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Novel corrole-based e-nose for methanol detection in wine

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Summary:

Corrole derivatives are a versatile class of coordination complexes successfully exploited in different applications, ranging from medical to environmental fields, due to their peculiar tunable properties. Herein, we report novel N-alkyl corroles-based gravimetric sensors obtained by the deposition of twelve different macrocycles on quartz microbalances (QMBs). Sensors were tested against 17 VOCs and 4 gases, showing notable sensitivities, particularly to CO, NO, and ethanolamine. Data analysis revealed clear trends related to the alkyl chain structure, confirmed through correlations with linear solvation equation relationship (LSER) parameters. Principal Component Analysis enabled the clustering of compound families and discrimination along homologous series (e.g. class of alcohols). The sensors demonstrated strong potential for analyte differentiation in complex mixtures as demonstrated by a study cases where methanol content was estimated in both real and synthetic wine samples.

Keywords: Quartz Microbalances, porphyrinoids, e-nose, array, VOCs, gas, methanol, wine

1. Introduction

Corroles and related macrocycles are widely employed in the field of chemical sensors, where they are used as sensing materials for optical, electrochemical, gravimetric and conductometric transducers [1]. Specifically, porphyrinoid-based Thickness Shear Mode Resonating sensors (TSMRs) have been widely studied and used with excellent results on different analytes and real samples [2]. An interesting attempt to increase the selectivity towards different analytes was proposed by our group in the past, exploiting a series of porphyrins having different chain lengths covalently linked in the peripheral positions [3]. However, the presence of the alkyl chains improves the metalloporphyrin thin film permeability but at the same time increases the magnitude of non-specific interactions, reducing the influence of the intrinsic metalloporphyrin selectivity. To address this issue, a novel class of N- alkylated free-base corroles is proposed here to be used as sensing material, in order to obtain more homogeneous and selective sensing layers [4]. The insertion of chains with different lengths and numbers in the core of the macrocycle would allow, at the same time, to obtain homogeneous films and an increase in selectivity. Here, we have composed an e-nose using an array of twelve different N-alkyl corroles deposited on QMB, and we have tested it towards different VOCs and gases in order to study the different responses and sensitivities. Thus, we have performed tests on six samples of Italian wines and artificial wines to verify the possible use of our platform for methanol detection.

2. Materials and methods

Free-base N-alkyl corroles are synthesized according to literature methods [5]. Thin layer films are prepared by drop-casting a chloroform solution of porphyrinoids directly onto quartz microbalances (QMBs). The covered QMB were allocated in a plastic chamber, where each sensor was connected to an individual oscillator circuit and frequency variations were measured by means of an integrated frequency counter and then stored on a computer. Organic vapors of the different analytes were generated by bubbling an N_2 stream into a liquid sample of the compound. The saturated vapor concentration of the volatile organic compound was calculated using Antoine's law. Different concentrations of nitric oxide (NO), carbon monoxide (CO), molecular hydrogen (H_2), and carbon dioxide (CO_2) were also tested. The six samples of wine were purchased in local stores. Relative changes in responses have been considered as features, and data analysis is performed in Matlab®.

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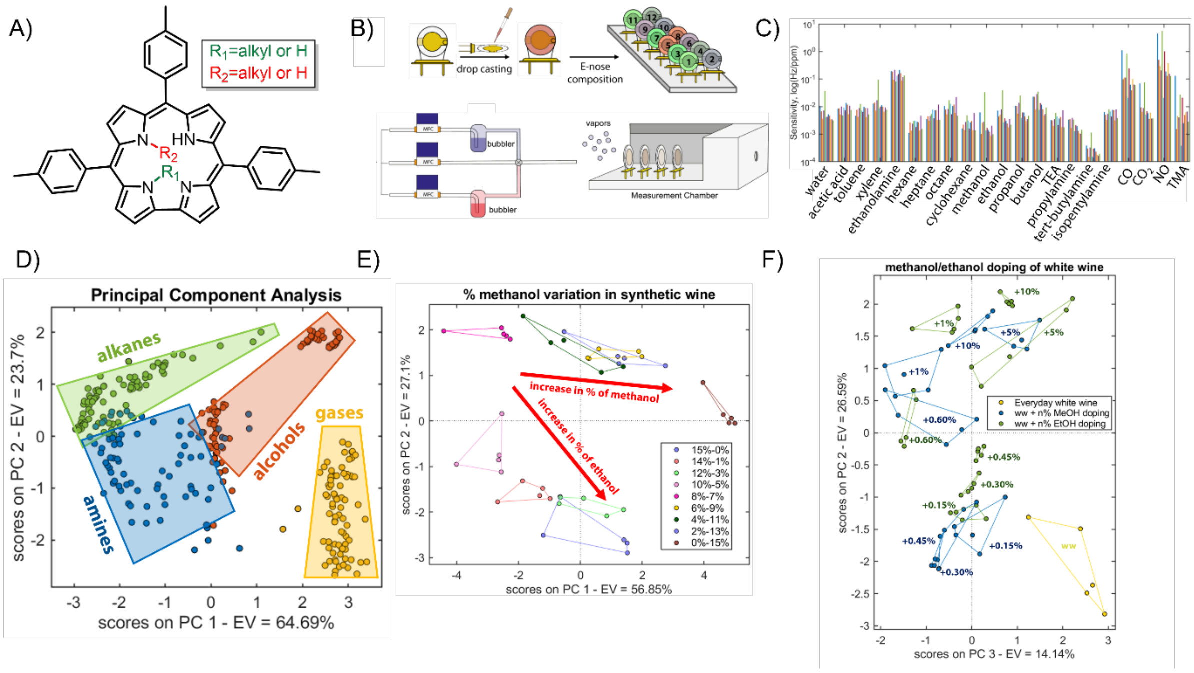

Fig. 1. A) Structure of an N-alkyl corrole B) Set-up for sensor fabrication, the e-nose arrangement and the functioning of the measure. B) Typical sensor response to an analyte. C) Sensitivity of the sensors based on the selected N-alkyl corroles. *D) PCA of experimental data considering responses from a QMB selection towards the classes of gases, alkanes, alcohols and amines. E) PCA of experimental data of methanol percentage variation in synthetic wine.F) PCA of experimental data of different solutions of methanol/ethanol doped white wine.*

3. Result and discussion:

Data analysis allowed the evaluation of sensor sensitivities, revealing strong responses, especially toward CO, NO, and ethanolamine. To understand the influence of the alkyl substituent on sensing performance, the sensors were grouped into series and correlated with LSER parameters of selected analytes. Pearson correlation matrices revealed differences according to the position and length of alkyl chains. Principal Component Analysis (PCA) showed a clear separation of the four main classes of compounds: gases, alkanes, alcohols, and amines. Moreover, a separation along the homologous series of alcohols and alkanes was observed based on the length of the analyte's alkyl chain. These findings confirm the ability of N-alkyl corroles to discriminate among different analytes and support the potentially useful presence of the alkyl chain. Following these results, we finally explored the possibility of using this array for the discrimination of methanol in wine, essential for regulatory compliance and product quality assurance. We first performed tests on six different varieties of Italian wines, obtaining a good separation based on the alcohol content and on the white and red varieties. Finally, two different studies were performed, the first testing wine samples doped with increasing concentrations of methanol and ethanol, the second on synthetic wine samples prepared using different ethanol/methanol ratios. Both studies confirmed the effectiveness of the array to discriminate between the two alcohols in different conditions, paving the way for several possible applications in environmental and agri-food monitoring.

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