## Colorimetric Sensor Arrays for the Detection of Aqueous and Gaseous Analytes

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In the past decade, there has been great interest concerning the development of artificial sensing devices; most notably optoelectronic tongues and noses.<sup>1-5</sup> Utilizing previous research on how the mammalian gustatory and olfactory systems operate, significant progress in mimicking these systems has been realized.<sup>6-9</sup> The turning point in this field of research has been the discovery that the mammalian senses of smell and taste are not based on specific receptors for each stimulant, but rather an array of semi-specific receptors that function simultaneously to produce a pattern. This pattern is interpreted in the brain, and classified either as a known stimulant or a new analyte similar to a known family of tastes or odors.

As a predominantly visual species, we are programmed to acknowledge visible reports to chemical reactions over alternative reporting methods. Thus, colorimetric sensing can be more advantageous than other techniques and can allow for a greater number of chemical reactions to be probed.

One colorimetric approach to sensing involves the immobilization of cross-responsive chemosensors capable of showing a color change upon reaction with analytes or mixtures of analytes.<sup>10-12</sup> The employment of porous glasses as an immobilization technique has allowed for facile detection of analytes, both aqueous and gaseous, by allowing dye-analyte interactions to occur while preventing the sensor dye from escaping from the matrix. In this manner, colorimetric sensor arrays have been fashioned that are capable of discriminating among structurally similar compounds such as sugars,<sup>13,14</sup> while retaining the ability to detect a wide range of analytes including toxic industrial chemicals.<sup>15,16</sup>



**Figure 1.** Color difference maps of six representative table-top sweeteners and one control. Sweeteners whose active ingredients are non-nutritive (e.g., Equal, Sweet'n'Low, Splenda) are differentiable, even by eye, from the natural or nature-based sweeteners.<sup>14</sup>

For aqueous detection, the newly developed porous glasses successfully immobilized otherwise soluble dyes that could detect changes in solution pH, caused by boronic acid-diol interactions. This allowed for rapid and sensitive detection and identification of natural and artificial sugars<sup>13</sup> and sweeteners. Further experiments showed the array's ability to differentiate between a selection of common table-top sweeteners such as Equal<sup>®</sup>, Sweet'N'Low<sup>®</sup>, Splenda<sup>®</sup>, and natural sugars.<sup>14</sup>

Gas sensing applications were made possible by slight modifications to the liquid sensing array. Hydrophobic silica precursors were added to limit the effect of changing humidity on the array, and printing onto flat, non-porous polymer surfaces gave fast and easy accessibility of incoming analytes to the immobilized indicators. Stable and sensitive colorimetric arrays for the detection and semi-quantification of a large number of toxic industrial chemicals was made possible by the inclusion of additional indicators capable of colorimetrically reporting changes in polarity, metal ligation, and redox reactions. The performances of these sensing arrays showed extremely low limits of detection, and were capable of identifying toxic gases within a large range of concentrations; ppb up to concentration immediately dangerous to life and health.



**Figure 2.** Schematic representation showing the premise behind a new and highly sensitive method for the detection and semi-quantification of gaseous formaldehyde. A change in local pH caused by the reactions between the analyte gas and the matrix are reported via polymer-immobilized indicators.<sup>17</sup>

In order to improve upon the detection limits for weakly responding gaseous analytes, such as formaldehyde, alternative methods were developed.<sup>17</sup> It was found that the immobilization of simple and stable color-changing dyes within chemically-reactive matrices could allow for facile and sensitive detection and quantification of formaldehyde. Optimization studies were carried out to assess the proper doping level of hydrophilic polymers with amine-appended polyethylene glycol.

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