Recent Progress in Amine Gas Sensors for Food Quality Monitoring: Novel Architectures for Sensing Materials and Systems

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**ABSTRACT:** The increasing demand for food production has necessitated the development of sensitive and reliable methods of analysis, which allow for the optimization of storage and distribution while ensuring food safety. Methods to quantify and monitor volatile and biogenic amines are key to minimizing the waste of high-protein foods and to enable the safe consumption of fresh products. Novel materials and device designs have allowed the development of portable and reliable sensors that make use of different transduction methods for amine detection and food quality monitoring. Herein, we review the past decade’s advances in volatile amine sensors for food quality monitoring. First, the role of volatile and biogenic amines as a food-quality index is presented. Moreover, a comprehensive overview of the distinct amine gas sensors is provided according to the transduction method, operation strategies, and distinct materials (e.g., metal oxide semiconductors, conjugated polymers, carbon nanotubes, graphene and its derivatives, transition metal dichalcogenides, metal organic frameworks, MXenes, quantum dots, and dyes, among others) employed in each case. These include chemoresistive, fluorometric, colorimetric, and microgravimetric sensors. Emphasis is also given to sensor arrays that record the food quality fingerprints and wireless devices that operate as radiofrequency identification (RFID) tags. Finally, challenges and future opportunities on the development of new amine sensors are presented aiming to encourage further research and technological development of reliable, integrated, and remotely accessible devices for food-quality monitoring.

**KEYWORDS:** volatile amines, biogenic amines, chemiresistive sensors, optical sensors, RFID, wireless sensors, electronic nose, optoelectronic nose, food evaluation

Food quality and safety are of increasing importance, and consumers are focused not only on the taste of food products but also on their quality, safety, and traceability along the supply chain.\(^1,^2\) For instance, consumption of tainted food causes more than 600 million illness cases and more than 400,000 deaths per year.\(^3\) The quality of dietary products can be directly affected along any point of the food chain by temperature variations, cross contamination during food handling, or improper storage. As a result, food quality is of prime importance for both consumers and the food industry, and this need is best addressed by nondestructive, rapid, and reliable methods able to detect and inform on food quality in real-time. Detecting signatures arising from specific volatiles in the headspace of food product packages is an excellent approach to enable food-quality determination without direct contact with the product.\(^7\)

Chemical sensors have been explored as inexpensive and reliable devices that can provide fast responses in the monitoring of gaseous compounds.\(^3,^7,^8\) These devices typically have a sensitive material capable of responding to the target analyte to produce a transduction event (e.g., change in an electrical, optical, or mass dependent mechanical property) to convert a molecular binding/reaction into a measurable signal.\(^9,^10\) Each kind of transduction process presents advantages and drawbacks, and can be chosen according to the intended application. There are cases where the food traceability is important and complementary to quality monitoring, whereas in other cases, the portability is best addressed using wireless communication. It is useful to consider two categories of sensors: those that are specific to individual compounds attained using highly selective recognition methods and those that identify analytes by pattern recognition approaches using sensors with cross-reactivity.\(^1,^12\) Different strategies have been explored for the detection of volatile analytes, including those designed for amines, in a

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variety of designs and transduction methods, as illustrated in Scheme 1. This review provides an overview of the role of volatile and biogenic amines in food-quality determination, followed by a summary of recent progress in amine sensors and sensor arrays, divided according to the transduction method. Lastly, we present an outlook and future trends of sensing devices capable of implementation for food-quality monitoring throughout the supply chain. A careful analysis of amine sensor characteristics and contributions to food-quality determination is expected to be useful in the design of new devices for reliable and fast analytics.

■ VOLATILE AND BIOGENIC AMINES AND THE RELATIONSHIP TO FOOD QUALITY

Food products with high levels of protein content are among the most perishable ones, in which decarboxylation and deamination reactions arise from amino acid degradation by the action of endogenous and microbial enzymes, leading to the formation of both toxic biogenic and volatile amines. These species increase with storage time and are part of the spoilage process. The most common biogenic amines are putrescine, cadaverine, spermidine, and spermine, whereas the most common volatile amines are ammonia, dimethylamine (DMA), and trimethylamine (TMA) (Figure 1). The volatile amines produce off-odors, diminishing the organoleptic quality of food products, and the biogenic amines (nonvolatile) are generally toxic when consumed and harmful to humans. Therefore, the monitoring of volatile and biogenic amine concentrations in food products is a reliable indicator of food freshness, quality, and safety. The characteristic amine compound produced during food spoilage and its concentration will depend on the type of food product. For example, ammonia alone is not a good indicator of fish freshness, and its determination cannot be effectively associated with fish quality. DMA can be considered an effective marker of meat freshness; however it is limited to those species that express the trimethylamine oxidase enzyme. TMA can be assumed to be an indicator of spoilage, but not freshness. It can be present at a constant level in some fresh foods, but its concentration can rise appreciably after 10 days of storage. As a result, the total volatile basic nitrogen (TVB-N) can be considered the best index to determine food freshness and is defined as the sum of primary, secondary, and tertiary volatile amines.

Figure 1. Molecular structure of main volatile and biogenic amines present in food products with their respective boiling points (bp) and melting points (mp).
amines. This approach is more robust and reduces the chances of mistakes or the need for calibration depending on the food product (fish species, red or white meat, red meat cuts—flank, loin, legs, chuck). Over the past years, both the scientific community and government agencies have been working to establish limits of TVB-N for identifying whether a food product with high protein content is fresh or spoiled. Most updated works/guidelines report a TVB-N of <0.15 mg g$^{-1}$ of pork, beef, lamb, or poultry and a TVB-N of <0.2 mg g$^{-1}$ of fish as admissible for intake, and spoilage onset is considered for values over 0.28 mg g$^{-1}$, which is classified as non-acceptable for human consumption.

It is also important to highlight that some national organizations are inclined to recommend more conservative limits of TVB-N. Most reports have focused on the development of amine sensors for food quality that primarily rely on measurement of ammonia or a combination of ammonia and one or two volatile amines.

### AMINE GAS SENSORS: MATERIALS AND MECHANISMS

Sensors designed for amine gas detection can be divided into two major categories: electrical and optical sensors. Electrically transduced gas sensors have been widely explored over the years owing to their design simplicity, low cost, and compatibility with standard electronic technologies. The key concept behind an electrical gas sensor is the variation of the electrical properties of conductive materials when interacting with the target gas analyte. These electrical properties include electrical conductivity/resistivity, the work function, and/or the dielectric constant, which are further translated into a measurable electrical signal, such as current, voltage, electrical resistance, capacitance, or impedance. Among the different types of electrical gas sensors, chemiresistive sensors, in which the resistance of the active sensing material changes upon interaction with the gas molecules, are the simplest and most widely applied devices for the analysis of amines in the gas phase as a result of their

[Figure 2. Schematic representation of the interaction of a typical volatile amine (ammonia) with (A) n-type MOS; (B) conjugated polymers by (i) charge doping, (ii) deprotonation, and (iii) swelling; (C) graphene oxide as general carbon-based material; (D) MoS$_2$ as general 2D material; (E) fluorometric probes via (i) turn-on and (ii) turn-off responses; and (F) metal nanoparticles as colorimetric probes due to the (i) particle aggregation or (ii) etching.]
ease of fabrication, simplicity of operation, cost-effectiveness, and low power consumption. Examples of materials for electrical sensors include the following: metal oxides semiconductors (MOS), conjugated polymers, carbon-based materials, and 2D nanomaterials. MOS are particularly interesting as sensing materials for electrical amine sensors because of their high surface-to-volume ratio, good chemical and thermal stability, high sensitivity, and fast response. Moreover, most of the MOS are n-type materials, which present an increased responsivity in the presence of volatiles with a high reducing power such as amines. N-type MOS have a high affinity for negatively charged oxygen species (e.g., \( \text{O}_2^\text{−} \)), resulting in an electron-depletion layer close to the grain boundaries, as represented in Figure 2A. The physical and/or chemical adsorption of amines onto the MOS surface transfer charge to the adsorbed oxygen species, releasing the entrapped charge carriers back into the MOS bulk, resulting in a decrease in the electrical resistance. Metallic nanoparticles and organic molecules are commonly added to MOS, resulting in hybrid devices. A summary of examples of MOS amine sensors is given in Table 1.

### Table 1. Sensing Approaches for Amine Detection in Gas Phase Employed in Food Quality Evaluation

<table>
<thead>
<tr>
<th>Amine</th>
<th>Sensing material</th>
<th>Transduction method</th>
<th>Sensing parameters</th>
<th>Matrix</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amine</strong></td>
<td><strong>Sensing material</strong></td>
<td><strong>Transduction method</strong></td>
<td><strong>Sensing parameters</strong></td>
<td><strong>Matrix</strong></td>
<td><strong>ref</strong></td>
</tr>
<tr>
<td>Ammonia</td>
<td>PPy/TiO₂ film</td>
<td>Gravimetry</td>
<td>Linear range: 10−250 ppm</td>
<td>Fish</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>CA-FITC/CA-PpIX film</td>
<td>Optical (Fluorimetric)</td>
<td>Linear range: ((5−2.5) \times 10^6 \text{ ppm})</td>
<td>Shrimp and crab</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>HPQ:Ac</td>
<td>Optical (Fluorimetric)</td>
<td>Concentration range: 10−360 ppm</td>
<td>Sensitivity: 0.097%</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Ag@MoS₂</td>
<td>RFID</td>
<td>LOD: 8.4 ppm</td>
<td>Pork</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>PTS−PAni</td>
<td>RFID</td>
<td>Linear range: 0−30 ppm</td>
<td>Pork</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>TiO₂/Ti₃C₆Tₓ</td>
<td>Electrical</td>
<td>Linear range: 50 ppb to 30 ppm</td>
<td>Fish</td>
<td>58</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>(β-D-GP)/silver ions/agarose hydrogel</td>
<td>Optical (Colorimetric)</td>
<td>Linear range: 28.5−114.9 nM</td>
<td>Fish</td>
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<tr>
<td></td>
<td>Au NRs/RMA/AgNO₃ hydrogel</td>
<td>Optical (Colorimetric)</td>
<td>Linear range: 11−200 nM</td>
<td>Salmon fish and beef</td>
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<tr>
<td></td>
<td>TPEBA-based fluorescent film</td>
<td>Optical (Fluorimetric)</td>
<td>Linear range: 1.7−26.4 ppm</td>
<td>Fish</td>
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</tr>
<tr>
<td></td>
<td>SWCNT−N₂F₂CO₂H</td>
<td>Electrical</td>
<td>Linear range: 5−40 ppm</td>
<td>Seafood</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Naphthyl end-capped terthiophene</td>
<td>Electrical</td>
<td>Linear range: 2,110−16,880 ppm</td>
<td>Pork, chicken, and fish</td>
<td>63</td>
</tr>
<tr>
<td>Cadaverine</td>
<td>porous PLA film/ CaCO₃ NPs</td>
<td>Optical (Colorimetric)</td>
<td>Linear range: 0.1−6.0 mg/mL</td>
<td>Pork</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>PTS−PAni</td>
<td>Optical (Colorimetric)</td>
<td>Linear range: 0−15 s</td>
<td>Pork</td>
<td>65</td>
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<tr>
<td></td>
<td>Double-walled chiral nanotubes</td>
<td>Optical (Colorimetric)</td>
<td>Linear range: 0.1−6.0 mg/mL</td>
<td>Pork</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>PTCN fluorescent tag</td>
<td>Optical (Colorimetric)</td>
<td>Linear range: 0−15 s</td>
<td>Pork</td>
<td>67</td>
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<tr>
<td>Putrescine</td>
<td>CMA-Cl</td>
<td>Optical (Fluorimetric)</td>
<td>Linear range: 0−200 mM</td>
<td>Fish</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>PPAB dyes</td>
<td>Optical (Colorimetric)</td>
<td>Linear range: 5−40 ppm</td>
<td>Pork</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>NPTH</td>
<td>Optical (Colorimetric)</td>
<td>Linear range: 5−40 ppm</td>
<td>Pork, salmon</td>
<td>70</td>
</tr>
</tbody>
</table>

**PPy**: polypyrrole; **CA**: cellulose acetate; **FITC**: fluorescein isothiocyanate; **PpIX**: protoporphyrin IX; **HPQ:Ac**: 2-(2-hydroxyphenyl)quinazolin-4(3H)-one; **PTS**: p-toluene sulfonate hexahydrate; **PAni**: polyaniline; **polyβ-D-GP**: β-D-glucose pentaacetate; **RRs**: nanorods; **RMA**: resorcino monoacetate; **TPEBA**: tetraphenylethylene derivative; **SWCNT-N₂F₂CO₂H**: sidewall modified single-walled carbon nanotubes with methyl 4-azido-2,3,5,6-tetrafluorobenzoate; **CMA-Cl**: 7-diethylaminocoumarin derivative; **PLA**: poly(lactic) acid; **NPs**: nanoparticles; **PPAB**: pyrrolopyrrole aza-BODIPY; **NPTH**: nitrated polythiophene.
Materials with improved sensitivity, selectivity, response recovery, and temperature of operation.\textsuperscript{5,31}

Conjugated polymers (including conducting and semiconducting ones) are versatile candidates for amine sensors, presenting good performance as active sensing elements in electrical sensors.\textsuperscript{31,32} Amines can interact with polymers by chemical interactions or intermolecular H-bonding, changing the electrical properties of the polymer.\textsuperscript{8} The sensing mechanism can be governed by the gas inducing a charge doping such as Lewis acid and base behavior (Figure 2B(i)). Another possible mechanism is the polymer deprotonation by the amine analyte, as reported for polyaniline (Figure 2B(ii)).\textsuperscript{8} Such a mechanism brings an advantage of high selectivity if other organic analytes, such as nonpolar volatile organic
compounds (VOCs), present a very weak interaction with conductive polymers. Besides these two mechanisms, polymers can also respond to gaseous amine as a consequence of swelling, which extend the interchain distance (Figure 2B(iii)), increasing the electrical resistance within the polymer network. Moreover, these mechanisms also justify gravimetric sensors (mass variation) and optical sensor (Lewis acid/base and hydrogen bonding) responses to amines. Disadvantages such as slow response and poor selectivity have been countered by the polymer arrangement in hierarchic designs such as fibrous membranes and molecular imprinted polymers.

Carbon-based materials have also been used in electrical sensors for amine detection. For example, carbon nanotubes (CNTs) can experience a shift in Fermi level when exposed to ammonia, reducing the material conductance. The CNT functionalization with metallic nanoparticles and side groups improves the selectivity, whereas hybrid CNT structures can improve the CNT sensitive performance. Other carbon-based structures employed in sensors for amine detection include graphene, graphene oxide (GO), and reduced graphene (rGO). The graphene sensitivity and selectivity can be tuned by controlling the presence of defects, dopants, and functional groups. Graphene-like materials have attracted attention because of the relatively low cost, possibility of large-scale production, and structures that are abundant in defects and chemical groups, facilitating gas adsorption. Despite the fact that amine can be considered a mild electron donor when interacting with GO, an improved response can be observed which might be attributed to the amino group interaction with the adsorbed species (OH−) (Figure 2C). The amine gas detection mechanism for graphene-based materials relies on this interaction and the consequent increase in charge density decreasing the material resistance.

Transition metal dichalcogenides (TMDs) (e.g., MoS2), metal organic frameworks (MOFs), and MXenes are 2D materials that have emerged as alternatives for amine detection, representing the future of sensing materials. Like MOS, the sensing mechanism of n-type inorganic 2D materials is based on increasing the surface charge density by the interaction with reducing amine vapors (Figure 2D). Besides, the adsorption of amine molecules on an n-type 2D nanomaterial can result in induced lower Fermi level, closer to the conduction band, decreasing Schottky barrier, and so resulting in an higher conductivity.

Among the different optical transduction mechanisms, colorimetric and fluorescent sensors are the most common approaches employed in the monitoring of amine vapors. The colorimetric approach can be based on either changes in the adsorption of amine molecules on an n-type 2D nanomaterial, or turn-on and turn-off responses. Sensors with turn-on behavior exhibit decreasing fluorescence intensity (fluorescence quenching) with increasing analyte concentration (Figure 2E(i)). In sensors with turn-off behavior, the analyte increases the fluorescence intensity as a function of analyte concentration (Figure 2E(ii)). The most important functional materials for optical sensing include organic and synthetic dyes, conjugated polymers, noble metal, and metal oxide nanostructures, and quantum dots. Since the pH shifts from low to high with the increase of TVB-N, synthetic dyes and naturally occurring compounds with the ability to change their colors with pH can be applied as spoilage indicators. These compounds undergo protonation/deprotonation, chemical or redox changes, resulting in structural and/or steric changes of the molecules. Synthetic polymers such as polydiacetylene (PDAs) can also be used as colorimetric indicators due to the sensitivity dependency of the amine interaction with PDA functional groups and amine molecular weight. Metal nanoparticles (e.g., Au and Ag), known to exhibit localized surface plasmon resonance (LSPR), have also been used as colorimetric probes. The plasmonic character of these nanomaterials varies as a function of particle aggregation or etching, and therefore their color in solution can be used as an analytical tool for the colorimetric detection of amines.

To date, a myriad of sensing platforms has been successfully prepared following different approaches for detecting volatile and biogenic amines in different high-protein foods. The different strategies employed for this purpose are discussed in the next section according to the transduction method, while Table 1 summarizes some interesting sensing approaches reported in the literature in the past few years.

### AMINE GAS SENSORS

**Electrical Sensors.** Conjugated oligomers and polymers have been widely employed in the development of chemiresistive sensors. For instance, Liu et al. studied the effect of naphthyl end-capping groups on the chemiresistive sensing performance of terthiophene derivatives, NA-3T-NA and NA-3T (Figure 3A(i)), toward aromatic biogenic amines (BAs) (e.g., dopamine, histamine, tryptamine, and tyramine) and TMA. The authors observed that the presence of two-end-capping naphthyl moieties in the NA-3T-NA enhanced the charge transport, improving the sensitivity of the corresponding film sensor. Specifically, as shown in Figure 3A(ii), they observed sensitivity increases of 28% for TMA, 68% for dopamine, 120% for histamine, 83% for tryptamine, and 198% for tyramine. With TMA as an example, the NA-3T-NA-based film sensor displayed a linear response over the concentration range from 2,110 to 16,880 ppm and a detection limit (LOD) of 22 ppm. Moreover, as illustrated in Figure 3A(iii), a thin-film sensor was successfully used for the evaluation of pork, chicken, and fish freshness by monitoring the presence of BAs for 5 days at 4 and 25 °C. Polyaniline (PANI) films have also been applied for food-quality monitoring. Specifically, PANI synthesized by in situ chemical oxidative polymerization was deposited by spray coating onto flexible interdigitated electrodes (IDE) and then used for ammonia gas detection. The authors observed that the electrical response increased linearly with the increasing of ammonia concentration, which was attributed to the reversible redox reactions accompanying ion exchange between the ammonia molecules and the PANI films. The sensor displayed a stable linear response to ammonia gas in the concentration range of 50–150 ppm and was able to evaluate meat and sheep liver freshness in real-time. Moreover, the sensor exhibited excellent mechanical stability and no lack in performance even after several bending cycles.

Chang and co-workers employed P3HT (poly(3-hexylthiophene)), a semiconducting conjugated polymer, as a sensing layer for the analysis of volatile amines from three types of spoiled fish (tilapia, beltfish, mackerel), as illustrated in Figure 3B.
The sensor was able to detect ammonia, DMA, and TMA in the ppb regime within 1 min. The reactions between the volatile amines and P3HT film were explained in terms of redox reactions, as follows: (i) the oxygen in air oxidizes P3HT creating hole charge carriers; (ii) the amine gases physically absorbed on the P3HT and react with the polarons to reduce the polymer chain; (iii) the hole concentration in P3HT then becomes lower resulting in a decrease of the film’s conductance. As shown in Figure 3B(iii), for all three kinds of fish storage at 25 °C, the effective ammonia concentration significantly increased with the storage time.

As previously mentioned, MOS (metal oxide semiconductors), which include n-type (ZnO, TiO$_2$, In$_2$O$_3$, SnO$_2$, and WO$_3$) and p-type (CuO, PdO, and NiO) materials, have been widely exploited as sensing materials for the fabrication of chemiresistive sensors as a result of their high sensitivity and low-cost. The surface-adsorbed oxygen ions play an important role for the sensing mechanism of these materials, and to activate the chemiresistive mechanisms in these materials and achieve reversibility, thermal energy is essential. Consequently, chemiresistive gas sensors based on MOS usually work at elevated temperatures (e.g., 150–400 °C), which can limit their practical application for food quality monitoring. As a result, in recent years, materials design efforts have been devoted to further improving the sensing performances of MOS devices. In this regard, several studies have shown that the sensing responses of MOS can be improved by adjusting their composition, pore structures, and morphologies. For instance, Srinivasan and Rayappan evaluated the influence of the grain features of twinned MnO$_3$ nanorods on their volatile amine sensing characteristics. These investigations were carried out by analyzing the role of microwave irradiation power (300, 450, and 800 W) used in the MnO$_3$ nanorod synthesis on sensing properties. The authors observed that nanorods prepared at 450 W provided a maximum sensing response ($S = R_{air}/R_{gas}$) of 413 toward 200 ppm of TMA, owing to their minimal (53.8 MΩ) grain boundary electrical resistance, thereby indicating that charge transport is facilitated by minimizing grain boundaries. The sensor exhibited a LOD of 1 ppm for TMA, which is lower than the threshold levels (10 ppm) indicative of spoilage in seafood. Doping has also been used to enhance the sensing performance of MOS, as recently demonstrated by Bruce and co-workers. They compared the sensing performance of ZnO and Pd-decorated ZnO nanoflowers with methylamine. Bare ZnO showed a resistivity change of 45.5% to 400 ppm methylamine, whereas the Pd-decorated ZnO sensor exhibited a response of 99.5% under the same conditions. In the same fashion, Wu et al. investigated the influence of Ce doping percentage on the sensing properties of TiO$_2$ nanostructures. BET analysis revealed an increase of the specific surface area and the pore volume with the increase of Ce doping concentration (from 0.17 to 0.43 at%). Consequently, TiO$_2$ nanocrystals doped with 0.43 mol % Ce displayed superior sensing performance at room temperature, including high response (23.99 @ 20 ppm), and LOD of 140 ppb. The improved sensing response was attributed to some factors, including (i) the large surface area (266.9 m$^2$/g), which can provide abundant adsorption sites and improve the efficiency of the interface redox reaction compared with pure TiO$_2$, (ii) the shorter distance between the NH$_3$ molecules and the surface, indicating that Ce incorporation significantly improved the gas adsorption and the electron transfer (Figure 3C(i)), and (iii) the increase in the oxygen vacancies (O$_{vac}$), as illustrated in Figure 3C(ii), which can enhance the donor effect, leading to more surface adsorbed oxygen species and a thicker depletion layer as well as a higher Schottky barrier. The practical application of the sensor was verified by using the Ce-TiO$_2$ nanocrystal gas sensor to detect amine gas generated from fish (Pangasius) spoilage. As shown in Figure 3C(iii), the sensor showed an increased response with the increase in NH$_3$ concentration. Specifically, in the first 6 h, the NH$_3$ concentration.
concentration does not exceed 5 ppm, indicating that the fish maintained acceptable freshness. However, after 12 h storage, the concentration of released gas rapidly exceeded 6 ppm, indicating the fish spoilage.

Recently, significant research efforts have also been concentrated on the development of composite materials. Sensors based on these hybrid materials have shown promising results in terms of sensitivity, detection limit, and capability to operate at room temperature compared to those relying solely on the individual phases, as a result of the synergistic properties of the constituent materials. Using this scheme, a room temperature gas sensor was fabricated with a pigment-sensitized TiO$_2$ thin film as sensing layer. Thin films were prepared by immersing porous TiO$_2$ coatings in solutions containing different natural pigment extracts from spinach, winter jasmine, red radish, and black rice. Films containing black rice extract, which had the highest anthocyanin content, generated the highest electrical response values. This behavior was attributed to the improved interaction between the TiO$_2$ and the hydroxyl and carbonyl groups of anthocyanins. The sensor response increased almost linearly with the methylamine concentration from 2 to 10 ppm. Additionally, the black rice pigment sensitized TiO$_2$ thin film was employed to monitor the freshness of pork meat during storage at 4–6 °C. In another work, Shi et al. developed a sensitive layer based on TiO$_2$-$\gamma$ polyaniline, and silk fibroin fiber (TiO$_2$–PANI/SFF) for the detection of ammonia at room temperature. The TiO$_2$–PANI/SFF sensor showed good sensing performance to 100 mg/L NH$_3$ with a response value ($S = (R_{sp} - R_{sp})/R_{sp}$) of 0.82 and a response time of 10 s. Moreover, the sensor exhibited a good correlation with TVB-N levels for monitoring pork meat, demonstrating its feasibility for meat freshness monitoring.

A diverse range of materials and their combinations, with specific dimensionalities and chemical/electrical properties, have also been explored in the design of amine gas sensors. CNTs, for example, have been proven to be sensitive to electron donating gases, such as amines, even at room temperature. Additionally, their electronic transport properties can be easily modulated by surface functionalization, as reported by Liu and co-workers. In their work, amine vapors were monitored by chemiresistive sensors based on single-walled carbon nanotubes (SWCNTs) noncovalently modified with cobalt meso-arylporphyrin complexes. By tuning the metal oxidation state, the ligand, and the primary coordination sphere of the compound, the sensor exhibited subppm sensitivity, a LOD of 0.5 ppm, and high selectivity for NH$_3$ compared to other tested analytes, as illustrated in Figure 4A(i). The application of the sensor in the monitoring of spoilage in raw meat and fish samples (e.g., chicken, pork, salmon, cod) over several days was evaluated for sample storage at 4 °C and room temperature (22 °C), as shown in Figure 4A(ii). Sidewall modified SWCNTs with perfluorooxyphenyl molecules bearing carboxylic acid or methyl ester moieties have also been employed for the detection of NH$_3$ and TMA at room temperature.

Field-effect transistor (FET)-type gas sensors have also been employed for the detection of amine vapors. For instance, a polymeric FET-based sensor was successfully applied for ammonia and amine detection. This FET sensor was designed using a PTTEH semiconducting polymer (Figure 4B), which is composed of thieno[3,4-b]thiophene units. The proposed sensor showed good selectivity and high sensitivity (down to 10 ppb) toward ammonia and volatile amines (triethylamine, piperidine, or aniline). Furthermore, the authors demonstrated the real-time freshness monitoring for pork and shrimp stored in a refrigerator (0–5 °C) and at room temperature (20 °C) for different times. All the sensing experiments were carried out at low voltages (5 V); therefore, the measurements can be easily powered by batteries, which is advantageous for practical applications.

**Wireless Chemoresistive Sensors.** Materials that present changes in their electrical conductivity in the presence of organic volatile compounds can be integrated with communication circuitry capable of transmitting/receiving information/signals through electromagnetic waves in the radiofrequency (RF) range, resulting in wireless chemoresistive sensors. Because of their typical desired applications (food safety, homeland security, law enforcement, etc.), wireless sensors incorporating complex, expensive, and large pieces should be avoided. Instead, devices must have the features of being lightweight, simple to operate, low-cost, and disposable. Radiofrequency identification (RFID) tags are commercially available devices that match all those characteristics, combining a communication antenna compatible with flexible substrates, with a microchip transponder that is responsible for storing data, processing data, as well as modulating and de-modulating the RF signal.

In an RFID communication event, a tag reader (transceiver), which can be a network analyzer, an impedance analyzer, a digital oscilloscope with fast Fourier transform (FFT) option, or even a mobile phone equipped with near-field connection (NFC) capability, emits (with the aid of a transmitting antenna) a radiofrequency request signal which is received by the tag antenna and decoded by the microchip, establishing a digital communication protocol. The information stored within or detected by the chip is then transmitted back by the tag antenna to the reader. An important characteristic of a RFID tag is related to the transponder power supply. Active tags have a battery, or another power source, attached to the microchip and periodically emit signal pulses containing the stored information to be read by the transceiver. Semipassive tags also have a small on-board battery, but the microchip is only activated when a signal request is received from the transceiver. The method saves power and is smaller and less expensive than active tags. The simplest, least expensive, and smallest options are completely passive tags, which operate without the need of a battery, using the RF power emitted by the tag reader to energize the chip and the transponding resonant RF circuit. Despite the smaller size and cost of completely passive tags, they require a much higher exposure to the RF (to provide enough power) emitted by the transceiver, are more prone to interference, and thereby only operate at shorter distances when compared to their active/semipassive counterparts.

The frequencies of commercial RFID tags are concentrated into bands internationally reserved for industrial, scientific, and medical (ISM) use, to prevent interference with telecommunications. High-frequency (HF) tags operate in a very narrow band centered at 13.56 MHz and have a short-read range (0.1–1 m), being widely used in area access control,
contactless payment cards, ID badges, and asset-tracking systems. Ultrahigh frequency (UHF) tags, on the other hand, are regulated for operation in the 865–868 MHz (European standard) and 902–928 MHz (EUA and Canada standard) ISM bands, presenting longer read ranges (1–12 m), and are being recommended in applications such as store item tracking and supply chain management. Both types of RFID tags have a low cost for bulk production and are compatible with passive communication technology. Although UHF tags permit higher data transfer rates than HF tags, UHF transceivers are considerably more expensive than HF tag readers and are more liable to interfere with other sensitive electronic equipment.

Recent advances in new active materials and devices used in chemical/biochemical sensors have allowed the development of modified RFID tags, which can be applied in intelligent food packing. The detection of volatile compounds in environments simulating food packing can be done by using a passive vapor sensor that presents changes in the resistance in the presence of determined volatile chemicals. By integrating the sensors to the RFID tag circuit, the output signal from the tag changes (signal amplitude, resonant frequency, and/or quality factor) and can be measured by a network analyzer.

The presence of amines released during the spoilage of fish samples could be detected from variations in the pH using a sensitive device based on a hydrogel electrolyte sandwiched between mixed metal oxide and silver/silver chloride (Ag/AgCl) electrodes. The junction capacitance of a varactor connected in parallel to a printed inductor coil (forming an RF-LC oscillator) changes because of variations in the potential difference between the electrochemical cell electrodes. The resonant frequency of the oscillator, wirelessly measured by a network analyzer, presented a linear dependence on the logarithm of ammonia vapor concentration, down to a limit of detection of 1.5 ppm, and the response was correlated with the bacterial growth in fish tissue. Another approach to monitor fish freshness used conductive PANI thin films coupled to HF RFID tags, which displays a modulation in the conductivity in response to the total volatile nitrogen compounds (including ammonia and biogenic amines) resultant from the microbial spoilage. These films showed increased impedance in the presence of ammonia resulting from PANI deprotonation, allowing the detection of concentrations as low as 500 ppt.

A different operation principle for wireless chemoresistive tags was proposed by Fiddes and Yan, wherein they used a set of 16 different polymers mixed with carbon black (CB) to modify commercial HF passive RFID tags that were tested in the presence of water, toluene, ethanol, and ammonia vapor. The swelling of the polymeric phase of the composites caused an increase in the spacing between CB particles, increasing the composite electrical resistance. The tag modification by the composite was done in such a way that a series resistance was added to the tag chip circuit, resulting in a decrease on the RF reflection signal when the composite swelled. Since each polymer has different swelling characteristics, a discriminate response for each volatile chemical was obtained by using an array of different polymer/CB composites. Moreover, the sensor’s initial resistance could be tuned by controlling the amount of composite material used to modify the RFID tags, resulting in calibration curves for each analyte and allowing the determination of the volatile compound concentration. Similar modifications in RFID tags were performed using poly-
(ethylene-co-vinyl acetate) (PEVA), maleic acid (MA), and carbon black composite as active sensing material to detect biogenic amines (putrescine, histamine, cadaverine, spermine, and spermidine). Although some amines resulted in a different response time for the RF reflection coefficient, the system was not able to have a clear discriminate response for each biogenic compound. However, an improved RFID tag response in the presence of the biogenic amine putrescine was obtained by using functionalized multiwalled carbon nanotubes (MWCNTs) as sensing materials.

The RF reflection coefficient, resonant frequency, and quality factor of the tag signal had a different exposure time dependence for each composite modified tag, and this feature allowed discrimination by considering the exposure time necessary to render the RFID tag signal irresponsive (below 30% of reflection at 13.56 MHz). These characteristic exposure times were also used as a quantitative parameter to determine a calibration curve for the putrescine concentration (in the 0−0.5 M range).

An important feature concerning modified RFID tags for detection/identification of chemical compounds described before is that the most important signal is not the digital information stored in the tag microchip, but the analog RF reflection signal, which requires a network analyzer or another laboratory benchtop instrument to be detected/measured. RFID tag readers/transceivers in the HF range are, nowadays, relatively inexpensive, and most mobile phones have the NFC functionality. Therefore, the development of RFID tags for detection of chemical compounds that can be read by widely available devices, such as mobile phones, represents a great opportunity to widely deploy sensors. The earliest report on such use was made by Azzarelli et al. where commercial HF RFID tags were modified to give rise to programmable chemically actuated resonant devices (p-CARDs) with a binary (on/off) response in the presence of different gas-phase compounds (ammonia, cyclohexanone, hydrogen peroxide, and water), at different concentrations. The p-CARD binary response to each analyte was programmed by controlling the series resistance introduced into the tag circuit as a result of the type (or amount) of material added to the circuit. The use of an array comprising four different p-CARDs resulted in a four-bits logic response able to discriminate different gas-phase analytes.

The p-CARDs response could be improved by using more selective and sensitive chemiresistive sensors based on p-toluene sulfonate hexahydrate (PTS) doped PANI nanostructures or hybrid (inorganic n-type/organic p-type) composites comprising SiO$_2$-ZnO nanofibers (NF) and functionalized SWCNTs. PTS−PANI modified tags have the advantage of being compatible with inkjet printing, presenting a high chemoresistive sensitivity ($\Delta R/R_0$) toward 5 ppm vapors of the biogenic amines putrescine (46%) and cadaverine (17%). Wireless sensors based on hybrid SiO$_2$-ZnO NF/SWCNTs structures (Figure 5A) presented a dosimetric sensitivity approximately 40 times higher for amines when compared to other VOCs, allowing the quantitative detection at concentrations as low as 2.5 ppm. Such p-CARDs were successfully tested for detection of biogenic amines released during the spoilage of different kinds of meat (beef, chicken, and fish), presenting a more pronounced response for chicken meat, which usually shows higher emission of volatile amines during spoilage.

Figure 6. (A) (i) Reaction of the fluorescent probe BZCO with amine vapors, (ii) digital image of paper-based BZCO sensor with fresh fish meat and spoiled fish, and (iii) digital image of filter papers loaded with BZCO under UV light with or without propylamine vapor. Reprinted with permission from ref 109. Copyright 2021 Elsevier. (B) (i) Mechanism of action of amine vapor detection using HPQ-Ac and (ii) emission spectra of paper-based platform and HPQ-Ac after exposure to ammonia vapor for 5 min. Reprinted with permission from ref 55. Copyright 2016 American Chemical Society. (C) Illustration of the mechanism of the cellulose-based ratiometric fluorescent material in the detection of ammonia. Reprinted with permission from ref 19. Copyright 2019 Springer Nature.
putrefaction. The variation in the NFC signal resulting from the storage of chicken meat for 72 h at room temperature was enough to change the mobile phone reading status from the “on” state to the “off” state, demonstrating a low cost wireless sensor for monitoring food quality. For meat refrigerated at 4 °C, the time needed for complete attenuation of the NFC signal using a mobile phone increased to 128 h, indicating a delay on the meat spoilage process when lower storage temperatures are used.

Wireless detection of ammonia and biogenic amines (putrescine and cadaverine) was also performed using UHF (in the vicinity of 1000 MHz frequency range) chip-less tags. These tags were produced by spray deposition of molybdenum disulide nanosheets decorated with silver nanoparticles (Ag@MoS₂) onto a nested split-ring resonator (SRR) produced by copper magnetron sputtering deposition through appropriate shadow masks (Figure 5B(i)). A highly sensitive, fast, and low detection limit (<1 ppm for ammonia) response was obtained by measuring the variation in the NFC signal, instead of the antenna reflection coefficient (S₁₁), with this method displaying low interference from environmental (humidity) and directional (antenna angle) conditions. However, a network analyzer was needed for measuring the RF response and considerable data treatment is required to obtain an output parameter. As a result, these sensors are more complex than the binary responses obtained from the NFC and a mobile phone, but the tags successfully monitored spoilage by detecting the presence of 20 mg of TVB-N/100 g from different kinds of meat (pork, mutton, beef, and chicken), as shown in Figure 5B(ii). The method was further demonstrated at a poultry farm to monitor the level of BA and ammonia in the atmosphere.

Optical Sensors. Fluorometric Sensors. Organic and inorganic semiconductors with optical properties can operate as fluorescent probes and are used to create gas sensors. They often provide excellent performance including sensitivity and selectivity, high signal-to-noise ratios, and simplicity of operation as advantages to be explored in food analyses.

Optical fluorescence detection has an advantage over optical absorption detection as a result of its greater sensitivity. In the absorbance methods, the signal is obtained through the difference in intensity between the light absorbed by the reference and the target sample, whereas in fluorescence the use of reference is not always necessary, and the signal intensity can be measured directly. Furthermore, absorbance is measured in the bright reference beam, and in ideal cases fluorescence is measured against a dark background, facilitating the detection of low levels of fluorescent light.

Organic fluorescent probes have been most widely used in the vapor phase detection of small molecules. Meng et al. reported a paper-based, portable sensor for the fluorescence detection of amine vapors with high sensitivity providing low detection limits and good selectivity, for food spoilage. The material used in the detection platform, BZCO, is an organic molecule based on benzoxazole and coumarin, as shown in Figure 6A. The sensor platform was prepared by coating filter paper with BZCO, which was found to produce an excellent sensory platform. BZCO’s band gap is 3.95 eV and the HOMO energy is deeper as a result of the bonding of the benzoxazole to oxygen of the coumarin, and the LUMO is located mainly on the lactone ring. Hence, in this configuration the benzoxazole moiety in BZCO interrupts the internal charge transfer, leading to weak fluorescence. When BZCO comes into contact with amine molecules, the ether bond is cleaved removing the benzoxazole, and a new chromophore with an intense fluorescence is generated. The authors reported a relatively low detection limit of 3.82 ppm and selectivity for distinguishing amine vapors from other volatile organic solvents.

In a similar approach, Gao and collaborators described the use of a fluorogenic organic molecule based on 2-(2-hydroxyphenyl)quinazolin-4(3H)-one (HPQ) to develop a portable turn-on sensor (HPQ-Ac) for the detection of amine vapors through bond cleavage reactions by aminolysis. This sensor is also paper-based and shows high fluorescence when exposed to amine vapors, and good potential for monitoring food spoilage. As depicted in Figure 6B(i), when in contact with amine vapors, HPQ-Ac undergoes cleavage of the O-acetyl bond and forms the product HPQ, which is highly emissive. The detection limit for ammonia vapor was obtained from the calibration curve (Figure 6B(ii)) and found to be 8.4 ppm, which confirms the suitability of the HPQ-Ac paper-based method for using in portable sensors for the detection of ammonia vapor.

Covalent modification of natural polymers such as cellulose can be used to design fluorescent sensor platforms. In this direction, Jia et al. prepared ratiometric fluorescent cellulose-based materials for the visual and real-time detection of amine compounds in evaluating fish freshness. In this effort, the compound fluorescein isothiocyanate (FITC) was reacted with hydroxyls in the cellulose acetate (CA) chain to generate an indicator, and protoporphyrin IX (PpIX) was attached similarly as an internal reference thereby producing green-light emitting CA-FITC, and red-light emitting CA-PpIX. The materials were electrospun into a high surface area nanofiber network to create a sensory platform to quickly and visually provide amine detection for the evaluation of freshness of shrimp and crabs. The dual emission cellulose-based materials were able to detect ammonia through the mechanism illustrated in Figure 6C. By mixing CA-FITC and CA-PpIX at a ratio of 5:1, the resulting material initially exhibited red fluorescence. Under exposure to ammonia, there were changes in the molecular structure, resulting in an increase in green fluorescence. The authors used fresh shrimp to test the sensor in real-world conditions by placing a smart tag for food freshness monitoring. After certain periods of time, the red fluorescent color of the membrane transformed to a yellowish emission and eventually to green and provided information on the deterioration of the shrimp.

In addition to organic molecules, the combination of photocatalytic, optical, and electrical properties of MOS offer opportunities to create effective gas sensors. Gupta et al. reported the synthesis of ZnO nanostructures for the detection of n-propyl amine (NPA) by calcining polymer fibers containing ZnO. The performance of these sensors depended on the surface area available for interaction with the analyte, and the use of nanostructures becomes very promising. In this work, the sensing potential of the nanomaterial was evaluated using photoluminescence (PL) and cyclic voltammetry. The ZnO nanostructures have a broad absorption band around 254 nm, and the emission spectra exhibited a band around 418 nm. When in contact with NPA vapors, the PL emission intensity of ZnO drastically decreased, a blue shift in the residual emission peak is observed. The PL bands of ZnO are attributed to point defects present in the nanostructures. Active defects are generally present in high density, leading to an intense PL
emission. The NPA vapor interacts with defects in the ZnO nanostructure and releases trapped electrons back into the conduction band, consequently reducing the PL emission intensity. In the fluorescence detection of NPA by the ZnO nanostructures, the authors reported a linear response over the concentration range of 0−500 ppm with a LOD of 12.54 ppm.

Metal−organic structures can also be used as platforms for the detection of amine vapors. For example, Mani et al. used a zinc-based coordination polymer to detect aliphatic amines using the turn-on method. Both coordination polymers (CPs) and MOFs are excellent fluorescence sensor platforms as a result of their fast reversible detection capabilities. MOFs or CPs can have different architectures and pore sizes, and this feature can control interactions at the molecular level between the structure and the analyte of interest. For amine vapor sensing, it is natural to target electron-deficient MOFs or CPs to interact with the electron donating amines and generate strong analytical signals. The detection limit for ethylenediamine found in this work was on the order of 166 μM.

The absence of substantial amine vapors can validate the freshness of fish in a nondestructive measurement. To this end, Lai et al. proposed the development of sensitive, fast,...
reversible, and nanometer-thick fluorescent films for the nondestructive evaluation of fish freshness. The detection was used to decrease the fluorescence in the presence of amines from a tetraphenylethylene (TPEBA) and a calix[4]-pyrrole derivative (CPTH) at a humid air/DMSO interface. The detection limit found for TMA was 0.89 ppm, and the response was fast and highly reproducible.

Quantum dots (QDs) (e.g., semiconducting QDs, carbon dots, graphene QDs) having outstanding fluorescent properties have also been widely explored for gas sensing applications. In this regard, a fluorescent sensor based on 3-mercaptopropionic acid (MPA)-capped indium phosphide/zinc sulfide QDs (MPA-InP/ZnS QDs) and sodium rhodizonate (SR) was designed to monitor bighead carp fish

Figure 8. (A) (i) SEM images of the BCG sol–gel sensing label with magnification of 500 times. Application of the BCG sol–gel sensing label to monitor fish freshness stored in the package at room temperature: (ii) turbot and (iii) yellow croaker. Reprinted with permission from ref 119. Copyright 2020 Elsevier. (B) (i) Schematic illustration of pH-dependent chemical structures of cyanidin derivatives. The position of each equilibrium and the resulting color of a solution are dependent on the substituents (R) and pH of the environment. (ii) Photographs of sensor films when exposed to ammonia, triethylamine, cadaverine, and pyridine at increasing concentrations from 1 to 450 ppm. Reprinted with permission from ref 124. Copyright 2018 Elsevier. (C) (i) General reaction for MAF-based amine sensor. MAF (1) reacts with ammonia or primary or secondary amine to form a colored product (2). (ii) Colorimetric responses (DE) of MAF-coated nylon filters after exposures to DMA and ammonia. (iii) Change in color of MAF-coated nylon filters over time in the presence of cod, tilapia, and air (control) at room temperature. Reprinted with permission from ref 125. Copyright 2017 Wiley-VCH.
freshness. As illustrated in Figure 7A(i,ii), the fluorescence of MPA-InP/ZnS QDs was first quenched by SR molecules due to the combined effect of the inner filter effect (IFE) and static quenching effect (SQE) at pH = 3. In the presence of NH3, the fluorescence was recovered, and the color changed from colorless to a bright orange/red color. As shown in Figure 7A(iii), the sensor exhibited a linear response to NH3 in the range from 0 to 500 ppm with a LOD of 1 ppm. In addition, the fluorescence response and ∆E of the sensor were linearly related to the TVB-N content accumulated during fish storage at room temperature (Figure 7A(iv)). In another work, a fluorescent histamine sensor was developed by combining carbon dots (CDs) and an inert red-emitting fluorescent dye (1-aminooanthraquinone, ANQ). As presented in Figure 7B(i), the CDs@ANQ exhibited an orange-red fluorescence under 365 nm UV light, which differs from the blue fluorescence of CDs and the red fluorescence of ANQ. The fluorescence intensity increased linearly with the histamine concentration from 0.2 to 20 μM, yielding a LOD of 0.036 μM. Moreover, a change in the fluorescent color from orange-red to violet was easily observed by the naked eye. Interestingly, unlike conventional pH-responsive sensors for BAs, the fluorescence intensity of the CDs was not affected by pH change (Figure 7B(ii)), demonstrating that the CDs are insensitive to basic environments. Moreover, common biological species including ions, amino acids, and proteins had negligible effects on the fluorescence of CDs (Figure 7B(iii)). Finally, test strips impregnated with CDs@ANQ were combined with a smartphone and applied to the quantitative analysis and monitoring of dynamic changes of histamine levels in real fish samples.

**Colorimetric Sensors.** Considering convenience and simplicity, colorimetric sensing is a powerful analytical approach, and the direct visualization output makes this a promising technology candidate for a variety of applications including point-of-care assays. In this regard, several synthetic pH dyes, e.g., bromocresol green,119 bromothymol blue,49,120,121 bromocresol purple,120 chlorophenol red,122 methyl red,120 or mixtures123 of different dyes, have been used for the detection of volatile amines. Liu et al.119 developed a colorimetric fish freshness sensing label using bromocresol green (BCG) and a filter paper coated with a sol–gel matrix layer. As shown in Figure 8A(i), the BCG sol–gel sensing label showed a fibrous structure, thus providing larger surface area to interact with the volatile amines generated during fish spoilage. The sol–gel layer was employed to prevent moisture from interfering with the sensor response. For instance, at a relative humidity of 76%, the moisture absorption in the BCG dip-coated paper and BCG sol–gel sensing layer were 14.1%, 9.0%, and 4.1%, respectively. By including the sol–gel layer, the BCG colorimetric sensing label had an accurate response to fish freshness and displayed intense color changes from yellow to green and then to dark blue tracking the fish spoilage. These changes could be easily detected by the naked eye, as shown in Figure 8A(ii,iii). Additionally, the sensing label response was found to correlate with the concentration of TVB-N in redfish (Sciaenops ocellatus) samples in the range of 16.4–23.1 mg/100 g at room temperature, and in the range of 9.3–24.1 mg/100 g at chilled temperatures.

Recently, Sutthasupa and co-workers124 reported the use of an alginate-methylcellulose blend hydrogel doped with bromothymol blue as a colorimetric indicator for monitoring minced pork spoilage. Hydrogels are particularly well suited for portable colorimetric platforms as a result of the typical negligible background colors, large carrying capacity, and controllable shape. In addition, gas molecules can be easily captured by porous hydrogel structures through diffusion, which facilitates subsequent detection.126 The hydrogel indicator demonstrated a color change at day 6 from orange to yellow upon detection of the TVB-N during minced pork storage at 4 °C, and the results revealed a positive correlation between the color change, TVB-N values, and pH change. For instance, the TVB-N levels at day 0 were 5.86 mg/100 g and increased to 12.8 mg/100 g on day 6, and the pH of minced pork was around 6 from days 1–6 and increased to 6.14 on day 7. Other reports have shown that the volatile amine analysis can be correlated with the color change of colorimetric sensors based on other compounds susceptible to pH change, such as azobenzene-based molecules,127 alizarin,128 and conjugated polymers.129

Since food safety is of the utmost importance, there is a growing demand for the use of nontoxic materials in order to avoid possible food contamination with compounds originating from the sensing material.130 In this direction, there is growing interest in colorimetric films made by the combination of natural dyes and biopolymers (e.g., chitosan, starch, cellulose), since they are nontoxic, safe, and biodegradable.131,132 In ideal cases the resulting films can be edible. For instance, Dudnyk et al.124 reported the development of a colorimetric sensor for monitoring meat and seafood freshness based on pectin and red cabbage. The red cabbage extract contains a significant amount of anthocyanins, which are natural pigments with the ability to change color when exposed to changes in pH, as illustrated in Figure 8B(i). The authors evaluated the response of the films to gaseous amines (namely, ammonia, triethylamine, tyramine, cadaverine, and pyridine) from 1 to 450 ppm at 54% RH. As shown in Figure 8B(ii), the sensor exhibited remarkable sensitivity with a visible color change even at low amine concentrations (1 ppm). Additionally, the sensor film displayed different colors when exposed to each of the gaseous amines, probably as a result of a mixture of different anthocyanins within the cabbage extract. Color changes were also evident when the sensor film was exposed to the headspaces above beef, chicken, shrimp, and fish samples during their degradation at 21 and 4 °C. In another work, a nanofiber halochromic pH sensor film based on curcumin, chitosan (CS), and poly(ethylene oxide) (PEO) was employed to monitor chicken freshness.133 The nanofiber film was fabricated by electrospinning, and the membranes displayed high porosity, large surface areas, and tunable surface functionality.134 The color of the curcumin/CS/PEO nanofiber films changed from bright yellow to reddish color when exposed to NH3 vapor, which was selected to mimic TVB-N. Moreover, the nanofiber film was applied to monitor the freshness of chicken breast samples, and the authors observed a TVB-N value of 23.45 mg/100 g at the end of the day 5, indicating that the meat sample was at the edge of the accepted quality level.

Colorimetric indicators based on extracts from flowers,135 mulberry,136 black carrot,137 butterfly pudding, purple sweet potato,138 as well as other anthocyanin extracts or mixtures of pH dyes have also been explored for detecting aging of different food samples. Despite the numerous works devoted to the development of pH dye-based indicators for food quality monitoring, unfortunately, evaluation of the color change reversibility, the selectivity for amines, stability of the sensors
with respect to humidity, temperature, and light, and to leaching was not performed in most cases.

Volatile and biogenic amines in gas phase can also be detected by studying their interactions with other compounds/materials. For instance, Meldrum’s activated furan (MAF) was synthesized and employed for the colorimetric subppm detection of amines.\textsuperscript{125} The reaction between activated furans and amines results in a distinct color change, discernible by the naked eye, as demonstrated in Figure 8C(i). To evaluate the sensitivity of MAF toward volatile amines, MAF coated nylon filter membranes were exposed to vapors of DMA and ammonia. Although MAF has a similar LOD for both vapors (0.4 and 0.5 ppm for DMA and ammonia, respectively), as shown in Figure 8C(ii), a more pronounced color change for DMA was observed, providing a pathway to distinguish between primary and secondary amines. Finally, MAF was used to detect volatile amines released from two fish samples, namely, cod and tilapia. The cod sample resulted in a noticeable change in color after 48 h, whereas the tilapia had a significantly delayed response, changing color only after 24 h (Figure 8C(iii)). Genipin can also experience change in color upon reaction with BAs, as demonstrated by Mallov and co-workers.\textsuperscript{139} The authors observed a color change from a colorless to a red-colored product when exposing the genipin-based sensor to the amine volatiles. This behavior was ascribed to the selectivity reaction of genipin with amines through a double condensation reaction, which produces an oxidatively unstable dihydropyridine intermediate. In addition, in the presence of oxygen, the red-colored intermediate further undergoes oxidative oligomerization/polymerization forming a blue product. The incorporation of genipin in calcium alginate beads allowed the detection of putrescine at a minimum concentration of 44 ppm. Moreover, the sensor was also shown to be effective at monitoring chicken freshness by naked eye detection.

Advances in materials science, nanotechnology, and fabrication techniques have provided a robust toolbox for the rational design of a variety of colorimetric sensors for food-quality monitoring. In this regard, a printable hydrogen-bonded cholesteric liquid crystal (CLC) polymer film was employed as a sensor for the detection of TMA.\textsuperscript{140} When the CLC films were exposed to the amine vapor, the hydrogen...

![Figure 9.](https://doi.org/10.1021/acssensors.2c00639)
bonded polymer network was disrupted, leading to a color change from green to red. Additionally, the amine-responsive material could be inkjet-printed on foil and used to evaluate the freshness of codfish.

Metallic nanoparticles have also been extensively explored as colorimetric sensors, as a result of their unique LSPR properties. Tseng and co-workers reported the fabrication of paper-based plasmonic refractometric sensors by embedding hollow Au–Ag alloyed (HGNs) nanoparticles onto commercial inkjet paper for the detection of BAs released from spoiled fish (Figure 9A(i)). The HGN-embedded paper exhibited a wavelength shift upon the adsorption of the amines. Interestingly, no shift was observed upon exposure to N₂, CO₂, and water vapor, highlighting the selectivity of the sensor platform. Moreover, the plasmonic sensing papers were used to monitor the freshness of spiked putrescine salmon sample (Figure 9A(ii)), showing an LOD of 13.8 ppm.

Plasmonic colorimetric sensors based on etched noble metal nanoparticles have also been developed for the detection of volatile amines. For instance, Heli et al. evaluated how corrosive ammonia gas exposure altered the size and the population density of silver nanoparticles (AgNPs) embedded in bacterial cellulose nanopaper. Upon ammonia vapor exposure, the nanopaper exhibited a color change from amber to light amber and from amber to a gray or taupe upon exposure to spoiled fish or meat. The color change was attributed to the decrease of the AgNPs population density from 1473 ± 227 AgNPs µm⁻² to 302 ± 38 AgNPs µm⁻², after ammonia exposure, which results in a decrease in the UV–vis plasmonic band. The plasmonic nanopaper exhibited a LOD of 28.7 µg of ammonia spontaneously volatilized in a sealed 50 mL container at room temperature during 8 h. Other sensor platforms based on plasmonic nanostuctures for visual monitoring of food spoilage have also been published.

Recently, Shi’s group demonstrated the sensing performance of portable functional hydrogels to monitor BAs for evaluating food spoilage. A smartphone-integrated colorimetric sensor based on a hydrogel functionalized with Au@MnO₂ core–shell NPs (Figure 9B(i)) and β-D-glucose penta-acetate (β-D-GP) was employed to detect TVB-N. Specifically, as shown in Figure 9B(ii), in the presence of TVB-N/OH⁻, the β-D-GP was hydrolyzed leading to the formation of β-D-glucose. Then, a redox reaction between β-D-glucose and MnO₂ etched the MnO layer of NPs. Consequently, the AuNPs were exposed, causing the blue shift of the LSPR absorption peak, which generated a colorimetric signal. The color change was analyzed by a smartphone and transformed into RGB signals. The R/(R + G + B) gray value was used to monitor the freshness of spiked putrescine salmon sample showing an LOD of 13.8 ppm.

Other Transduction Methods. Microgravimetric sensors, which are used for measuring changes in mass, have also been proposed as an alternative approach for the analysis of amine compounds in gas phase. For instance, increased mass resulting from captured gas analytes can bend a cantilever or shift the resonant frequency of a quartz crystal microbalance (QCM), to produce an analytical signal. Costa and co-workers reported the evaluation of meat and fish freshness by functionalized cantilever-based sensors. Silicon nitride cantilevers were functionalized with cyclam (1,4,8,11-tetraazacyclotetradecane) by the drop-casting method. Then, the cantilever resonance frequency was measured for 5 consecutive days when exposed to meat and fish samples, and the changes from the mass increase (cadaverine binding) were determined using optical beam reflection. The cumulative mass of cadaverine increased during spoilage reaching 3 μg of cadaverine bound on the cantilever sensor. The cumulative mass of cadaverine increased in the following order: fish, chicken, beef, and finally pork. Evans et al. employed 2D covalent organic frameworks (COFs) thin-film selectors on a QCM for volatile amine sensing. Specifically, boronate-ester-linked 2D COFs were prepared as colloidal nanoparticle ink solutions and spray-coated. The resulting 2D COF films exhibited high porosity and Lewis acidity, which performed suitably for detecting volatile amines, showing a LOD of 10 ppb for TMA, which is below the freshness target detection limit for meat spoilage. In another work, a QCM sensor based on polypyrrole/TiO₂ nanocomposite thin films was used to monitor fish freshness over 1 week. The sensor showed an ultrasensitive response with the frequency signal varying from 175 to 390 Hz for ammonia concentrations of 10 to 50 ppm.

There are limited reports of volatile amine sensors using electrochemical transduction for meat freshness, which indicates that this area should be further explored. Electrochemical volatile amine detection is based on solid electrolyte sensors and is a result of amine oxidation reaction in the electrochemical cell. The electrochemical reaction results in a current flow through the electrodes, and, in appropriate diffusion conditions, the electrochemical reaction rate is proportional to the concentration of exposed amine. Regarding gaseous analytes, the electrochemical detection can be favored by adsorption membranes as diffusion barriers to enhance the analyte detection. Besides, adsorption membrane properties can be tailored to control the relative humidity, by using hydrophobic membranes, or yet limiting the interferents percolation by controlling the membrane porosity. Electrochemical gas sensor characteristics are dependent on the electrode materials chemical composition and grain size.

### MAIN LIMITATIONS FOR AMINE GAS SENSORS

Considering the survey of sensors for amine in gas phase presented here, it is possible to affirm that nanomaterials development has evolved in a way to overcome the many drawbacks and limitations of sensors made from bulk materials. In some cases, the performance of these sensors has reached a level of efficiency and reliability better than traditional analytical techniques such as gas chromatography. However, the translation to commercial devices is still challenging when considering the food package and storage conditions (e.g., temperature and humidity). For example, electrical sensors are
sensitive, selective, and fast for very low concentrations of amine vapors. Despite these advantages, long-term stability, portability, integration with easy-to-read systems, and performance at low temperatures (along the food supply chain) remain as unsolved questions toward real applications. As an alternative to overcome the portability limitation in electrical sensors, we have previously discussed the integration of electrically responsive materials with wireless technology and smartphone recognition. The same problems of portability and integration can be cited for fluorometric sensors, while colorimetric sensors are more versatile regarding portability and specific conditions of operation when focusing on food packaging. Considering the presence of several amines at the same time and the need for reliable sensing measurements, the combination of more than one material in a sensor array is presented in the next section as an alternative.

One last concern regarding amine gas determination in food products applies to the toxicity and biocompatibility of the material employed as sensing elements, which might eventually be in direct contact with the food product. Alternative porous covers might be efficient additions to avoid food product contamination, but further studies are required to better understand the implications in the sensor performance.

### SENSORS ARRAYS FOR AMINE IN GAS PHASE

An alternative to overcome the limitations of traditional sensors that operate as single devices (including the very specific selectivity or poor performance in complex environments) is the use of an array of sensors, which provide new dimensions to the collected data, creating patterns that can be associated with the sample characteristics. Sensor arrays are versatile and can be associated with many transduction methods. Next, we present a discussion regarding chemoresistive and colorimetric sensor arrays and provide some relevant examples.

**Chemoresistive Sensor Array.** Chemoresistive sensor arrays use multiple sensing units to simultaneously analyze many components present in complex samples. Such devices are frequently referred to as electronic noses (e-noses) since the use of multiple cross-reactive sensors was inspired by the biological olfactory system. In addition to the multisensory array, an e-nose is usually aided by pattern recognition methods in the data processing. An imperative characteristic of these analytical instruments is the cross-sensitivity wherein the sensors respond simultaneously to different components in the sample that is under analysis. To capture an entire complex odor, the collective sensor array must respond to a broad spectrum of analytes, instead of specific interaction with a single target analyte. However, high differential sensitivity of different sensors is necessary, and selectivity for key analytes will improve the accuracy of an e-nose. To attain the desired characteristics, the choice of the electrode’s composition, the sensing materials, and the data processing all play crucial roles in determining sensor performance.

E-noses have been broadly employed for food quality and spoilage evaluation. Different gas compositions presented by similar foodstuffs give rise to specific sample fingerprints, allowing for evaluation of each sample’s differences. The characteristic odors released upon food deterioration enable the detection of contaminants and the estimation of a product’s shelf life. Given the cross-sensitivity characteristics of e-noses, in most cases these devices are not devoted to detecting a single analyte in food quality monitoring applications, but instead to respond simultaneously to various components present in a complex sample. Besides amines, the presence of alcohols, aldehydes, ketones, and other VOCs in the analyzed samples is frequently reported. There are also some reports that do not make a classification of the analytes, and in these cases food spoilage is determined through patterned responses obtained after data treatment using visualization techniques.

E-noses have been widely reported in the detection of amines and consequently to evaluate food deterioration. In line with e-nose methods, the amine compound detected may not be specified, and multiple analytes can be detected simultaneously. In such cases, the strategy is to train the e-nose system with defined concentrations of known isolated amine compounds likely to be present in real samples to be analyzed. In this way, the pattern responses for the various amine compounds can be known, and their quantitative detection in the food sample can be performed using the responses obtained before. For instance, Lorwongtragool et al. used this approach with an e-nose based on polymers and carboxylic-functionalized single-walled carbon nanotubes (SWCNT-COOH) to evaluate sun-dried snakeskin gourami stored for 4 days. The mechanism associated with the detection of the analytes was found to be related to the percolation of the gases throughout the polymer matrix leading to a decrease in the electrical conductance. To this end, poly(vinyl chloride) (PVC), cumene terminated polystyrene-co-maleic anhydride (cumene-PSMA), poly(styrene-co-maleic acid) partial isobutyl/methyl mixed ester (PSE), and polyvinylpyrrolidone (PVP) were used as matrices, and embedded carbon nanotubes were employed to provide conducting channels. The system was first tested against dimethylamine, dipropylamine, pyridine, and ammonium hydroxide at concentrations ranging from 50 to 1000 ppm. The response of the sensing material to the amine compounds was associated with the basicity and mobility of the volatile amines analyzed. In this way, the capability of the amine to diffuse into the matrix and their electron-donating properties resulted in different sensitivities, giving rise to a fingerprint for each gas. With the information obtained for each analyte, the evaluation of the fish odors at different storage days was performed. The results revealed that the change in resistance increased with storage times, indicating an increase in the production of amine vapors. Through principal component analysis (PCA), the samples could be clearly distinguished based on days of storage. In another work, Lorwongtragool and coauthors also used an e-nose based on polymers and SWCNT to detect amine compounds, in which the e-nose could effectively distinguish different dried seafoods, namely, fish, squid, and shrimp based upon their distinct rates of amine production during spoilage.

An alternative method to identify amines present during food spoilage is correlating the e-nose performance and response patterns with the analyses collected using other analytical methods such as gas chromatography–mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) methods. El Babri used GC-MS to identify volatile species related to the degradation of sardines stored for 15 days and corroborated the results obtained using an e-nose based on commercially available...
Ten compounds were identified using the GC-MS method, including TMA, ketones, and alcohols. Increases in the storage days produced more volatile gases, and new species and the e-nose presented an increase in conductance. The data was processed using PCA, and stored sardines could be grouped in fresh (days 1−3), medium (days 5−7), and aged (days 9−15) samples. It is also possible to observe that there is a relation between the values of PC1 and the storage days. Specifically, as the storage time increases, the PC1 value decreases, and the results obtained with the e-nose were supported by mass spectroscopy analyses.

Wojnowski et al. also used GC-MS to detect the concentration of BAs and correlated the results with data collected using an electrochemical e-nose for the evaluation of the freshness of chicken meat samples. Cadaverine (CAD), histamine (HIST), putrescine (PUT), and tyramine (TYR) were detected in increasing concentrations within 5 days using the GC-MS method. The same samples were also analyzed with the e-nose to establish a relationship between the two strategies. Using the collected data, an artificial neural network (ANN) model was developed and indicated that the estimated amount of BAs obtained using the e-nose device was highly correlated with the predicted results with a coefficient of determination of 0.954.

Li and coauthors used HPLC to analyze the responses obtained using a commercial e-nose in the evolution of BAs and VOCs in smoked bacon under refrigerated storage for 45 days. Through HPLC, it was found that BAs concentrations increased with storage time, especially PUT, CAD, HIST, and TYR. Then, the responses collected by the e-nose were treated using the partial least-squares regression (PLSR), which showed that the e-nose was capable of identifying bacon in different stages of storage as well as indicated the same BAs as also being involved in the spoilage process. Since BAs are produced by microbial growth and metabolism, the authors argued that the e-nose could be used to evaluate the freshness of the bacon as well as its storage time.

As mentioned before, sensor arrays are generally used for nonspecific detection of amines. Thus, the response of these devices when analyzing other gases or even interferents is rarely reported. The mechanisms of amine detection by e-noses are mainly related to changes in the conductivity of the sensors after interaction with the analytes. Hence, it is expected that other volatile compounds, in addition to amines, which can interact with the sensor material, will also cause a change in the conductivity of the sensor units. Nevertheless, electronic nose devices will still fulfill their fundamental task of monitoring the concentration evolution of amine compounds originating from aging food. In these works, the different response patterns are obtained for different analytes and data processing tools, and additional analytical techniques ensure the detection of the target analytes.
Although less frequently reported, the detection of a single specific amine compound can also be performed using e-noses. In such cases, a specific recognition element must be employed in order to perform this specific detection. To this end, Lee et al. used a bioelectronic nose based on a novel microfluidic system to detect TMA. For this, the authors functionalized single-walled carbon nanotube-field effect transistors (SWCNT-FETs) with olfactory receptor-derived peptides (ORPs). The device was able to use ten sensing units simultaneously. A schematic illustration of the fabricated system is shown in Figure 10A(i). Conductance measurements were employed for detection with TMA at concentrations ranging from 1 ppt to 10 ppb. Interestingly, a microfluidic system, which was designed for analyses of liquid media, showed good results in the detection of the gaseous TMA. The selectivity of the e-nose was tested against dimethylamine, 2-methyl-1-propanol, acetic acid, and acetone. A much stronger response was observed for TMA than for the other analytes. The bioelectronic nose was also applied to evaluate the quality of oysters using the detection of TMA generated from the spoilage process. As shown in Figure 10A(ii), the presence of the ORPs was fundamental in the monitoring of this process. Moreover, the amount of oysters was related to the response intensity obtained by the system. The estimation of the TMA generated by the spoilage process reached values as low as 10 ppb, below the human threshold (210 ppt). The system was used to fabricate the FET sensors. The device presented high sensitivity with a minimum limit of detection of 10 ppb. The sensor was also tested with PUT, hydroxylamine (HA), glutamine (Glu), and tryptamine (TryA), and showed high selectivity to these analytes. The bioelectronic nose applicability was evaluated by analyzing samples of beef and salmon. As shown in Figure 10B(ii), the response of the sensor array increased in proportion to the spoilage period for 4 weeks, while no signal was observed for fresh foods, indicating the ability of the sensor to discriminate spoiled food by the selective detection of CAD.

As reported in this section, e-nose enables the monitoring of food decomposition by evaluating complex samples containing multiple gas compounds, including amines. Detection of a specific analyte can also be performed through the use of specific recognition elements. In general, analyses on food samples are mostly conducted using meat, fish, or pork. Sensor arrays have yet to overcome some limitations necessary for commercial use, including the large-scale production of sensor arrays with repeatability of responses and properties, so that the system does not require recalibration after the replacement of a sensor unit. In this sense, the use of more robust tools for data processing represents an interesting alternative. There is a growing interest in artificial intelligence and neural networks to treat and analyze the collected responses and enhance the system performance. Another trend is the miniaturization of devices to perform measurements in situ.

**Colorimetric Sensor Array.** Colorimetric sensor arrays are optical arrays based on chemoresponsive colorants, e.g., dyes and nanoporous pigments, and constitute another example of an electronic nose that mimics in function the mammalian olfactory system. Hence, colorimetric sensor arrays have also been called optoelectronic noses. However, instead of collecting electrical responses upon analyte interaction, the colorimetric sensor arrays generate unique colorimetric patterns caused by color changes of the sensor materials upon interactions with the analyte(s). The sensing units of the colorimetric array are chosen to respond specifically to a given analyte or a class of analytes, and the interactions may not provide differentiation between similar compounds. Cross-sensitivity is a desired characteristic in colorimetric arrays and when paired with more specific sensing elements provides for a very effective method for analysis of odors.

Colorimetric sensor arrays are obtained by depositing chemoresponsive sensors on solid supports that are often white in color to provide maximum contrast. The advantage is that visual detection can be achieved without sophisticated equipment, but can still allow for the necessary sensitivity, low cost, nondestructive sampling, and fast analysis. Therefore, this approach presents an enormous potential to be employed for food “odor visualization” and quality monitoring.

As previously mentioned, the detection of the gas analyte occurs by interactions of molecules/compounds with the sensing material. In this regard, stronger interactions often lead to enhanced sensitivity. In amine detection, high binding enthalpies are possible, ranging from ~40 to ~300 kJ mol⁻¹. These largely irreversible processes have been reported for the detection of volatile amines using colorimetric sensor arrays. Earlier works using optical sensor arrays to detect amines did not usually report or validate the results using real food samples to directly monitor the spoilage process. However, colorimetric arrays to evaluate the spoilage process of foodstuffs have recently gained attention.

Similar to the application of e-noses for food quality monitoring, some studies have succeeded in monitoring the food spoilage process without necessarily determining which amine compounds are interacting with the colorimetric sensor array. For instance, Salinas and coauthors used a colorimetric sensor array based on 16 dyes and a partial least-squares (PLS) prediction model to monitor chicken aging. In another work, Salinas and coauthors reported the monitoring of pork sausage spoilage using an optoelectronic nose based on pH indicators and selective chromogenic reagents. The array was able to differentiate samples with clear clustering and 85% correct classification if the storage time had been over 52 days. Li et al. evaluated pork freshness with an optoelectronic nose fabricated by printing 12 chemically responsive dyes on a silica-gel flat plate. Linear discriminant analysis and ANN were used in data treatment, and values of discrimination rates of 100% and 97.5% for the training and prediction were obtained, respectively. Although in these works the amine compound was not distinguished, the food spoilage process produces amines and provided information. However, there are also reports of the use of colorimetric sensor arrays combined with traditional methods to evaluate the specific amines produced during food aging. For instance, Xiao-Wei et al. developed a colorimetric gas sensor array based on four natural pigments to...
evaluate pork freshness. PUT, CAD, spermidine (SPD), and spermine (SPM) were also detected in this study by HPLC experiments. The color difference before and after exposure to the analytes was evaluated from scanned RGB images. By using the PCA tool, the system was able to clearly separate daily samples over 7 days. A good correlation (0.77 and 0.73 in calibration and validation, respectively) between the responses collected using the sensor array and conventional methods was obtained using PLS models, indicating the robustness of the sensor for pork spoilage.

To assess the shelf life of squid in cold storage, Zaragoza fabricated an optoelectronic nose containing six dye sensing materials. The decomposition of squid has been associated with dimethylamine, formaldehyde, and TMA production, generating the characteristic odor of spoiled food. In this regard, TVB-N and trimethylamine nitrogen (TMA-N) contents were determined by steam-distillation. The spoilage process was followed by packing the squid samples and the colorimetric array in cold storage for 12 days, and the TVB-N varied from 91.93 mg/100 g (day 0) to 138.95 mg/100 g (day 12). PCA was used in the analysis of the color change data and revealed that the optoelectronic nose was able to cluster the data according to storage time (group one: control and day 0; group two: days 5–7; and group three: days 10–12).

The detection of TMA was also performed by Xiao-Wei using a nanoporous colorimetric sensor array composed of a TiO$_2$ nanoporous film as substrate and 16 sensing materials. The sensor was able to detect TMA at different concentrations from the permissible exposure limits, from 10 ppm to 60 ppb, exhibiting different patterns for each concentration tested. PLS was used as a prediction model, and the sensor array was employed to assess the evolution of TMA content in Chinese squid.
Yao-meat. Figure 11A shows the increase in TMA production during 35 days and the resulting color change of the colorimetric array. The TMA values exceeded 1.0 mg/100 g after 30 days, which is the accepted shelf life of the Yao-meat. A portable optoelectronic nose was developed by Li and Suslick for meat freshness monitoring.\textsuperscript{12} The device was obtained from printing chemically responsive dyes and combined with a hand-held analyzer for on-site assessment and monitoring of the meat freshness. Figure 11B(i) shows the sensing device that contains a colorimetric sensor array inside the electronic hand-held analyzer. The authors used Brønsted/ Lewis acidic or basic dyes to detect biogenic amines. The sensor was first used in the quantification of CAD, TMA, and other two sulfides (H\textsubscript{2}S and (CH\textsubscript{3})\textsubscript{2}S), and the differentiation of the analytes at subppm concentration was possible with visual inspection. The responses toward TMA and CAD to the vapochromic species, pH indicators, and metal-containing dyes were in alignment with the expected changes in local polarity and Brønsted basicity. Because the sensor responded to a variety of analytes beyond amines, such as sulfides and other VOCs, it presented the ability to discriminate the spoilage process in five different meat products rather than only a single meat. Figure 11B(ii) shows the obtained pattern from the array for beef, chicken, fish, pork, and shrimp after storage for 48 h at room temperature. The sensor showed that up to 4 days, the spoilage process was dominated by the release of biogenic amines. By using PCA, hierarchical cluster analysis (HCA), and support vector machine (SVM) as statistical tools for data treatment, the system was able to predict the freshness of the meat samples.

Guo et al.\textsuperscript{214} combined cross-reactive colorimetric barcode combinatorics and deep convolutional neural networks (DCNNs) to develop a colorimetric portable sensor array for meat freshness. The barcode was made of porous nano-composites comprising dye-containing chitosan nanoparticles embedded in a cellulose acetate matrix (CNP-Dye/CA) (Figure 11C(i)). As shown in Figure 11C(ii), the multiplex barcode was composed of 20 different CNP-Dye/CA. Each type of CNP-dye responded to a different pH range and as a result covered the detection range of gases emitted from rotting meats, including bioamines. The protonation and deprotonation of the halochromic dyes with amine interactions produced pH and color changes of the sensing units. Moreover, SEM showed that the CNP-Dye was well distributed on the interwoven fibers that form the porous 3D structure of the CNP-Dye/CA (Figure 11C(iii)). Such a porous 3D structure can provide abundant gas sensing sites. Using PCA and HCA, the system was able to discriminate NH\textsubscript{3}, MA, TMA, CAD, and PUT amine compounds in concentrations from 20 to 100 ppm. The use of DCNN showed a classification accuracy of 98.5\% for the assessment of the freshness of chicken, fish, and beef samples. In this way, DCNN was incorporated in a smartphone application to obtain a portable user-friendly device for meat freshness determination. The authors used 3475 images as training and 686 as testing. The applicability of the system was then tested in real refrigeration situations, in which the colorimetric barcode was integrated into fish packages stored at 4 °C. Based on TVB-N analyses, the system was able to predict the freshness of fish, i.e., fresh, less fresh, and spoiled samples, with 92.0\% of accuracy.

The visual analysis of a colorimetric array is only a qualitative indicator, and the quantification of the analytes requires the use of digital image processing devices or optical characterization techniques to quantitatively determine the color changes induced by analyte interactions. In addition, other quantitative or analyte recognition techniques are frequently required to determine the specific compound being detected.\textsuperscript{199,200}

When compared to traditional electronic noses, the miniaturization and portability of colorimetric sensor arrays are more easily accomplished. Qualitative portable arrays can be used in packages and in other parts of the supply/distribution chain for monitoring of food quality. Automation of the systems is required in order to make colorimetric sensor arrays best suited for food analyses. Electronic devices when combined with colorimetric arrays can produce fast, accurate, and nondestructive sensors. Optoelectronic noses using new data processing techniques (e.g., machine learning) that generate improved responses promise to yield high sensitivity and selectivity. The selectivity to be attained is, however, not for a specific compound or molecule, but for a class of food and its decomposition products. Data treatment tools can also help in the understanding of the interaction of the sensing units with the gas analyzed and guide additional sensor development.

**FINAL REMARKS AND FUTURE TRENDS OF AMINE GAS SENSORS**

In this review, the past decade of developments and advances in sensors for amine vapor detection related to food quality were surveyed. Volatile amines are generated by the degradation of proteins, and an index of the total volatile amines, TVB-N, has been determined as a reliable measure of the stage of food degradation which increases with storage time and temperature. Although there are different recommendations of volatile amine limits for food freshness, the sensors reported in the literature over the past decade operating under distinct transduction methods with varied sensitivity, selectivity, response, and long-term stability indicate their potential to detect TVB-N at low concentrations. As discussed throughout the review, the continuing development and improvement in the sensing materials, sensor devices, and sensors arrays (e-noses) can provide different patterns that are indicative of food quality.

The ongoing relevance of amine gas sensors is revealed by more than 25 publications per year and the increased literature citations over the past decade (Figure 12A). In terms of transduction methods (Figure 12B), electrical sensors are the most popular for gas monitoring. Fluorometric and colorimetric methods have also been widely used to develop amine gas sensors. The reliability of electronic and optoelectronic noses is expected to increase with the aid of computer-assisted techniques (e.g., artificial intelligence, neural networks, etc.). Finally, wireless chemoresistive sensors that can be easily integrated into the food package and remotely accessed and controlled are very attractive from the prospects of portability and integration into intelligent packaging.

Despite the large number of excellent papers on this subject, challenges in fielding a robust food freshness sensor that can be used and understood by consumers still exist. Ongoing developments to create the most diverse/robust sensors (in some cases with the aid of 3D printing) producing devices capable of automated actionable outputs employing complex data processing, and the development of low-cost systems are likely to meet these challenges in the near future.
Volatile amines, low-volatility amines abundantly present in protein-rich food products and generally used as indicators of food spoilage. Examples include putrescine, cadaverine, spermidine, and spermine. TVB-N, total volatile basic nitrogen (TVB-N) is an index calculated by the sum of primary, secondary, and tertiary amines exhaled by food products and is used to determine food freshness. TVB-N values between 0.15 mg g\(^{-1}\) and 0.2 mg g\(^{-1}\) are indicative of nontoxic food, and values over 0.28 mg g\(^{-1}\) are alarming for potential toxicity.

Wireless sensors, devices capable of analyte recognition operating through wireless power and/or wireless measurement/communication.

RFID, radiofrequency identification is based on the radiofrequency communication between a transponder and a transceiver, which are electromagnetically coupled through their respective resonant antenna circuits.

Electronic nose (e-nose), analytical tool composed of an array of nonspecific sensing units capable of responding distinctly to different classes of volatiles under analysis. The overall response of the sensor array generally forms a recognition pattern that can be appropriately analyzed using multivariate data processing methods.

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**Notes**

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**VOCABULARY SECTION**

Volatile amines, nitrogenous compounds in gas phase abundantly present in protein-rich (or high-protein) food products and generally used as indicative of food spoilage. Examples include ammonia, dimethylamine (DMA), and trimethylamine (TMA).

Biogenic amines, low-volatility amines abundantly present in protein-rich food products and generally used as indicators of food spoilage. Examples include putrescine, cadaverine, spermidine, and spermine.

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**Figure 12.** (A) Number of citations per year related to amine gas sensors. (B) Distribution of published articles according to the transduction method. Data obtained from Web of Science accessed in June 2022 using the keywords “volatile amine sensors.”
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