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Near infrared chemo-responsive dye intermediaries spectra-based in-situ quantification of volatile organic compounds

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ABSTRACT

Volatile organic compounds (VOCs) detection and measurement in materials with near infrared spectroscopy (NIRS) have been an unresolved constraint till date. This paper focused on the use of NIRS for rapid detection and quantification of pure VOCs (ethanol, ethyl acetate and acetic acid) in mixed VOCs via employing sensitive intermediary chemo-responsive dyes as capture probes, whose NIRS spectra were scanned, preprocessed and used to build partial least squares (PLS) prediction models. Average predicted rates based on the PLS-built prediction models for the pure VOCs in the mixed VOCs yielded 98.60 ± 17.41%. 78.26% of the pure VOCs prediction rates ranged between 85 and 114% and normally distributed. The high prediction rates achieved imply the technique may be deployed as a panacea to widen the usage scope of NIRS and e-nose based colorimetric sensors for rapid detection and quantification of VOCs content in materials which hitherto had been a constraint for both systems.

1. Introduction

This paper attempted the rapid detection and quantification of volatile organic compounds (VOCs) based on NIRS chemo-responsive dyes spectral data extraction technique. NIRS has been applied to detect chemical compounds in liquids and solids [1,2], but has limitation for the detection of chemicals in gaseous substances like VOCs albeit these volatile compounds provide essential information on the quality and safety of various edible and inedible materials. Currently, NIRS and e-nose based sensors cannot be used for pure VOCs quantification in materials. Porphyrins dyes are known to bind with various volatiles leading to intense colour changes [3,4], as a result of their strong molecular interactions [5,6]; and the coordination mechanism of their central metals with VOCs [7,8]. Porphyrins dyes are sensitive to a wide range of volatiles [9,10] with none known to be specifically sensitive to any VOC [11]. Porphyrins-based dyes have been variously applied in colorimetric sensors for the detection of groups of closely related volatiles [12,13]. Although triacetone triperoxide (TATP) detection has been attempted using the colorimetric sensors [14], they have not yet been exhaustively explored for detecting and quantifying specific VOCs. Moreover, volatile organic compounds have been reportedly used for monitoring the quality or otherwise conditions of various edible and inedible materials – detection of adulteration and classification of food into different quality grades [15,16] and the diseased conditions of patients based on their breath odour [17,18]. Although various VOCs have been used to monitor quality or diseased conditions of materials in the aforementioned studies, specific VOCs have been reported in other studies as the precise indicators or signals of state or conditions – ethylene as an indicator of ripeness in apple [19]; and hydrogen sulphide, rottenness of egg [20]. It therefore presupposes that the quantification of specific VOCs in materials may enable ascertainment of their respective thresholds of specific VOCs that may necessitate the description of materials as being quality or otherwise with speed and on nondestructive basis. To address such a challenge, the development of an innovative technique with the capability of quantifying VOCs rapidly becomes relevant since no known technique exists currently for addressing this concern. Gas chromatography combined with mass spectrometry (GC–MS), a hyphenated technique is currently the most accurate system for VOCs quantification in materials but requires time and lacks nondestructive ability because it requires sample pretreatment. Electronic nose systems employing different types of sensors such as metal oxide sensors (MOS), polymer coated surface acoustic wave (SAW) devices among others have been utilized successfully for the identification and discrimination of different volatile organic compounds [21,22]. However, e-nose based sensors lack chemical specificity, hence unable to distinguish between closely related VOCs to allow for their quantification [13]. Albeit the e-nose systems based on col-

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orimetric sensors arrays (CSA) which are composed of cross reactive porphyrin dyes and designed with the underlying principle of dye-analyte interactions have been reported to produce a comparatively high specificity for chemical compounds in complex mixtures, their application is currently limited to identification and discrimination of VOCs in complex mixtures in agricultural and biological materials [16]. Nonetheless, no attempt has yet been reported on the use of e-nose based CSA for quantification of VOCs. Hence, an attempt to design a technique that harnesses the binding potential of porphyrin-based dyes to VOCs, and the subsequent acquisition of the NIRS spectra of the bound VOCs to chemo-responsive dyes for the quick detection and quantification of pure VOCs is germane towards providing an antidote to the existing NIRS and e-nose VOCs quantification limitations. In addition, this technique holds promise and potential for broadening the usage scope of NIRS and e-nose systems as well as their application in monitoring occurrences (natural or artificial), and their effects in terms of indicating quality and safety precipitated by the presence of different estimated amount of specific VOCs in materials nondestructively and speedily. The success of this attempt consequently will enable quality and safety assurance for materials whose quality and safety are VOCs dependent such as food and biological materials.

In the quest to design a system with high potentials for above stated applications, this paper explored the binding ability of two selected porphyrin-based dyes namely: 5,10,15, 20-Tetraphenyl-21H,23 H-porphine zinc (TPP-Zn); 2,3,7,8,12, 13,17,18-Octaethyl-21H,23H porphine manganese (III) chloride (OEP-Cl-Mn); and a pH indicator, bromocresol green (BMG); by exposing them to pure and mixed VOCs made up of ethanol (C_2H_6O), ethyl acetate ($CHCOOC_2H_5$) and acetic acid ($C_2H_4O_2$) as capture probes highly sensitive to each of the respective pure VOCs in their volatile mixtures. Thereafter, NIRS spectra data prior and post chemo-responsive dyes and VOCs interactions were captured, and used via the aid of partial least squares (PLS) built chemometric algorithm models, to attempt the identification and quantification of each pure VOC in the mixed VOCs nondestructively and rapidly. This pioneering attempt at exploring the use of NIRS data on porphyrin based dyes interactions with VOCs for odour 'measuring' may revolutionize the use of NIRS for gaseous compounds identification and quantification in materials; quantification of odour by e-nose systems; as well as applied to the detection and measurement of VOCs leakages in materials whose variations and threshholds may denote and allow the prediction of various natural and artificial occurrences in agricultural and biological materials, thus enable their quality and safety monitoring to be carried out rapidly and noninvasively.

2. Materials and methods

Ethanol, ethyl acetate and acetic acids were selected for this study to explore the potential of this innovative technique for their quantification, with the fore knowledge of the close relatedness of the three VOCs. For instance, the mixing of acetic acid and ethanol results in the production of ethyl acetate. The choice of the pure VOCs used is based on the assumption that the ability of the technique to distinctly identify and quantify these closely related VOCs may prove it as more potent for the identification and quantification of other distantly related VOCs such as benzene, xylene, aldehyde, chlorinated compounds among others, some of which are known to be harmful to humans.

The porphyrin dyes used in the study were selected based on quantum chemistry calculations and verified by experiments

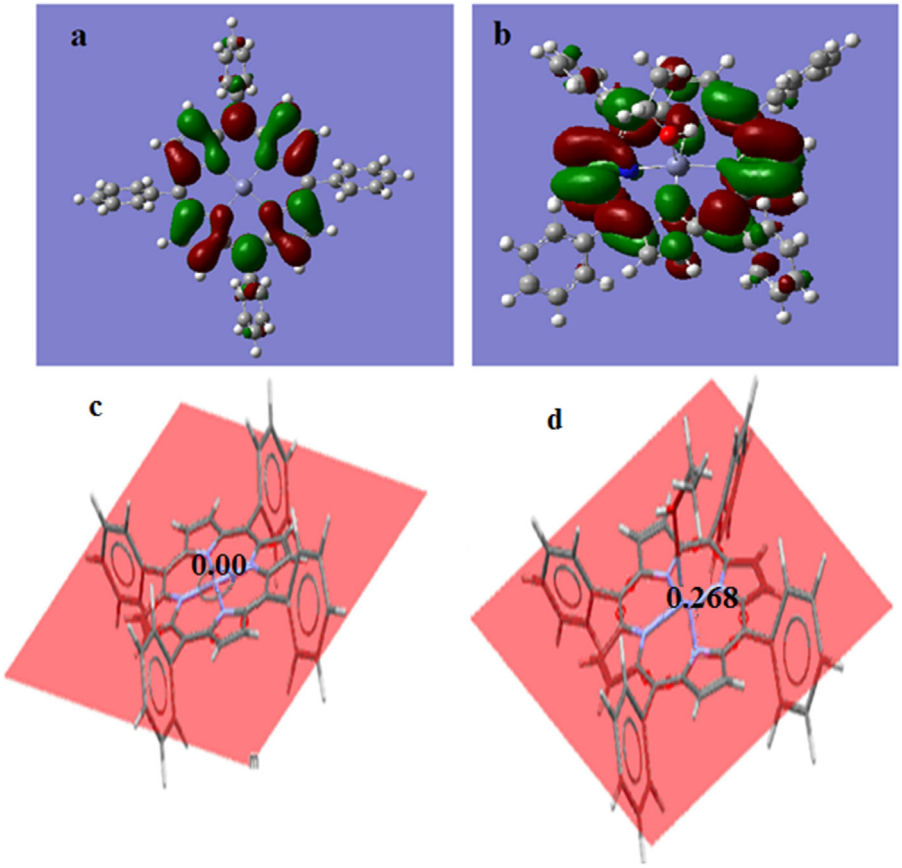

Fig. 1. Model of porphyrin-dyes based on TDDFT calculations at B3LYP/6-31G (d) level **(a)** prior VOCs exposure, and **(b)** post VOCs exposure; change in the horizontal displacement deviations from the plane of the ZnTPP **(c)** before and **(d)** after exposure to ethanol.