

Polymer-Coated Quartz Microbalance Array for Discriminating VOCs and Ammonia

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Summary:

A quartz microbalance array coated with polymeric sensing layers was investigated for the detection of volatile compounds and ammonia at room temperature. The array included chitosan and polylactic acid based coatings. Measurements performed with isopropanol, xylene, pentanol, octane and ammonia showed analyte dependent response patterns over concentration ranges relevant to environmental monitoring. Chitosan electrospinning coatings provided the largest absolute responses, while signal normalization highlighted complementary sensitivities across the array. t-distributed Stochastic Neighbor Embedding (t-SNE) confirmed that the collective response of the sensors enables discrimination among the tested compounds.

Keywords: quartz microbalance, polymer coatings, volatile organic compounds, sensor array

Background, Motivation and Objective

Quartz microbalances are attractive platforms for room temperature gas sensing because they provide real time mass sensitive transduction with simple readout electronics. Their analytical performance strongly depends on the physico-chemical properties of the coating, which control sorption, swelling and specific interactions with the analytes [1-3]. In this context, arrays combining different functional layers are particularly promising, since partial selectivity can be exploited to recognize complex vapors through multivariate analysis. The aim of this work is to evaluate whether a heterogeneous set of polymeric coatings can provide discriminative fingerprints for selected volatile organic compounds and ammonia.

Description of the New Method or System

The sensing platform consists of a set of seven quartz microbalance array coated with different active layers, including chitosan based, polylactic acid (PLA) based materials. The array include four sensors based on a chitosan and gelatine blend coatings, which differ in percentages of the components in the mixture, in microstructure (crosslinked or not) and type of deposition (electrospray or electrospinning), and three sensors coated with PLA by electrospray, using different set-up conditions (Tab. 1). Figure 1 shows the surface arrangement of Chitosan 2.5% /Gelatin 10% 7/3 in high Acetic acid, deposited by electrospinning (Fig. 1A) and PLA layer deposited by electrospray (Fig. 1B). The array was tested with

isopropanol, xylene, pentanol, octane and ammonia in concentration ranges of about 3500 to 14200 ppm, 544 to 2170 ppm, 88 to 350 ppm, 840 to 3300 ppm and 5 to 20 ppm, respectively. Sensor responses were evaluated as resonance frequency shifts, and the resulting datasets were analyzed both in terms of single sensor sensitivity and collective response using t-distributed Stochastic Neighbor Embedding (t-SNE).

Results and Discussion

All analytes produced concentration dependent responses, with significant differences among coatings. Chitosan 2.5% /Gelatin 10% 7/3 in high Acetic acid (electrospun-Chito 1) and Chitosan 1% /Gelatin 5% 6/4 diluted, crosslinked and deposited by electrospray (Chito4) layers showed the largest absolute signals, especially toward xylene, octane and ammonia, whereas the other coatings contributed more moderate but complementary patterns (Fig. 2). Ammonia emerged as the most sensitive target across the full array, while isopropanol generated the weakest signals (Fig. 3). Pentanol and xylene showed intermediate sensitivities and a stronger dependence on the coating composition, indicating that the array can exploit both adsorption strength and pattern diversity. t-SNE of the linear-normalized responses, calculated using Euclidean distance, provided a good separation of the five vapors, especially for alcohols, supporting the use of the platform for analyte discrimination rather than simple threshold sensing (Fig. 4).

Tab. 1: Sensing material characteristics

Name	Material	Deposition technique
Chito 1	Chitosan 2.5% /Gelatin 10% 7/3 in high Acetic acid	Electrospin (V=19kV, Flow=2 μ L/min, Dep. Time= 5s, T=40°C)
Chito 2	Chitosan 2.5% /Gelatin 10% 7/3 in high Acetic acid	Electrospray (V=21kV, Flow=3 μ L/min, Dep. Time= 90s, T=25°C)
Chito 3	Chitosan 2.5% /Gelatin 10% 7/3 in high Acetic acid	Electrospray (V=21kV, Flow=3 μ L/min, Dep. Time= 90s, T=25°C)
Chito 4	Chitosan 1% /Gelatin 5% 6/4 diluted & crosslinked	Electrospray (V=20kV, Flow=20 μ L/min, Dep. Time= 540s, T=25°C)
PLA 1	PLA 5%	Electrospray (V=20kV, Flow=5 μ L/min, Dep. Time= 30s, T=25°C)
PLA 2- PLA 3	PLA 5%	Electrospray (V=20kV, Flow=5 μ L/min, Dep. Time= 180s, T=25°C)

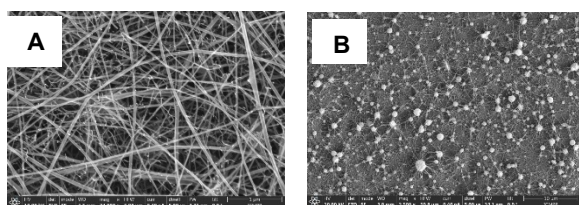


Fig. 1. Surface arrangement of (A) electrospun chitosan-based and (B) electrosprayed PLA-based sensing layer

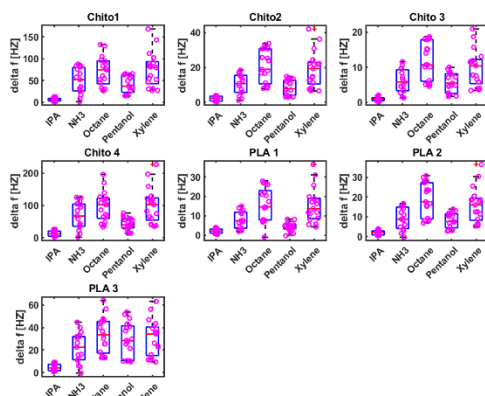


Fig. 2. Box plots of sensor responses to the different considered analytes

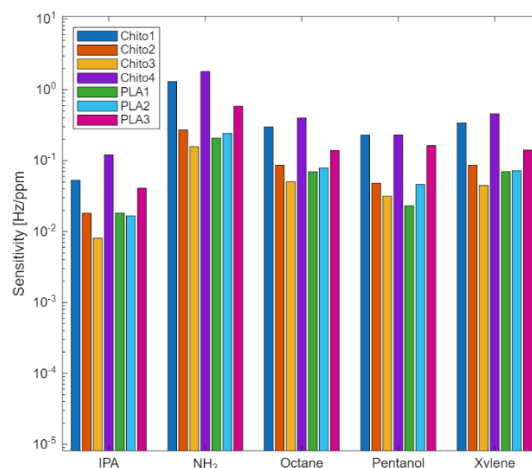


Fig. 3. Bar plot reporting the sensitivity of each sensor to the different analytes

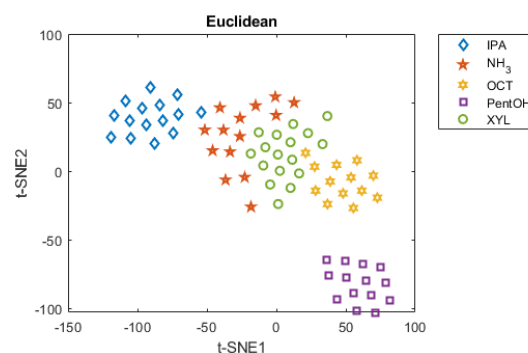


Fig. 4. t-SNE of the linear-normalized sensor responses, calculated using Euclidean distance

Conclusions

These preliminary results indicate that polymer coated quartz microbalance arrays are suitable for room temperature recognition of volatile compounds and ammonia. The combination of high response chitosan based layers with complementary lower amplitude coatings improves the multidimensional fingerprint of the system and enables robust separation in t-SNE space. The study therefore supports further optimization of the coating set and measurement protocol toward an electronic nose strategy for environmental or process monitoring applications.

References

- [1] G. Magna, R. Belugina, F. Mandoj, *et al.*, Experimental determination of the mass sensitivity of quartz microbalances coated by an optical dye, *Sensors and Actuators B: Chemical* 320, 128373 (2020); doi: 10.1016/j.snb.2020.128373
- [2] A. Catini, R. Kumar, R. Capuano, *et al.*, An Exploration of the Metal Dependent Selectivity of a Metalloporphyrins Coated Quartz Microbalances Array, *Sensors* 16, 1640 (2016); doi: 10.3390/s16101640
- [3] K. Triyana, A. Sembiring, A. Rianjanu, *et al.*, Chitosan-Based Quartz Crystal Microbalance for Alcohol Sensing, *Electronics* 7, 181 (2018); doi: 10.3390/electronics7090181