film, (B) Rb film

(A)

(B)

Figure 8.2. Chromatograms showing the effect of different alkali metals on DMMP peak polarity.
(A) K film, (B) Na film

Figure 8.3 Effect of the alkali metal on power requirements for DMMP detection.

We discovered that the temperature in which the thermionic cathode film is operated has a strong effect on the selectivity and sensitivity of our μ NPD devices. However, given the nonlinear TCR of our Si-based devices we were not accurately able to measure temperature directly. Instead we used device voltage as a surrogate for temperature in the knowledge that as device voltage power increases so does the temperature of the film.

In most cases we discovered that the highest selectivity for P or N compounds was at the power level which coincided with a rapid increase in background thermionic emission. When the power level was increased to levels above this transition the signal increased but the selectivity decreased. In essence, the signal from hexane increased at a faster rate with temperature than DMMP or DIPEA. Another general trend noticed was that for a given device the power level at which maximum DIPEA selectivity was observed was slightly higher (tenths of watts) than the power necessary to achieve maximum DMMP selectivity.

Figure 8.3. contains data showing what happens to a blank uncoated p-doped Si device when its temperature increases. As the temperature increases, as noted by an increase in device voltage, we measure an exponential increase in background thermionic emission current. Figure 8.4 contain data showing the effect of having a Cs(DMP) silicate thin film sprayed on the same type of device. The film lowers the work function of the device from 5.2 eV to 4.5 eV and is responsible for a dramatic increase in thermionic emission of about five orders of magnitude. We have found that we achieve the best selectivity for DMMP just after the point in which the background thermionic emission beings increasing exponentially. While increasing the temperature above this point does allows you to optimize the sensitivity of DMMP detection it comes at the cost of reduced selectivity.

Figure 8.3. Current-Voltage behavior of an uncoated p-doped Si microhotplate.

(A)

(B)

(C)

Figure 8.4. Effect of temperature on DMMP selectivity and sensitivity for a Cs(DMP) silicate thin film coated on a Si microhotplate.

9.0 INSIGHT INTO μ NPD DETECTION MECHANISM

The effect of alkali ions on the selective ionization of phosphorus and halogen-containing organics was first observed in modifications to an FID detector.⁹ Later designs incorporated alkali-containing glasses but proposed a gas phase ionization mechanism rather than a surface catalyzed mechanism for the selective ionization of heteroatomic analytes.¹⁰ According to this model, neutral alkali atoms (Cs or Rb) in electronically excited states were evaporated from the surface of a doped silicate glass bead at high temperature. In the gas phase these excited atoms collisionally transferred an electron to the analyte molecule, forming a negative molecular ion and a positive alkali metal ion. With a negative accelerating potential applied to the substrate, the molecular ion would be repelled toward a collection anode while the metal ion would be accelerated back toward the emitter surface. Upon collision with the surface the ion would be neutralized by a negative free charge carrier in the emitter material, and thus the alkali metal would become available for subsequent evaporation cycles.

This “gas phase selective NPD mechanism” has since been discredited by several experimental observations. Using an AlGaAs diode laser, McMahon and Schofield modulated the population of excited-state Rb atoms above the surface of a ceramic bead and monitored the effect on NPD detector current.¹¹ Although they did see evidence for evaporation of Rb atoms there was no correlation between the excited state population and the NPD response current. We note that the evaporation of Rb atoms may be responsible for the limited lifetime of thin-film Rb-doped silicate emitter cathodes, without necessarily requiring a gas-phase collisional ionization mechanism for selective NPD operation.

A modification of the gas-phase collisional mechanism was proposed by Lynch, et al., based upon their observation that a sodium borosilicate glass bead without Rb or Cs doping could be used to obtain a selective NPD response under appropriate conditions.¹² We note that the Na-doping is still a group I metal and that the experiment in principle does not preclude the possibility of a gas-phase ionization mechanism, but rather removes the specific possibility for neutral excited states available to Rb rather than lower-Z Na atoms. However, we note that if excited state gas-phase neutral sodium atoms are required for the selective ionization mechanism of the NPD, then our Rb- and Cs-doped silica solgel films, nominally with no sodium, would not exhibit NPD selectivity. Again, this does not necessarily preclude the existence of a gas phase collisional ionization mechanism, but would require the existence of multiple selective ionization mechanistic pathways, with different choices operative under different conditions and material compositions. This is a daunting possibility but one that is consistent with the complexity of the NPD ionization results.

An indirect but more compelling argument in support of a surface adsorption-catalyzed selective ionization mechanism is provided by the observation of a maximum ionization current vs. emitter temperature as discussed by Olah et al. and as observed in our data (Figure 7.4, *vide supra*).⁸ The salient point here is that desorption of an adsorbed analyte species competes with the activated but surface-catalyzed charge transfer reaction. As the surface temperature increases the lack of adsorbed intermediates precludes access to the charge transfer reaction channel.

This unfortunately leaves open the question of the specific shape of the potential energy barrier to reaction (ionization) of the adsorbed species. It is certainly qualitatively reasonable to expect that the potential energy surface for the kinetics of the ionization reaction(s) will change depending on the structure of the surface-adsorbed intermediate(s). This accounts for the complexity of the observed selectivity for the μ NPD across the range of different analytes studied under this project: Alkanes, phosphonates, and aliphatic vs. aromatic amines. Our data indicate that a simple parameter related to basicity of the nitrogen site in amines is insufficient to explain variation across molecular classes. At best, a relatively weak effect is observed within the homologous series of anilines. Stability of the anion due to aromatic delocalization is a candidate mechanism as well, but cannot be the whole story due to the wide variation in selectivity between aniline and pyridine.

We note that other structural factors can also affect selectivity. Carlsson et al. explored the effect of N-H acidity of a range of carbazoles.¹³ This is a credible explanation for the observed selectivity within a homologous range of carbazoles: Loss of H⁺ from the adsorbed molecule forms a negative fragment ion at the surface, rather than direct transfer of an electron from the emitter substrate to the adsorbate molecule. However, this cannot explain the selectivity of response to pyridine or other molecules with no protic hydrogens near the heteroatom(s).

In summary, our data are generally consistent with the proposed surface catalyzed ionization, in particular the observation of non-monotonic selectivity with substrate temperature. However, the details of the kinetic energy barriers to charge transfer into the adsorbate(s) are unfortunately quite complex and subject to change based on adsorbate structure.

Progress in elucidating such surface catalysis kinetics will be extremely challenging. This will require investigations of adsorbate structure at elevated temperature as well as localized measurement of charge carrier mobility and work function at high temperature. In addition, catalytic reaction rates may be determined by the translational and/or internal energy state of reactant molecules as they approach the surface – the so called “pressure gap” in heterogeneous catalysis studies, where relatively stable, low energy (“frozen”) surface intermediate structures do not surmount the kinetic energy barriers to reaction. Thus, further mechanistic studies must be able to address the possible effect of high-energy reactant gas molecules (the high energy “tail” of the Boltzmann distribution).

10.0 RECOMMENDED FUTURE WORK

To help further elucidate the NPD detection mechanism we believe two sets of studies should be done if future work on this project takes place. The first relates to understanding why some cathode films generate negative polarity DMMP peaks while others generate positive peaks. The second relates to continuing to explore the role the chemical bonding environment plays on N-analyte selectivity. To address the peak polarity question we propose to continue efforts to collect *in situ* work function data. The UHV kelvin probe equipment is assembled but more work is necessary to tune the instrument. To address the N atom bonding environment question we propose to continue studying different classes of N containing analytes similar to what we have done with the aniline series.

11.0 REFERENCES

1. Patterson, P. L., The Nitrogen-Phosphorus Detector. In *Detectors for Capillary Chromatography*, John Wiley & Sons, Inc.: 1992; Vol. 121, pp 139-168.
2. (a) Patterson, P. L., Selective responses of a flameless thermionic detector. *Journal of Chromatography* **1978**, 167, 381-97; (b) Patterson, P. L.; Howe, R. L., Thermionic nitrogen-phosphorus detection with an alkali-ceramic bead. *Journal of Chromatographic Science* **1978**, 16 (7), 275-80; (c) Patterson, P. L., New uses of thermionic ionization detectors in gas chromatography. *Chromatographia* **1982**, 16, 107-11; (d) Patterson, P. L.; Gatten, R. A.; Ontiveros, C., An improved thermionic ionization detector for gas chromatography. *Journal of Chromatographic Science* **1982**, 20 (3), 97-102; (e) Patterson, P. L., A specific detector for nitrogen and halogen compounds in TLC on coated quartz rods. *Lipids* **1985**, 20 (8), 503-9; (f) Patterson, P. L. Thermionic detector with a multiple layered ionization source. 1983-471282 4524047, 19830302., 1985; (g) Patterson, P. L., A comparison of different methods of ionizing GC effluents. *Journal of Chromatographic Science* **1986**, 24 (11), 466-72; (h) Patterson, P. L., Recent advances in thermionic ionization detection for gas chromatography. *Journal of Chromatographic Science* **1986**, 24 (2), 41-52; (i) Patterson, P. L., Organic fuel flames in selective ionization detectors for chromatography. *Chromatographia* **1993**, 36, 225-33; (j) Patterson, P. L., Selective Detection of Formic Acid in Wine and Other Alcoholic Beverages. *Abstracts, 39th Western Regional Meeting of the American Chemical Society, Sacramento, CA, United States, October 27-30 2004*, GEN-120.
3. Manginell, R.; Frye-Mason, G. Chemical preconcentrators with integral thermal flow sensor. 6527835, 2003.
4. (a) Chambers, S. A.; Droubay, T.; Kaspar, T. C.; Gutowski, M.; van Schilfgaarde, M., Accurate valence band maximum determination for SrTiO₃(001). *Surf Sci* **2004**, 554 (2-3), 81-89; (b) Garcia, M. A.; Wolter, S. D.; Kim, T. H.; Choi, S.; Baier, J.; Brown, A.; Losurdo, M.; Bruno, G., Surface oxide relationships to band bending in GaN. *Appl Phys Lett* **2006**, 88 (1), 013506; (c) Fairley, N.; Carrick, A., *The Casa Cookbook*. Acolyte Science: Cheshire, 2005.
5. Morrison, R. T.; Boyd, R. N., *Organic Chemistry*. Allen and Bacon: Boston, 1973.
6. (a) Lias, S. G.; Liebman, J. F.; Levin, R. D., Evaluated gas phase basicities and proton affinities of molecules; heats of formation of protonated molecules. *Journal of Physical and Chemical Reference Data* **1984**, 13 (3), 695-808; (b) Hunter, E. P. L.; Lias, S. G., Evaluated Gas Phase Basicities and Proton Affinities of Molecules: An Update. *Journal of Physical and Chemical Reference Data* **1998**, 27 (3), 413-656.
7. *Advanced Chemistry Development Laboratories Software Version 11.02* 11.02; Chemical Abstracts Service (CAS) SciFinder®: 2012.
8. Olah, K.; Szoke, A.; Vajta, Z., On the mechanism of Kolb's nitrogen-phosphorus selective detector. *Journal of Chromatographic Science* **1979**, 17 (9), 497-502.
9. Karmen, A.; Giuffrida, L., Enhancement of the Response of the Hydrogen Flame Ionization Detector to Compounds Containing Halogens and Phosphorus. *Nature* **1964**, 201, 1204-5.
10. Kolb, B.; Auer, M.; Pospisil, P., Reaction mechanism in an ionization detector with tunable selectivity for carbon, nitrogen, and phosphorus. *J. Chromatographic Sci.* **1977**, 15, 53-63.

11. McMahon, A. W.; Schofield, p. A. In *Probing the response mechanism of the thermionic detector by resonance enhanced ionization spectroscopy*, Resonance Ionization Spectroscopy, 1998; 1998; pp 301-304.
12. Van de Weijer, P.; Zwerver, B. H.; Lynch, R. J., Spectroscopic investigation of the mechanisms of the alkali bead detector for gas chromatography. *Analytical Chemistry* **1998**, *60* (14), 1380-1387.
13. Carlsson, H.; Robertsson, G.; Colmsjoe, A., Response mechanisms of thermionic detectors with enhanced nitrogen selectivity. *Analytical Chemistry* **2001**, *73* (23), 5698-5703.

12.0 Distribution

1	MS0892	Robert Simonson	1716
1	MS0892	Larry Stotts	1716
1	MS1349	Timothy Boyle	1815
1	MS0899	Technical Library	9536 (electronic copy)
1	MS0359	D. Chavez, LDRD Office	1911