



Analytical Methods

Discrimination of fresh fruit juices by a fluorescent sensor array for carboxylic acids based on molecularly imprinted titania



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ABSTRACT

Design of chemical sensor arrays that can discriminate real-world samples has been highly attractive in recent years. Herein a fluorescent indicator-displacement sensor array for discrimination of fresh fruit juices was developed. By coupling the unique high affinity of titania to electron-donating anions and the cross-reactivity of molecularly imprinted materials to structurally similar species, a small array was fabricated using only one rhodamine-based fluorescent dye and three synthesized materials. Citric, malic, succinic and tartaric acids were chosen as indices. The recognition mechanism was investigated by spectrofluorimetric titration using a non-linear Langmuir-type adsorption model. The proposed method was applied to discriminate thirteen fruit juices through their carboxylic acid contents. Principal component analysis of the data clearly grouped the thirteen juices with the first principal component owning 98.2% of the total variation. The comparison of the sensor array with HPLC determination of the carboxylic acids was finally made.

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1. Introduction

Design of chemical sensor arrays that can identify multiple analytes and complex mixtures has been attracting tremendous analysts' interest (Albert et al., 2000; Wright & Anslyn, 2006). The pattern-based response obtained not from any single selective sensor but an assembly of cross-reactive sensors composes a unique fingerprint for each analyte. The excellent works of Anslyn (Edwards, Sager, McDevitt, & Anslyn, 2007; Gallagher et al., 2012; Zhang, Anslyn, & Qian, 2012; Zhang, You, Anslyn, & Qian, 2012), Anzenbacher (Anzenbacher, Li, & Palacios, 2012; Palacios, Nishiyabu, Marquez, & Anzenbacher, 2007), and Suslick (Musto, Lim, & Suslick, 2009; Suslick, Feng, & Suslick, 2010; Zhang, Bailey, & Suslick, 2006; Zhang & Suslick, 2007) have highlighted the recent shift in the application of chemical sensor arrays from single analytes to complex mixtures. Impressive examples include the identification of red wines (Gallagher et al., 2012), black teas (Zhang, Anslyn, et al., 2012), soft drinks (Edwards et al., 2007; Zhang et al., 2007), toothpastes (Palacios et al., 2007), beers (Zhang et al., 2006), and coffee grounds (Suslick et al., 2010).

Conventional methods to construct chemical sensor arrays typically involve the synthesis of individual receptors and chromophores/fluorophores as sensing elements or the selection of

commercially available indicators. Inspired by the pioneer works of Shimizu and co-workers (Greene, Morgan, & Shimizu, 2004; Greene & Shimizu, 2005; Shimizu & Stephenson, 2010), we have proposed an alternative approach for chemical sensor arrays. Our previous works have been based on molecularly imprinted silica and achieved the discrimination of metal ions and saccharides by the use of 8-oxyquinoline and phenylboronic acid appended triethoxysilane as functional monomer, respectively (Tan, Wang, & Yan, 2009a, 2009b). For a specific group of analytes, however, design and preparation of effective fluorescent functional monomer proved to be challenging. Besides, the synthesized functional monomer can only be applied to the given group of analytes. To overcome these limitations, it is necessary that the molecularly imprinted sensor be cross-responsive to several different kinds of target. To this end, we chose titania as the host material instead of silica. Taking advantage of its unique high affinity to electron-pair donating compounds such as the ionized carboxylic and sulphonic in aqueous solutions (Nawrocki, Dunlap, McCormick, & Carr, 2004), we have recently reported the functional monomer-free synthesis of titania-based molecularly imprinted materials for the solid-phase extraction (SPE) of nicotinic acid (Tan, Li, Li, & Jiang, 2013) and sulphonic acid food colourants (Li, Li, Tan, & Jiang, 2013), respectively. Here, we report the exploitation of this approach to the facile construction of molecularly imprinted sensor array for carboxylic acids.

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Carboxylic acids are an important group of organic acids in fruits and their products. Citric, malic, succinic, and tartaric acids are natural carboxylic acids most commonly found in fruits (Fig. 1). The profile and concentration levels of these organic acids are significant parameters for fruits' products such as juices and wines. The contents of these low molecular weight organic acids differ much in different fruits. For instance, malic and citric acids are the most characteristic acids in apples and lemons, respectively. They are also the predominant organic acids in pears and oranges, however, the contents of the two acids are distinct in different kinds of fruit. Even for a same kind of fruit, the contents of carboxylic acids vary in different varieties and geographical origins (Flores, Hellín, & Fenoll, 2012; Liu, Ding, & Tang, 2014; Nawirska-Olszańska, Biesiada, Sokół-Łętowska, & Kucharska, 2014; Scherer et al., 2012).

While several analytical methods are feasible for the analysis of carboxylic acids (Mato, Suárez-Luque, & Huidobro, 2005), array-based sensing provides an alternative approach for the discrimination of carboxylic acids. Davey, Zuccheri, Trapp, and Bunz (2011) constructed a small array composed of three reactive cruciform fluorophores in six different solvents. The array can identify ten different aromatic carboxylic acids based on protonation-induced fluorescence shifts. Gallagher et al. (2012) developed a 3×3 array composed of three boronic acid and guanidinium group functionalized tripodal receptors and three fluorescent indicators, and achieved the discrimination of three organic acids and six wine varieties. Herein, we design a molecularly imprinted sensor array using only one fluorescent indicator and avoiding the use of traditional functional monomer. We utilize the titania-based molecularly imprinted sensor array to discern four common carboxylic acids and show the feasibility of applying the array to differentiate fresh fruit juices of different kinds and varieties.

2. Materials and methods

2.1. Materials and chemicals

All reagents used were of at least analytical grade and used without any further purification unless otherwise specified. Ultrapure water was used throughout the experiments. Citric acid (CA), L-malic acid (MA), succinic acid (SA), L-tartaric acid (TA), HCl, NaOH, ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25%), and formamide were obtained from Guangfu fine chemical research institute (Tianjin, China). Lissamine rhodamine B (LRB) was purchased from Jingchun Reagent Co., Ltd. (Shanghai, China). H_3PO_4 , NaH_2PO_4 , and MeOH of chromatographic grade were bought from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Titanium isopropoxide ($\text{Ti}(\text{OPr}^i)_4$) was purchased from Taichang Chemical Co., Ltd. (Tianchang,

China). Thirteen kinds of fresh fruit including four varieties of apple (Fuji apple, Red Delicious, Ralls Genet, and Gala apple), four varieties of pear (Snowflake pear, Crystal pear, Yantai pear, and Huangguan pear), and five kinds of Citrus fruit (Tangerine (*Citrus tangerina*), Mandarin orange (*Citrus reticulata*), Orange (*Citrus sinensis*), Grapefruit (*Citrus paradise*), and Lemon (*Citrus limon*)) were bought from local supermarket.

Carboxylic acid stock standard solution (1 mmol L^{-1}) was prepared by dissolving the required amount of carboxylic acid in water. The stock solution was stored in the dark at 4°C and was stable within 1 week. Working solutions of lower concentrations were freshly prepared from the above stock solution prior to use.

2.2. Instrumentation

Scanning electron microscopy (SEM) images were taken on an SS-550 microscope (Shimadzu, Japan) operated at 15 kV. UV-vis absorption spectra were measured with a U-3900 UV-vis spectrophotometer (Hitachi, Japan). IR spectra ($4000\text{--}400 \text{ cm}^{-1}$) in KBr were recorded on a Magna-560 spectrometer (Nicolet, USA). Fluorescent spectra were obtained with a 970CRT fluorescent spectrometer (INESA, China). HPLC analysis was operated with an Agilent 1200 system (Agilent, USA) consisting of an isocratic pump (model G1310A), a UV detector (model G1314B) and an injection valve (model G1328B) with a $20 \mu\text{L}$ loop. An Alltima™ C18 column ($250 \text{ mm} \times 4.6 \text{ mm I.D.}$, $5 \mu\text{m}$, GRACE, USA) was used with a Yamatake HT-230A column oven.

2.3. Materials synthesis

In a typical synthesis of molecularly imprinted material, HCl (0.82 mL, 10 mmol) was added to $\text{Ti}(\text{OPr}^i)_4$ (2.85 g, 10 mmol) under ice bath and stirring condition. The mixture was stirred for 5 min, and water (3.16 mL) in which template (0.4 mmol) was dissolved in advance was drop-wisely added to the mixture. Consequently, formamide (0.4 mL, 10 mmol) was added to the mixture. The homogeneous solution was stirred for another 5 min and then poured into a glass tube, sealed with parafilm and allowed to gel at 30°C for 1 day. Subsequently, the resultant gel was aged at 30°C and 60°C each for 2 days, and then dried in ovens at 100°C for 1 day. The obtained dried gel was ground into fine powder in a mortar, extracted with 200 mL 0.1 M NaOH to remove the template, rinsed with copious water and dried in vacuum. The final dried material was sieved through steel sieves. The particles between 200 and 400 meshes were collected for further use. CA and MA were chosen as the template and hence CA imprinted material (CAIM) and MA imprinted material (MAIM) were obtained. The control blank non-imprinted material (NIM) was prepared in parallel in the same way just without the addition of template.

2.4. Fluorescence measurements

In the spectrofluorimetric titration with LRB, to a set of 10 mL calibrated test tube 5.0 mg of the materials and a given concentration of LRB solution were sequentially added. In the spectrofluorimetric titration with carboxylic acids, to a set of 10 mL calibrated test tube 5.0 mg of the materials, 1.0 mL of 10^{-5} M LRB and a given concentration of carboxylic acids solution were sequentially added.

In the array study for four carboxylic acids, to a set of 10 mL calibrated test tube 5.0 mg of the materials, 1.0 mL of 10^{-5} M LRB and 1.0 mL of 10^{-4} M carboxylic acid solution were sequentially added. The four carboxylic acids were tested against the array (NIM, CAIM and MAIM) for five times.

In the test of real-world samples, fresh fruits were washed, peeled and cored. Fresh juices were obtained by squeezing the

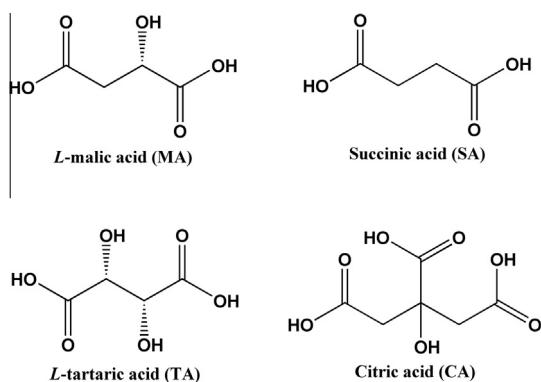


Fig. 1. Chemical structures of four carboxylic acids commonly found in fruits.

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