

Class Specific Discrimination of Volatile Organic Compounds Using a Quartz Crystal Microbalance Based Multisensor Array

Stephanie R. Vaughan, Nicholas C. Speller, Pratap Chhotaray, Kevin S. McCarter, Noureen Siraj, Rocío L. Pérez, Yue Li, Isiah M. Warner



www.elsevier.com/locate/talanta

PII: S0039-9140(18)30601-5  
DOI: <https://doi.org/10.1016/j.talanta.2018.05.097>  
Reference: TAL18738

To appear in: *Talanta*

Received date: 17 April 2018  
Revised date: 28 May 2018  
Accepted date: 30 May 2018

Cite this article as: Stephanie R. Vaughan, Nicholas C. Speller, Pratap Chhotaray, Kevin S. McCarter, Noureen Siraj, Rocío L. Pérez, Yue Li and Isiah M. Warner, Class Specific Discrimination of Volatile Organic Compounds Using a Quartz Crystal Microbalance Based Multisensor Array, *Talanta*, <https://doi.org/10.1016/j.talanta.2018.05.097>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**Class Specific Discrimination of Volatile Organic Compounds Using a Quartz Crystal Microbalance Based Multisensor Array**

Stephanie R. Vaughan,<sup>a</sup> Nicholas C. Speller,<sup>a,1</sup> Pratap Chhotaray,<sup>a,2</sup> Kevin S. McCarter,<sup>b</sup> Noreen Siraj,<sup>a,3</sup> Rocío L. Pérez,<sup>a</sup> Yue Li,<sup>a</sup> Isiah M. Warner<sup>a\*</sup>

<sup>a</sup> Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

<sup>b</sup> Department of Experimental Statistics, Louisiana State University, Baton Rouge, LA 70803, USA

<sup>1</sup> Present Institution, Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA

<sup>2</sup> Present Institution, Department of Chemistry, Indian Institute of Technology Delhi, Delhi 110016, India

<sup>3</sup> Present Institution, Department of Chemistry, University of Arkansas at Little Rock, Little Rock, AR 72204, USA

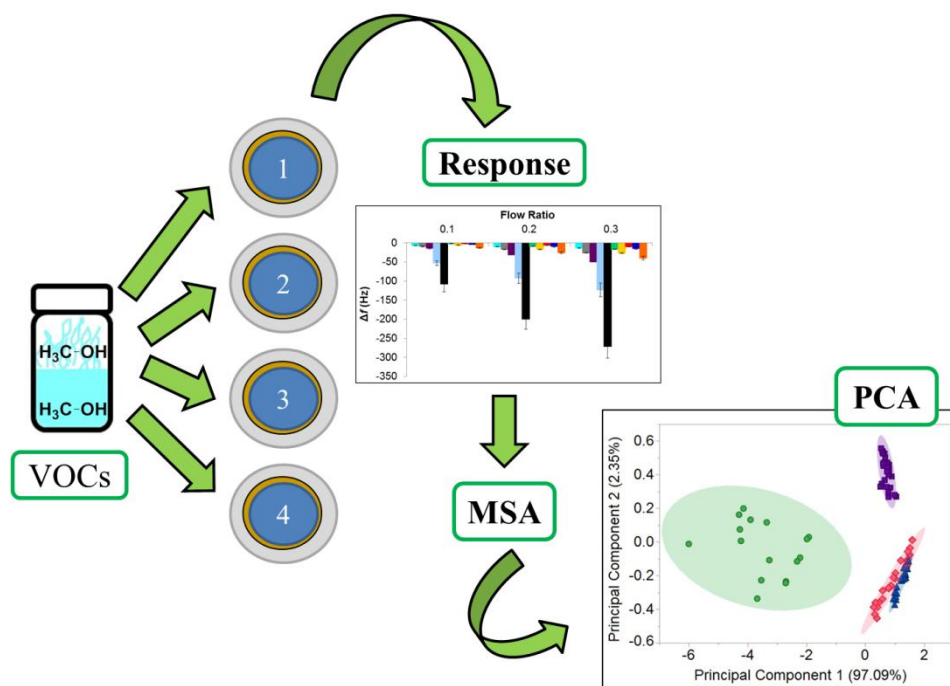
\*Corresponding Author

\*Fax: 1-225-578-3971 Tel.: 1-225-578-2829 E-mail: [iwarner@lsu.edu](mailto:iwarner@lsu.edu)

436 Choppin Hall, Louisiana State University, Baton Rouge, LA 70803, USA

**Abstract:** The use of quartz crystal microbalance (QCM) sensor arrays for analyses of volatile organic compounds (VOC) has attracted significant interest in recent years. In this regard, a group of *uniformed materials* based on *organic salts* (GUMBOS) has proven to be promising recognition elements in QCM based sensor arrays due to diverse properties afforded by this class of tunable materials. Herein, we examine the application of four novel phthalocyanine based GUMBOS as recognition elements for VOC sensing using a QCM based multisensor array (MSA). These synthesized GUMBOS are composed of copper (II) phthalocyaninetetrasulfonate ( $\text{CuPcS}_4$ ) anions coupled with ammonium or phosphonium cations respectively (tetrabutylammonium (TBA), tetrabutylphosphonium ( $\text{P}_{4444}$ ), 3-(dodecyldimethylammonio)propanesulfonate (DDMA), and tributyl-n-octylphosphonium ( $\text{P}_{4448}$ )). These materials were characterized using ESI-MS and FTIR, while thermal properties were investigated using TGA. Vapor sensing properties of these GUMBOS towards a set of common VOCs at three sample flow rate ratios were examined. Upon exposure to VOCs, each sensor generated analyte specific response patterns that were recorded and analyzed using principal component and discriminant analyses. Use of this MSA allowed discrimination of analytes into different functional group classes (alcohols, chlorohydrocarbons, aromatic hydrocarbons, and hydrocarbons) with 98.6% accuracy. Evaluation of these results provides further insight into the use of phthalocyanine GUMBOS as recognition elements for QCM-based MSAs for VOC discrimination.

## Graphical Abstract



**Keywords:** QCM, Sensor Array, GUMBOS, VOCs, Phthalocyanine

## 1. Introduction

Although many volatile organic compounds (VOCs) are non-toxic, many of them can cause harmful health and environmental effects including, but not limited to, headaches, nerve disease, or cancer[1, 2]. Furthermore, VOCs play a critical role in food quality control, [3, 4]

explosives detection, [5-7] and medical diagnostics [8-10]. Therefore, it is very important to develop vapor-sensing techniques for detection and discrimination of various types of VOCs.

A variety of techniques, including optical sensors and colorimetric sensors, have been used for VOC analysis [11-14]. However, more recent use of electronic noses (e-nose) has gained considerable popularity[15] since e-nose devices are designed to mimic the human nose. In this regard, when the human nose encounters a scent, a signal travels from multiple receptors in the nose to the brain, which processes the receptor response pattern and identifies the scent. A mechanized analogue of an e-nose will typically comprise multiple chemically distinct coatings that act as cross reactive elements within a multisensor array [16, 17]. Upon exposure to vapors, sensor-vapor interactions generate analyte specific response patterns that can be analyzed using statistical analyses such as artificial neural networks (ANN), cluster analysis, analysis of variance (ANOVA), principal component analysis (PCA), and discriminate analysis (DA). E-noses can be categorized into many classes, including metal oxides, gas chromatography-mass spectrometry (GC-MS), and many others [15]. However, these approaches have distinct disadvantages; for example, GC-MS is complex, expensive, and typically requires an expert operator[18], while metal oxides require operation at high temperatures, high power consumption, and have a limited selection of sensor coating materials [19]. To overcome these disadvantages, use of a quartz crystal microbalance (QCM) as an e-nose has been proposed due to its good precision, high sensitivity, and diverse range of sensor coating materials [19].

The QCM is a thickness shear mode device that consists of an AT-cut quartz crystal resonator (QCR), sandwiched between two metallic electrodes and based on the reverse piezoelectric effect. In such a system, an external voltage is applied causing the QCR to oscillate, resulting in the generation of an acoustic shear wave. At the interface of a QCR and coating material, the shear wave undergoes an attenuation and phase shift, resulting in a

change in frequency [20]. The operating principle of a QCM is based on the Sauerbrey equation:

$$\Delta f = -\frac{n}{c} \Delta m = -\frac{n}{c} \rho_f t_f,$$

where  $\Delta f$  is change in resonance frequency,  $n$  is harmonic number,  $c$  is mass sensitivity which is  $17.7 \text{ ngcm}^{-2}\text{Hz}^{-1}$  for a 5 MHz AT-cut crystal as used in this study;  $\rho_f$  is the density of the film, and  $t_f$  is film thickness [21]. Essentially, change in mass on the QCR surface is directly related to change in frequency on the oscillating crystal as reflected in the above equation. Thus, change in frequency allows an estimation of the mass of analyte adsorbed onto the surface of the QCR. Since these terms are directly proportional, the resonance frequency should decrease as mass is added to the QCR surface, which is characterized as ideal Sauerbrey behavior. In essence, the QCM has commonly been used simply as a mass detector. Selectivity and sensitivity of a QCM sensor depends on the characteristics of the coating material. In this regard, QCM sensors typically employ chemosensitive materials such as ionic liquids, imprinted polymers, and composite materials [6, 22-24]. However, there are some limitations associated with use of such materials including complex synthesis, intricate deposition procedures, and slow response times [6, 22-26].

Phthalocyanines and their derivatives are an appealing class of sensing materials due to their flexible synthesis and ability to interact with a large number of organic vapors [27-29]. In addition, conversion of these materials into GUMBOS may allow optimization of both sensitivity and selectivity [30]. The acronym GUMBOS is derived from **g**roup of **u**niformed **m**aterials **b**ased on **o**rganic **s**alts as coined by Warner, et al. [31]. This class of compounds are similar to ionic liquids (ILs) in that both are organic salts using similar counterions; however, GUMBOS represent solid phase organic salts with melting points between 25°C and 250°C [31], while ILs have melting points below 100°C and are typically liquid at room temperature. Both classes of

compounds have tunable properties such as hydrophobicity, melting point, toxicity, etc. simply by alteration of the counterion.

Herein, a QCM based multisensor array is described for class specific discrimination of VOCs. To achieve this goal, a novel set of GUMBOS were synthesized using copper (II) phthalocyanine tetrasulfonate as anions and four different cations as recognition elements for VOC detection. Thin films of each compound were deposited on the surface of the QCRs via use of electrospray and then exposed to a set of ten VOCs in order to evaluate gas-sensing properties. The set of sensors exhibited cross-reactive patterns, thus rendering them as adequate candidates for development of a sensor array. The resulting data from these four sensors were then used to develop a statistical model for distinguishing four classes of compounds (alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, and chloro-hydrocarbons). PCA was used to assess the dimensionality of the observed sensor data and to obtain a visual representation of separation among the four compound classes. DA was used to develop the predictive model for distinguishing among the present compound classes, using the four sensor variables directly as predictor variables. It is often necessary to reduce the dimensionality of the predictor space in an experiment because of small sample size, and PCA can be used in this regard. However, in this manuscript, and for this analysis, compound classes are predicted rather than individual compounds, and thus adequate data allows use of the four sensor variables directly as predictor variables in this DA.

## 2. Materials and Methods

### 2.1. Materials

Copper (II) phthalocyaninetetrasulfonic acid ( $\text{CuPcS}_4$ ) tetrasodium salt, tetrabutylammonium (TBA) bromide, tetrabutylphosphonium ( $\text{P}_{4444}$ ) bromide, 3-(dodecyldimethyl-ammonio)propanesulfonate (DDMA), anhydrous methanol, anhydrous 1-propanol, anhydrous dichloromethane (DCM), anhydrous chloroform, anhydrous toluene, anhydrous heptane, hexane, and anhydrous benzene were purchased from Sigma-Aldrich (St.

Louis, MO USA). Tributyl-n-octylphosphonium ( $P_{4448}$ ) bromide was purchased from TCI (Portland, OR USA). Xylenes was purchased from Mallinckrodt (Paris, KY USA) and ethanol was purchased from Koptec (King of Prussia, PA USA). All chemicals were used as received without further purification.

## 2.2. Instrumentation

A Q-Sense QCM-D E4 system and associated QCRs were purchased from Biolin Scientific (Stockholm, Sweden). Each QCR is an AT-cut gold-coated quartz crystal with a diameter of 14 mm, thickness of 0.3 mm and fundamental frequency of 4.95 MHz  $\pm$  50 kHz. Both readout equipment (Model 5878) and mass flow controllers (Model 5850E) were obtained from Brooks Instrument, LLC (Hatfield, PA, USA).

## 2.3. Synthesis and Characterization of GUMBOS

GUMBOS were synthesized using a biphasic metathesis reaction [30]. As an example of a typical synthetic procedure,  $[Na]_4[CuPcS_4]$  was dissolved in water while  $[TBA][Br]$  was dissolved in DCM at a 1:4 mole ratio. Prepared solutions were mixed together and left to stir in the dark for 48 hours to obtain  $[TBA]_4[CuPcS_4]$ . Following completion of the reaction, the DCM layer was rinsed several times with water to remove byproducts (NaBr). DCM was removed by rotary evaporation and any residual water was removed via freeze-drying. The reaction procedure referenced above was followed to obtain remaining GUMBOS by reacting  $[Na]_4[CuPcS_4]$  with  $[P_{4444}][Br]$ , DDMA, and  $[P_{4448}][Br]$  to obtain  $[P_{4444}]_4[CuPcS_4]$ ,  $[DDMA]_4[CuPcS_4]$ , and  $[P_{4448}]_4[CuPcS_4]$ , respectively. The final products for all GUMBOS were blue, tacky solids. Structures of starting materials are shown in Figure S1 (supporting information).

All compounds were characterized using electrospray ionization mass spectrometry (ESI-MS) and Fourier transform infrared spectrometry (FT-IR). ESI-MS was accomplished using an Agilent 6210 system in positive and negative ion modes. FT-IR was performed using a Bruker Alpha & Tensor 27 FT-IR instrument. Thermal properties were also investigated using



thermogravimetric analysis (TGA), which was completed using a Hi-Res Modulated TGA 2950 instrument (TA instruments).

#### 2.4. Preparation and Characterization of Sensing Films

Prior to coating, each QCR was cleaned using RCA standard clean 1 solution (5:1:1 deionized water, 30% hydrogen peroxide, and ammonium hydroxide).[32] Stock solutions of [TBA]<sub>4</sub>[CuPcS<sub>4</sub>], [P<sub>4444</sub>]<sub>4</sub>[CuPcS<sub>4</sub>], [DDMA]<sub>4</sub>[CuPcS<sub>4</sub>], and [P<sub>4448</sub>]<sub>4</sub>[CuPcS<sub>4</sub>] (1 mg/mL) were prepared using DCM in 20 mL borosilicate glass scintillation vials. A fairly uniform deposition of GUMBOS onto each QCR was achieved using electrospray. Parameters for electrospray remained constant for each thin film: deposition time of 2 minutes, flowrate of 100  $\mu$ L/min, current of 30  $\mu$ A, voltage of 16.6 kV and a working distance of 7 cm. After coating, films were blown with nitrogen and subsequently stored in a desiccator for at least 24 hours. The change in frequency between coated and uncoated QCRs in all of the studied GUMBOS was maintained at  $\sim$  -2000 Hz. Once coated with GUMBOS, QCRs are referred to as sensors. GUMBOS thin films were analyzed using scanning electron microscopy (SEM).

#### 2.5. Data Collection

In these studies, analyte vapors were generated using a flow type system. In brief, each analyte was exposed at three different instrumentally controlled dilutions of flow rate ratios (0.1, 0.2, and 0.3  $F_s/F_{tot}$ ) which correspond to 10%, 20%, and 30% of equilibrated headspace in a 20 mL vial of VOC and argon gas. This flow system consisted of two independent gas flow channels, one for sample vapors and the other for carrier gas (ultrapure argon). To begin, a stable baseline was established by purging the system with ultrapure argon. After a stable baseline was obtained, a vial containing the VOC of interest was bubbled with argon to generate a sample of equilibrated headspace. The sample and carrier channels merged to allow dilution of the sample flow to yield respective flow rate ratios [33]. Digital mass flow controllers were used to control and adjust the total flow rate to 100 sccm. VOC vapors mixed across 1-meter

length of tubing and then flowed over each sensor. Analyte vapor was removed from sensors by purging the system with argon at room temperature until the baseline was recovered. A schematic of the system described is shown in Figure 1.

## 2.6. Data Analysis

A single data set was acquired from vapor sensing studies expressed by change in frequency ( $\Delta f$ ) in units of hertz (Hz). PCA was used to assess the dimensionality of the observed sensor data and to obtain a visual representation of separation among the four compound classes with respect to the principal components. DA was used to develop the predictive model for distinguishing four VOC classes, using the four sensor variables directly as predictor variables.

## 3. Results and Discussion

### 3.1. Characterization of GUMBOS

Each synthetic compound was confirmed using ESI-MS (Fig. S2 – S6) and FT-IR (Fig. S7 – S10). Thermal properties of our GUMBOS were evaluated using TGA and these curves are shown in Fig. S11 – S14. All four compounds exhibited good thermal stability. The onset temperature of decomposition for [TBA]<sub>4</sub>[CuPcS<sub>4</sub>], [P<sub>4444</sub>]<sub>4</sub>[CuPcS<sub>4</sub>], [DDMA]<sub>4</sub>[CuPcS<sub>4</sub>], and [P<sub>4448</sub>]<sub>4</sub>[CuPcS<sub>4</sub>] is found to be 256°C, 172°C, 175°C, and 364°C, respectively.

### 3.2. Characterization of Sensing Films

GUMBOS sensing films were analyzed using SEM. Here, the entire sensor was investigated using SEM. However, the images represent only a portion of the sensor. SEM images shown in Fig. S15 – S18 show that most of the QCRs surface are covered with GUMBOS.

### 3.3. Evaluation of Vapor Sensing Properties

Four QCM sensors with [TBA]<sub>4</sub>[CuPcS<sub>4</sub>], [P<sub>4444</sub>]<sub>4</sub>[CuPcS<sub>4</sub>], [DDMA]<sub>4</sub>[CuPcS<sub>4</sub>], and [P<sub>4448</sub>]<sub>4</sub>[CuPcS<sub>4</sub>], respectively, as recognition elements were inserted into QCM-D chambers to

evaluate vapor sensing properties. All sensors were introduced to a set of ten VOCs that included: methanol, ethanol, 1-propanol, dichloromethane, chloroform, xylenes, toluene, heptane, hexane, and benzene. Sensors were exposed to three different instrumentally controlled sample flow rate ratios (0.1, 0.2, and 0.3  $F_s/F_{tot}$ ) of respective VOCs at 3-minute intervals for a total exposure time of ~10 minutes and changes in resonance frequency were measured. Three replicate measurements were performed for each VOC. Plots of  $\Delta f$  versus flow rate ratios are depicted for each sensor, [TBA]<sub>4</sub>[CuPcS<sub>4</sub>], [P<sub>4444</sub>]<sub>4</sub>[CuPcS<sub>4</sub>], [DDMA]<sub>4</sub>[CuPcS<sub>4</sub>], and [P<sub>4448</sub>]<sub>4</sub>[CuPcS<sub>4</sub>] in Figures 2, 3, 4, and 5, respectively. Each sensor was determined to have a stable baseline and reversible sorption, thus rendering them reusable (data shown in Fig. S19 – S20). Furthermore, sensor responses were stable and reproducible. Due to inherent differences in chemical properties of the tested VOCs, flow rate ratios for different VOC vapors are not the same when expressed as concentrations in milligram per liter (mgL<sup>-1</sup>); calculated concentrations are presented in Table S1. Thus, to compare sensitivity of each thin film towards a set of analytes, sensitivities were calculated. The sensitivity of GUMBOS has been previously defined as sensor response corresponding to 1 mgL<sup>-1</sup> of an individual VOC vapor [34]. Figure 6 illustrates the calculated sensitivities while Tables S2 and S3 summarize calculated sensitivities and detection limits of [TBA]<sub>4</sub>[CuPcS<sub>4</sub>], [P<sub>4444</sub>]<sub>4</sub>[CuPcS<sub>4</sub>], [DDMA]<sub>4</sub>[CuPcS<sub>4</sub>], and [P<sub>4448</sub>]<sub>4</sub>[CuPcS<sub>4</sub>]. Based on calculated sensitivities and sensor responses, these sensors demonstrated cross reactivity, which allowed for MSA fabrication. To fabricate a MSA, the complete data set must be analyzed. Notably, each sensor produced analyte specific response patterns, but more specifically three of the four sensors exhibited class specific responses. For instance, the sensor coated with [TBA]<sub>4</sub>[CuPcS<sub>4</sub>] in Figure 2, exhibited its highest sensor responses to the chlorohydrocarbons (chloroform and DCM), followed by alcohols (methanol, ethanol, and 1-propanol), aromatic hydrocarbons (benzene and toluene) and minimal response to aliphatic hydrocarbons (hexane and heptane). Interestingly, the response of xylenes was comparable to that of the aliphatic hydrocarbons with minimal

response as compared to aromatic hydrocarbons. Sensor  $[P_{4444}]_4[CuPcS_4]$  exhibited similar class specific responses to that of  $[TBA]_4[CuPcS_4]$ ; however, an increased response to hexane, heptane and xylenes as compared to  $[TBA]_4[CuPcS_4]$  sensor can be seen in Figure 3. Similarity in sensitivities and sensor responses for  $[TBA]_4[CuPcS_4]$  and  $[P_{4444}]_4[CuPcS_4]$  could be attributed to chemical similarity in the cations heteroatoms and carbon chain length. As shown in Figure 4, the  $[DDMA]_4[CuPcS_4]$  sensor demonstrated an overall lower response as compared to other sensors, with maximum change in frequency being approximately -40 Hz. It can also be seen that contrary to the  $[TBA]_4[CuPcS_4]$  and  $[P_{4444}]_4[CuPcS_4]$  sensors,  $[DDMA]_4[CuPcS_4]$  sensor had an increased response to both aromatic and aliphatic hydrocarbons compared to alcohols. This response pattern and lower sensitivity could be attributed to the zwitterionic charge of DDMA; however, more experiments are being explored to fully understand the mechanism of this interaction. In comparison to previous sensors, the  $[P_{4448}]_4[CuPcS_4]$  sensor exhibited its highest response to the chlorohydrocarbons. However, it does not show class specific responses to the remaining VOCs (Fig. 5). Although  $[P_{4448}]_4[CuPcS_4]$  does not demonstrate class specific responses for all VOCs; it does have increased sensitivities for most analytes as compared to previous sensors. This may be attributed to the  $P_{4448}$  cation having a longer carbon chain length. These observations lead us to infer that increasing the carbon chain length of GUMBOS will likely result in a more homogenous coating on the QCR, which in turn would make the sensor more sensitive. This hypothesis is supported by the SEM images (Fig. S15 – S18).

### 3.4. Evaluation of MSA

Due to the unique responses of the reported sensors, it was hypothesized that the MSA could discriminate between these ten different VOCs by compound classes. To accomplish this, the raw  $\Delta f$  data collected from the four sensors were used in developing a predictive model using DA. The hypothesis that the covariance matrices associated with the four sensor variables

were the same across all four compound classes was strongly rejected ( $p$ -value < 0.0001); thus, quadratic DA (QDA) was used, which fits a model that estimates the covariance matrices separately for each compound class.

The first two principal components accounted for 99.44% of the variability in the four predictors. The first principal component, which accounted for 97.09% of the variability, essentially represents the sum of the four sensor measurements. The second principal component, which accounted for an additional 2.35% of the total variation, represents a comparison between the [DDMA]<sub>4</sub>[CuPcS<sub>4</sub>] and [P<sub>4446</sub>]<sub>4</sub>[CuPcS<sub>4</sub>] sensor measurements. Based on a plot of the first two principal component scores, shown in Figure 7, the principal components provided a great visual separation between chloro-hydrocarbons and alcohols, as well as between chloro-hydrocarbons and the combined classes of aliphatic hydrocarbons and aromatic hydrocarbons. However, the first two principal components provided no visual separation between the aliphatic hydrocarbons and aromatic hydrocarbons. This suggested that there may be difficulty in distinguishing between these two classes of compounds with the model produced by DA. The values for the first two principal components could be used as predictor variables in DA for developing the predictive model. However, due to the large number of observations within each compound class, this was not necessary and the measurements from the four sensors were used directly as predictor variables.

To assess the predictive accuracy of the resulting QDA, cross-validation classification was used. Cross-validation provides a less biased and more accurate assessment of the predictive accuracy of a model than the default resubstitution method, which is biased upwards. Using cross-validation, the QDA predictive model accurately classified, with exception of only one, all of the compounds into their correct compound classes. The one misclassification was due to an aliphatic hydrocarbon being classified as an aromatic hydrocarbon. It was previously mentioned that aliphatic hydrocarbons and aromatic hydrocarbons completely overlapped in a

plot of the PCA scores (Fig. 7). Therefore, it was an interesting result that only one of these compounds was misclassified. Using uniform prior classification probabilities, the overall error rate was estimated to be 1.39%, corresponding to an overall accuracy rate of 98.6%.

For comparison purposes, in a QDA model using just the first principal component as a predictor, which again accounted for 97.09% of the variation in the sensor variables, the overall cross-validation classification error rate was 19.91%. In that model, two (2) of the alcohols were misclassified as hydrocarbons, seven (7) of the 27 aromatic hydrocarbons were misclassified as alcohols while another eleven (11) were misclassified as aliphatic hydrocarbons, and one (1) aliphatic hydrocarbon was misclassified as an aromatic hydrocarbon. In a QDA using the first two principal components as predictors, the overall cross-validation classification error rate dropped to 5.09%. In that model, four (4) aromatic hydrocarbons were misclassified as aliphatic hydrocarbons, and one (1) aliphatic hydrocarbon was misclassified as an aromatic hydrocarbon. Therefore, when all four sensor variables were used as predictors in the QDA, a more accurate predictive model was achieved than when the first two principal components were used as predictors.

#### 4. Conclusion

In this study, four novel GUMBOS using copper (II) phthalocyanine tetrasulfonate were synthesized, and their gas-sensing properties were investigated using a QCM based MSA. These GUMBOS showed good thermal stability, sensing characteristics, and cross-reactive responses for use in a MSA. By employing this phthalocyanine based GUMBOS multisensor array, ten different analytes were able to be discriminated into four classes with 98.6% accuracy. It should be noted that this high accuracy is achieved by using the original data set as predictor variables in QDA, as compared to the first two principal components, which is traditionally used. While the exact interaction of VOC vapors with GUMBOS sensing films is still being investigated, this work has given considerable insight into their use as VOC sensors using

a MSA. When one considers the high accuracy in discriminating classes of VOCs, this sensor array shows great potential for use in applications such as food quality control [3, 4].

**Conflicts of interest**

There are no conflicts of interest to declare.

**Acknowledgements**

This material is based upon work supported by the National Science Foundation under Grant No. CHE-1508726 and partially supported by the National Institutes of Health under award number R25 GM069743. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation or National Institutes of Health.

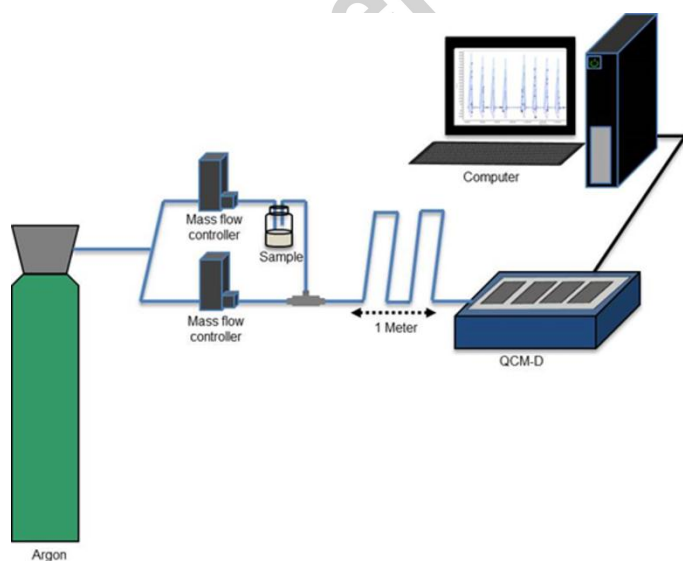
## References

- [1] M. Kampa, E. Castanas, Human health effects of air pollution, *Environmental pollution* 151(2) (2008) 362-367.
- [2] Volatile Organic Compounds' Impact on Indoor Air Quality, 2016. <https://www.epa.gov/indoor-air-quality-iaq/volatile-organic-compounds-impact-indoor-air-quality>. (Accessed February 2017).
- [3] R. Toniolo, A. Pizzariello, N. Dossi, S. Lorenzon, O. Abollino, G. Bontempelli, Room temperature ionic liquids as useful overlayers for estimating food quality from their odor analysis by quartz crystal microbalance measurements, *Analytical chemistry* 85(15) (2013) 7241-7247.
- [4] N. Barié, M. Bücking, M. Rapp, A novel electronic nose based on miniaturized SAW sensor arrays coupled with SPME enhanced headspace-analysis and its use for rapid determination of volatile organic compounds in food quality monitoring, *Sensors and Actuators B: Chemical* 114(1) (2006) 482-488.
- [5] J.M. Schnorr, D. van der Zwaag, J.J. Walish, Y. Weizmann, T.M. Swager, Sensory Arrays of Covalently Functionalized Single-Walled Carbon Nanotubes for Explosive Detection, *Advanced Functional Materials* 23(42) (2013) 5285-5291.
- [6] A. Rehman, A. Hamilton, A. Chung, G.A. Baker, Z. Wang, X. Zeng, Differential solute gas response in ionic-liquid-based QCM arrays: elucidating design factors responsible for discriminative explosive gas sensing, *Analytical chemistry* 83(20) (2011) 7823-7833.
- [7] T. Ponrathnam, J. Cho, P. Kurup, R. Nagarajan, J. Kumar, Investigation of QCM sensors with azobenzene functionalized coatings for the detection of nitroaromatics, *Journal of Macromolecular Science, Part A* 48(12) (2011) 1031-1037.
- [8] N. Queralto, A.N. Berliner, B. Goldsmith, R. Martino, P. Rhodes, S.H. Lim, Detecting cancer by breath volatile organic compound analysis: a review of array-based sensors, *Journal of breath research* 8(2) (2014) 027112.
- [9] X. Chen, M. Cao, Y. Li, W. Hu, P. Wang, K. Ying, H. Pan, A study of an electronic nose for detection of lung cancer based on a virtual SAW gas sensors array and imaging recognition method, *Measurement Science and Technology* 16(8) (2005) 1535.
- [10] C. Brunner, W. Szymczak, V. Höllriegl, S. Mörtl, H. Oelmez, A. Bergner, R. Huber, C. Hoeschen, U. Oeh, Discrimination of cancerous and non-cancerous cell lines by headspace-analysis with PTR-MS, *Analytical and bioanalytical chemistry* 397(6) (2010) 2315-2324.
- [11] H.-C. Liao, C.-P. Hsu, M.-C. Wu, C.-F. Lu, W.-F. Su, Conjugated Polymer/Nanoparticles Nanocomposites for High Efficient and Real-Time Volatile Organic Compounds Sensors, *Analytical chemistry* 85(19) (2013) 9305-9311.
- [12] K. Kanda, T. Maekawa, Development of a WO<sub>3</sub> thick-film-based sensor for the detection of VOC, *Sensors and Actuators B: Chemical* 108(1) (2005) 97-101.

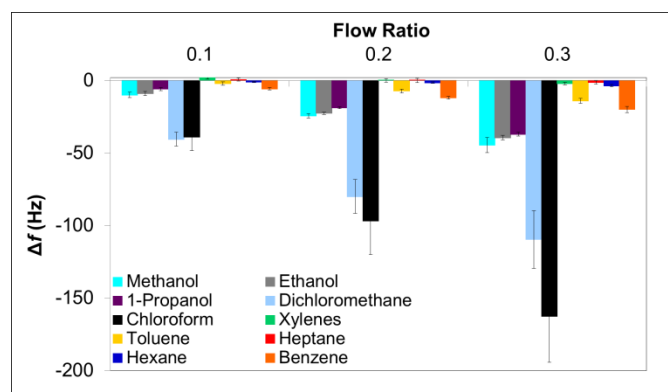


- [13] C. Elosua, I.R. Matias, C. Bariain, F.J. Arregui, Volatile organic compound optical fiber sensors: A review, *Sensors* 6(11) (2006) 1440-1465.
- [14] J. Yoon, S.K. Chae, J.-M. Kim, Colorimetric sensors for volatile organic compounds (VOCs) based on conjugated polymer-embedded electrospun fibers, *Journal of the American Chemical Society* 129(11) (2007) 3038-3039.
- [15] E.A. Baldwin, J. Bai, A. Plotto, S. Dea, Electronic noses and tongues: Applications for the food and pharmaceutical industries, *Sensors* 11(5) (2011) 4744-4766.
- [16] A.P. Umali, E.V. Anslyn, A general approach to differential sensing using synthetic molecular receptors, *Current opinion in chemical biology* 14(6) (2010) 685-692.
- [17] K.J. Albert, N.S. Lewis, C.L. Schauer, G.A. Sotzing, S.E. Stitzel, T.P. Vaid, D.R. Walt, Cross-reactive chemical sensor arrays, *Chemical reviews* 100(7) (2000) 2595-2626.
- [18] N. Fens, M. Schee, P. Brinkman, P. Sterk, Exhaled breath analysis by electronic nose in airways disease. Established issues and key questions, *Clinical & Experimental Allergy* 43(7) (2013) 705-715.
- [19] Y.K. Yoo, M.-S. Chae, J.Y. Kang, T.S. Kim, K.S. Hwang, J.H. Lee, Multifunctionalized cantilever systems for electronic nose applications, *Analytical chemistry* 84(19) (2012) 8240-8245.
- [20] D. Johannsmann, I. Reviakine, R.P. Richter, Dissipation in films of adsorbed nanospheres studied by quartz crystal microbalance (QCM), *Analytical chemistry* 81(19) (2009) 8167-8176.
- [21] G. Sauerbrey, Use of quartz vibration for weighing thin films on a microbalance, *Z. phys* 155 (1959) 206-212.
- [22] P.-G. Su, Y.-L. Sun, C.-C. Lin, A low humidity sensor made of quartz crystal microbalance coated with multi-walled carbon nanotubes/Nafion composite material films, *Sensors and Actuators B: Chemical* 115(1) (2006) 338-343.
- [23] X. Fan, B. Du, Selective detection of trace p-xylene by polymer-coated QCM sensors, *Sensors and Actuators B: Chemical* 166 (2012) 753-760.
- [24] N. Cheng, L. Zhang, J. Joon Kim, T.L. Andrew, Vapor phase organic chemistry to deposit conjugated polymer films on arbitrary substrates, *Journal of Materials Chemistry C* 5(23) (2017) 5787-5796.
- [25] A. Palaniappan, X. Li, F.E. Tay, J. Li, X. Su, Cyclodextrin functionalized mesoporous silica films on quartz crystal microbalance for enhanced gas sensing, *Sensors and Actuators B: Chemical* 119(1) (2006) 220-226.
- [26] A.K. Burrell, R.E. Del Sesto, S.N. Baker, T.M. McCleskey, G.A. Baker, The large scale synthesis of pure imidazolium and pyrrolidinium ionic liquids, *Green Chemistry* 9(5) (2007) 449-454.

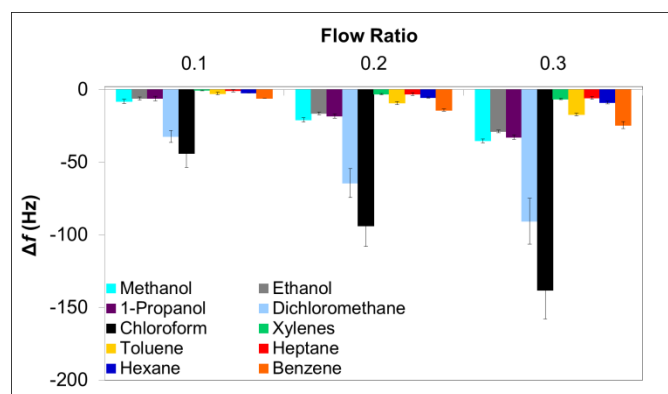
- [27] S. Kurosawa, N. Kamo, D. Matsui, Y. Kobatake, Gas sorption to plasma-polymerized copper phthalocyanine film formed on a piezoelectric crystal, *Analytical Chemistry* 62(4) (1990) 353-359.
- [28] K.-D. Schiebaum, R. Zhou, S. Knecht, R. Dieing, M. Hanack, W. Göpel, The interaction of transition metal phthalocyanines with organic molecules: a quartz-microbalance study, *Sensors and Actuators B: Chemical* 24(1-3) (1995) 69-71.
- [29] R. Zhou, F. Josse, W. Göpel, Z. Öztürk, Ö. Bekaroğlu, Phthalocyanines as sensitive materials for chemical sensors, *Applied Organometallic Chemistry* 10(8) (1996) 557-577.
- [30] B.P. Regmi, W.I.S. Galpothdeniya, N. Siraj, M.H. Webb, N.C. Speller, I.M. Warner, Phthalocyanine-and porphyrin-based GUMBOS for rapid and sensitive detection of organic vapors, *Sensors and Actuators B: Chemical* 209 (2015) 172-179.
- [31] I.M. Warner, B. El-Zahab, N. Siraj, Perspectives on moving ionic liquid chemistry into the solid phase, *Analytical chemistry* 86(15) (2014) 7184-7191.
- [32] W. Kern, The evolution of silicon wafer cleaning technology, *Journal of the Electrochemical Society* 137(6) (1990) 1887-1892.
- [33] N.C. Speller, N. Siraj, S. Vaughan, L.N. Speller, I.M. Warner, QCM virtual multisensor array for fuel discrimination and detection of gasoline adulteration, *Fuel* 199 (2017) 38-46.
- [34] I. Capan, Ç. Tarımcı, R. Capan, Fabrication of Langmuir–Blodgett thin films of porphyrins and investigation on their gas sensing properties, *Sensors and Actuators B: Chemical* 144(1) (2010) 126-130.



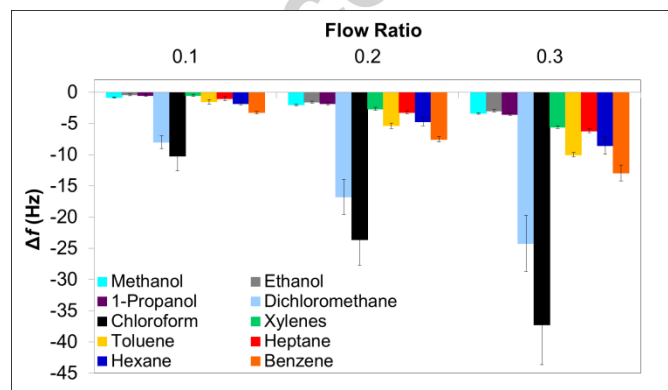
**Figure 1.** Schematic of QCM flow system.



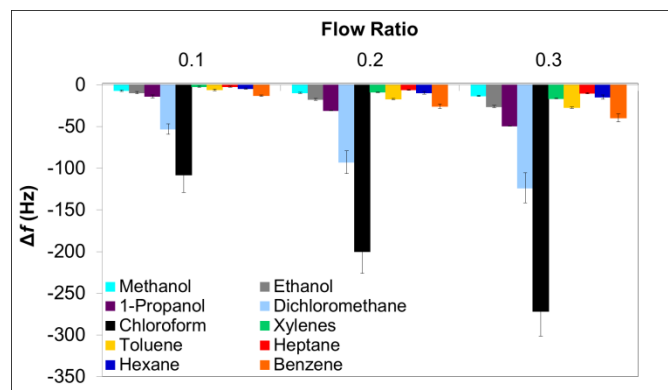
**Figure 2.** Sensor response when coated with  $[TBA]_4[CuPcS_4]$  and exposed to ten VOCs at three saturated vapor pressures. Error bars represent standard deviation for three replicate measurements.



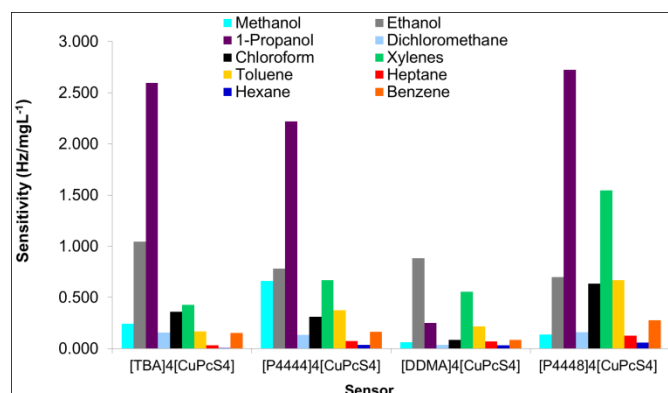
**Figure 3.** Sensor response when coated with  $[P_{4444}]_4[CuPcS_4]$  and exposed to ten VOCs at three saturated vapor pressures. Error bars represent standard deviation for three replicate measurements.



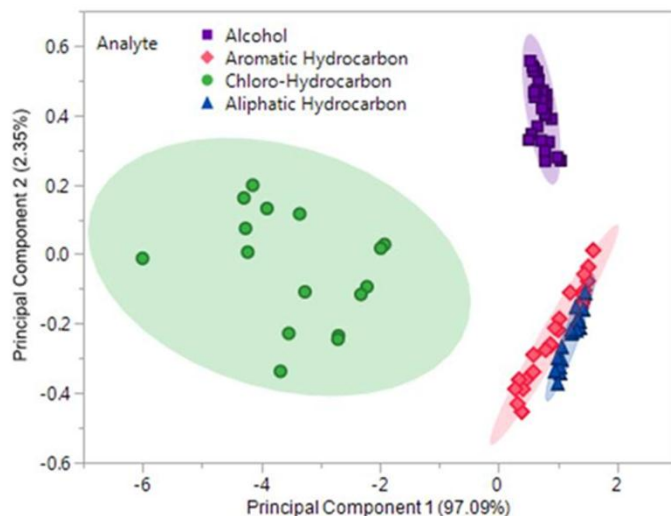
**Figure 4.** Sensor response when coated with  $[DDMA]_4[CuPcS_4]$  and exposed to ten VOCs at three saturated vapor pressures. Error bars represent standard deviation for three replicate measurements.



**Figure 5.** Sensor response when coated with  $[P_{4448}]_4[CuPcS_4]$  and exposed to ten VOCs at three saturated vapor pressures. Error bars represent standard deviation for three replicate measurements.



**Figure 6.** Graphical representation of calculated sensitivities of  $[TBA]_4[CuPcS_4]$ ,  $[P_{4444}]_4[CuPcS_4]$ ,  $[DDMA]_4[CuPcS_4]$ , and  $[P_{4448}]_4[CuPcS_4]$  sensors.



**Figure 7.** Principal component plot for discrimination of ten VOCs based on classes with respect to a four sensor MSA. Plot considers 90 total measurements consisting of three replicate measurements at three different flow ratios for each VOC (9 measurements per sample).

#### Highlights

- Four novel GUMBOS using copper (II) phthalocyanine tetrasulfonate were synthesized.
- GUMBOS showed good thermal stability and cross-reactive responses.
- Class specificity of ten analytes was achieved with 98.6% accuracy.
- High accuracy was achieved using original data set as predictor variables in QDA.