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Investigations into the chemical structure based selectivity of the microfabricated nitrogen-phosphorus detector

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ABSTRACT

Nitrogen and phosphorus atoms are constituents of some of the most toxic chemical vapors. Nitrogen-phosphorus gas chromatograph detectors (NPDs) rely on selective ionization of such compounds using ionization temperatures typically greater than 600 °C. NPDs have previously been reported to be $7 \times 10^4 \times$ and $10^5 \times$ more sensitive for nitrogen and phosphorus, respectively, than for carbon. Presented here is an investigation of the structure-based selectivity of a microfabricated nitrogen-phosphorus detector (μNPD). The μNPD presented here is smaller than a dime and can be placed in a system that is 1/100th the size of a commercial NPD. Comparison of responses of such devices to homologous anilines (p-methoxyaniline, p-fluoroaniline, and aniline) revealed that detection selectivity, determined by the ratio of μNPD to nonselective flame ionization detector (FID) peak areas, is correlated with acid disassociation pK_a values for the respective analine. Selectivity was determined to be greatest for p-methoxyaniline, followed by p-fluoroaniline, with aniline having the smallest response. The limit of detection for a nitrogen containing chemical, p-methoxyaniline, using the μNPD was determined to be 0.29 ng compared to 59 ng for a carbon chemical containing no nitrogen or phosphorus, 1,3,5-trimethybenzene. The μNPD presented here has increased detection for nitrogen and phosphorus compared to the FID and with a slight increase in detection of carbon compounds compared to commercial NPD's sensitivity to nitrogen and carbon.

1. Introduction

A nitrogen phosphorus gas chromatograph detector (NPD) is a thermionic detector first created by Kolb and Bischoff, and commercialized by Patterson [1]. Heating of a solid surface, typically of a Cs- or Rb-doped silicate ceramic bead, causes an increase in current emission in the presence of electronegative samples [2]. This increase in current emission allows for detection, seen as a change in current emission over a period of time. The NPD is a particular thermionic detector which is selective for molecules containing nitrogen and phosphorus [3]. Two broad classes of thermally induced ionization mechanisms have been proposed in the literature: a gas phase ionization theory proposed by Kolb and Bischoff, and surface ionization theory proposed by Patterson [3,4]. Attempts to detect gas phase ionization intermediates by laser-induced fluorescence have been unsuccessful, lending some indirect support for surface-mediated rather than gas-phase ionization. However, details of the selective ionization mechanism(s) involved are still not understood.

Commercial NPDs typically exhibit sensitivities of $7 \times 10^4 \times$ and $10^5 \times$ for nitrogen and phosphorus heteroatoms, respectively, as compared to carbon [2]. This specificity is extremely advantageous for detection of trace amounts of N- and P-containing toxic chemicals such as toxic industrial chemicals, nitrogen-containing explosives, or pesticides, particularly in complex sample matrices containing significant hydrocarbon background concentrations.

μNPD chemical detection uses the detection of electron emission based on the chemical exposed to the device. Creating a sensitive detector for N and P required us to look into factors that alter thermionic electron emission current. Thermionic electron emission current from a hot surface follows the Richardson–Dushman equation as seen in Eq. (1) [5].

$$J = AT^2 \exp\left[-\frac{\phi}{kT}\right] \tag{1}$$

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where J is the current density, A is the Richardson's constant, T is temperature, k is Boltzmann's constant, and ϕ is the work function of the surface.

Although the relation between free electron emission described by Eq. (1) and selective molecular ionization is indirect, the response of the NPD is a strong function of substrate temperature. In the experiments reported here the μNPD is run at temperatures in the range of 400–550 °C, somewhat lower than typical operating temperatures for macroscopic NPD operation. This operating temperature range is a compromise between increased ionization signal and operating lifetime of the relatively thin μNPD emitter coatings. These coatings consist of emitters that were spray coated with porous silica containing alkali metals. Rubidium (Rb) and cesium (Cs) are commonly used for the alkali metal in the spray coating in order to lower the work function of the heated surface. A lower work function allows for increased thermionic emission of electrons at a lower temperature [2], due to the exponential term in Eq. (1).

Typically NPD systems including a benchtop gas chromatograph with an NPD cost approximately $15,000 to $40,000 and are ~2 ft^3 or larger [6]. The gas cylinders required to run the gas chromatograph also adding considerably to system size. Detectors with high sensitivity come at the price of large size, increased detection time, and the need for a skilled operator. There are currently commercially available benchtop NPDs which have detection limits of 10 ppb N, with ~10× better detection for P [6]. The limit of detection for p-methoxyaniline μNPD corresponds to 64.9 ppm N. This indicates that our portable, handheld μNPD has a somewhat reduced detection ability versus the commercial NPD, but at 1/100th the size. The μNPD was designed with the idea that it would be most beneficial to people working in the field. Fig. 1 shows a μNPD device which is much smaller than a dime, 6.7 × 4.6 mm, and can be placed in handheld chemical detection systems.

In what follows, we describe our microfabricated nitrogen phosphorus detector (μNPD) and present results for detection of a series of homologous amines as well as the comparison to the common flame ionization detector used with gas chromatographs. Specifically, substituted anilines were tested to determine variations in selectivity due to the addition of functional groups to the aniline ring. This research was performed in order to seek insight into the thermal ionization mechanism(s) of the μNPD by attempting to vary the electron affinity of the functional groups on the aniline. An improved understanding of detection selectivity can help to understand detection mechanisms, with the ultimate goal of improving detection limits for chemicals that are toxic in trace amounts.

2. Materials and methods

2.1. μNPD design

The μNPD device is a Pt–ZnO microhotplate which contains Pt as a base with a ZnO adhesion layer. We at Sandia National Laboratories created a material system for use as a Micro Electro Machined System (MEMs) thin film heater. This is the first report of that material system and its performance in a sensor 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 common failure mechanism of thin films at high temperature. The ZnO layer was deposited via sputter deposition and patterned using photoresist lift-off.

Fig. 1. Uncoated μNPD (microhotplate) device next to a dime.

2.2. Cesium hydroxide/rubidium hydroxide sol–gel

In a fume hood, cesium hydroxide monohydrate (50 wt% solution) or rubidium hydroxide (50 wt% solution) was mixed with water and tetraethyl orthosilicate (TEOS). A TEOS:water ratio of 1:5, and a cesium (or rubidium):silicon ratio of 3:1 was used to make the sol–gel mixture. The sol–gel was then stirred for about 3 h until the two phase solution (the organic TEOS on top of the aqueous metal ion solution) became monophasic. Once monophasic, the solution was loaded into a syringe, placed in an automated syringe pump, and spray coated. The region coated is on the backside of the μNPD devices, in the material holding cup. The μNPD device was coated on the backside in order to prevent delamination of the wiring as a result of sol–gel ZnO interactions.

2.3. Spray coating

The μNPD sensor surface was prepared by heating it to approximately 480 °C for 10 min prior to spray coating. This allowed annealing of the Pt to the ZnO prior to coating and heating. Spray coating μNPD devices was conducted using an ultrasonic spray coater produced by Sono-Tek Corporation. The ultrasonic nozzle power was set at 2.5 W at room temperature. Devices were coated using a flow rate of 10 mL/h and 15 passes. After being coated, the devices were placed in a tube furnace and heated to 350 °C under flowing nitrogen gas for 2 h. The ramp up and down rate was set at 60 °C/h. This heating set is thought to increase the rate of the cross-linking reaction and to burn off excess solvent. After the devices are removed from the furnace they are ready for use in the NPD fixture. Devices were then heated to 450 °C in the μNPD fixture for approximately 20 min prior to taking data in order to remove any excess solvent remaining after being in the furnace.

2.4. μNPD testing fixture

A fixture, composed primarily of stainless steel with Macor® (machinable glass ceramic) inserts, the white pieces in Fig. 2, was developed to provide a testing interface for the coated μNPD device [7]. The fixture, shown in Fig. 2, integrates all of the electrical and gas flow connections into a single setup, and features coaxial line connections to the collector electrodes and pogo pin connections to the μNPD device. 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 μNPD testing. The total stainless steel dimensions are roughly 1.5″ × 2″. Macor® inserts were used to hold the NPD device and the electrical connections, in order to keep them from shorting to the metal walls. In addition, excess air volume was minimized by the Macor® inserts. The design features electrical connections to the μNPD that position the backside of the