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PII: S0925-4005(19)31448-0

DOI: <https://doi.org/10.1016/j.snb.2019.127249>

Reference: SNB 127249

To appear in: *Sensors and Actuators: B. Chemical*

Received Date: 24 July 2019

Revised Date: 4 October 2019

Accepted Date: 8 October 2019

Please cite this article as: González-Ceballos L, Melero B, Trigo-López M, Vallejos S, Muñoz A, García FC, Fernandez-Muiño MA, Sancho MT, García JM, Functional aromatic polyamides for the preparation of coated fibres as smart labels for the visual detection of biogenic amine vapours and fish spoilage, *Sensors and Actuators: B. Chemical* (2019), doi: <https://doi.org/10.1016/j.snb.2019.127249>

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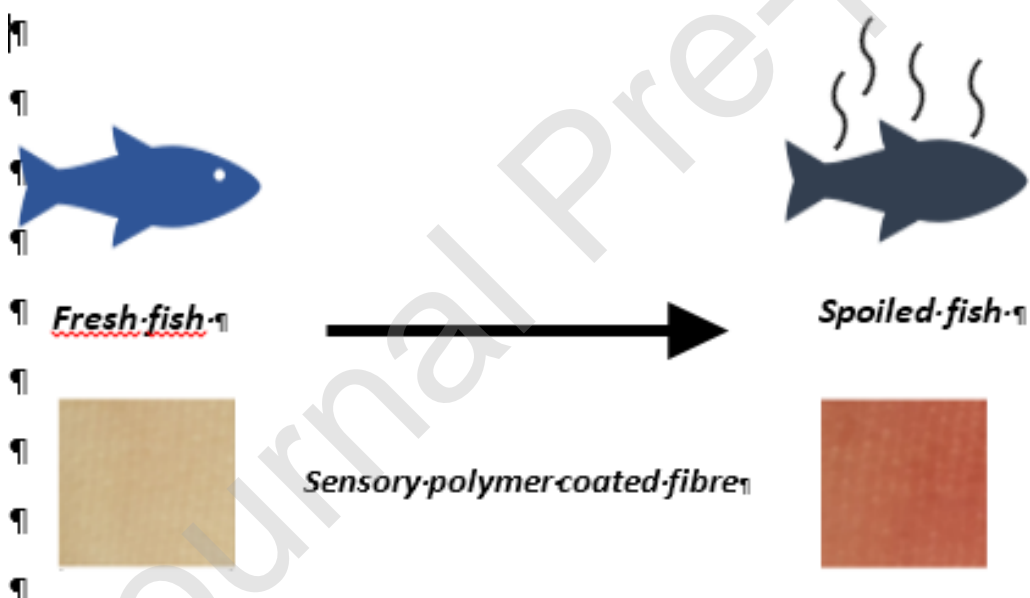
Functional aromatic polyamides for the preparation of coated fibres as smart labels for the visual detection of biogenic amine vapours and fish spoilage

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Graphical abstract



HIGHLIGHTS

- Colorimetric sensory polymer labels towards biogenic amines
- Sensory polymer coated fibres as manageable solid sensory kits
- Naked eye detection of biogenic amines released from spoiled fish
- A picture taken to the labels allowed to obtain the colour definition parameters (RGB)
- The RGB data were correlated with conventional techniques for following food spoilage

ABSTRACT:

We have prepared high-performance functional aromatic polyamides with sensory pendant groups toward amines. These polymers are colourless. The pendant groups have bromonaphthalimide motifs that react with amines rendering coloured arylamines by nucleophilic aromatic substitution of the halide. Thus, these materials are colorimetric sensors toward amines. In the interest of saving costs, while having a sensory material with a high specific surface, cotton fabrics were coated, in order to render coated fibres as smart colorimetric labels toward amines. Moreover, as fish spoilage by microorganism increases the biogenic amines in food, we have applied the smart labels to visually follow the food spoilage. Also, a picture taken to the films allowed to obtain, in seconds, the digital colour definition parameters (RGB) that were correlated with the results of expensive and time-consuming conventional techniques used to obtain relevant food quality data, such as total amine concentration (treatment of the sample and HPLC), colony-forming unit (microbiological assays), total volatile basic nitrogen (TVB-N), and organoleptic test (sensory test). The smart labels are inexpensive, granting in seconds, the visual qualitative evaluation of the food quality, or even quantitative, and they comply with the European food contact materials regulation.

KEYWORDS:

Amine sensors; biogenic amines; polymer chemosensors; smart labels; fish spoilage

1. INTRODUCTION

The detection and quantification of chemical species are one of the main topics of chemistry. These tasks are undertaken by skilled personnel using sophisticated methods and techniques developed by scientists and technicians, such as titrimetry, electroanalytical methods, spectroscopy, chromatography, gravimetry, microscopy, and so on [1]. In recent years there has been an increase in the interest in chemical sensors, or chemosensors, as alternative analysis techniques for the *in-situ*, inexpensive and rapid determination of chemical species, especially in environmental, biomedical, security and food control applications [2,3,4,5,6,7,8,9,10,-11]. A chemosensor, or probe, is a molecule that interacts selectively with target species with a concomitant variation of at least one microscopical property that can be

detected and correlated with the target species concentration in the so-called transduction or response.

When the response is a variation of the colour of the system, we have chromogenic chemosensors, and the detection can be carried out visually, even by untrained personnel [12,13,14,-15]. Moreover, a simple picture of the chemosensory system can be used to precisely quantify the concentration of the target species [16,17].

However, chromogenic probes are usually organic molecules that can only be exploited in organic solution or, at most, in organic/water solutions. We have overcome this drawback by preparing polymeric chemosensors that have a number of advantages compared with conventional organic probes: a) hydrophobic organic sensory motifs can be anchored to hydrophilic polymer structures to render water-soluble polymers, for sensing water resources and environmental samples; b) solid sensory films can be prepared for sensing not only in water but also for sensing target gases and vapours; c) the anchored sensory motifs cannot migrate to the measuring media and can be easily recovered; and d) the polymer backbone can be chemically designed for tuning the response of the sensory motifs in terms of selectivity, sensitivity and response times.

Accordingly, we have prepared sensory high-performance aromatic polyamides [18,19] as solid colorimetric chemosensors of biogenic amine vapours as intelligent labels for visually following the food spoilage. Biogenic amines are a group of nitrogenous compounds with low-molecular-weight, generated in food by decarboxylation of free amino acids, through the metabolism of different microorganisms grown in the process through which fish gets spoiled [20]. Thus, the amount of biogenic amines and the microbial counts are a good indicator of the fish freshness and quality [21,22]. Another good quality indicator is total volatile basic nitrogen (TVB-N) [23,24], along with the subjective organoleptic study carried out by sensory evaluation.

2. EXPERIMENTAL SECTION

2.1. Materials

All of the materials and solvents are commercially available and were used as received unless otherwise indicated: *N*-bromosuccinimide (99%, Sigma-Aldrich), dimethylformamide (DMF, 99%, Sigma-Aldrich), acenaphthene (97%, Alfa Aesar), ethanol (Absolute, VWR), glacial acetic acid (100%, VWR), sodium dichromate dihydrate ($\geq 99.5\%$, Sigma-Aldrich), 5-aminoisophthalic acid ($\geq 98\%$, VWR), sodium acetate ($\geq 99.5\%$, Fluka), thionyl chloride (SOCl_2) ($\geq 99\%$, VWR),

heptane ($\geq 99\%$, VWR), aniline ($> 99\%$, Alfa Aesar), piperazine (99%, Sigma-Aldrich), morpholine ($\geq 99\%$, Sigma-Aldrich), β -ethylendiamine (99%, Alfa Aesar), 1-butylamine (99%, Alfa Aesar), β -phenethylamine (99%, Sigma-Aldrich), tyramine (99%, Sigma-Aldrich), triptamine (98%, Aldrich), putrescine ($> 98\%$, Alfa Aesar), cadaverine ($\geq 97\%$, Fluka), spermine (97%, Alfa Aesar), spermidine ($\geq 99\%$, Sigma-Aldrich), histamine (97%, Acros Organics), trimethylamine (40% solution in water, VWR). *m*-Phenylenediamine (MPD) is commercially available ($> 99\%$, Sigma-Aldrich) and was purified by double vacuum sublimation and stored under a nitrogen atmosphere. Isophthaloyl dichloride ($> 99\%$, Sigma-Aldrich), was purified by double crystallization from dry heptane. *N,N*-dimethylacetamide (DMAc) (99%, Sigma-Aldrich) was vacuum-distilled over phosphorous pentoxide twice and then stored over 4 Å molecular sieves.

For the HPLC analysis the following materials were used as received: sodium hydroxide (VWR, 99%), benzoyl chloride (99%, Sigma-Aldrich), sodium chloride (99.5%, Sigma-Aldrich), hydrochloric acid (37%, VWR) diethyl ether (99.9%, VWR), methanol (HPLC grade, 99.8%, VWR), cadaverine hydrochloride (98%, Sigma-Aldrich), tyramine hydrochloride (98%, Sigma-Aldrich), histamine dihydrochloride (99%, Sigma-Aldrich), putrescine hydrochloride (99%, Sigma-Aldrich), trichloroacetic acid (99.5%, PanReac)

For the microbiological analysis, Plate Count Agar (PCA), (Scharlau) and Ringer solution (OXOID) were used.

For the total volatile basic nitrogen (TVB-N) determination, magnesium oxide (90%, Merckmilipore), boric acid ($\geq 99.5\%$, Sigma-Aldrich), trichloroacetic acid ($\geq 99.5\%$, PanReac) and hydrochloric acid (37%, VWR) were used as received.

2.2. Instrumentation and measurements

Nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded in deuterated dimethylsulfoxide (DMSO- d_6) as the solvent, with a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, respectively.

Infrared spectra (FT-IR) were recorded with a FT/IR-4200 FT-IR Jasco Spectrometer with an ATR-PRO410-S single reflection accessory.

High-resolution electron impact mass spectra (EI-HRMS) were obtained at 70 eV on a 6460 Triple Quad (Agilent) mass spectrometer.

Thermogravimetric analysis (TGA) data were recorded for a 5 mg sample under a nitrogen or synthetic air atmosphere on a TA Instrument Q50 TGA analyzer using the next procedure: First, the polyamides were heated from RT to 100 °C at 10 °C·min⁻¹ and kept at that temperature for 5 min to eliminate the moisture content, then, the polyamides were heated at 10 °C min⁻¹ to 800 °C to complete the TGA analysis. The limiting oxygen index (LOI) was estimated using the experimental Van Krevelen equation: $LOI = 17.5 + 0.4 CR$, where CR is the char yield weight percentage at 800 °C obtained from the TGA measurements under a nitrogen atmosphere.

The polymer solubility was determined with 10 mg of the polymer together with 1 mL of a solvent and stirring for 24 h at 20 °C. The polymer was considered soluble at room temperature if a homogenous solution was obtained. If the polymer was insoluble at room temperature, the mixture was heated to reflux for 2 h, and considered soluble on heating if a homogeneous solution was obtained this way. Otherwise, the polymer was considered insoluble.

Water sorption was calculated gravimetrically. 200 mg of sample was dried for 24 h at 60 °C in an oven with phosphorous pentoxide, and then placed in a closed box at 20 °C with a saturated aqueous solution of NaNO₂ to provide a relative humidity of 65 %. The samples were weighed periodically for 8 days until a constant weight was obtained.

The intrinsic viscosity $[\eta]$ was calculated by measuring the inherent viscosities, η_{inh} , of the aramids at different polymer concentrations (0.5, 0.3, 0.1, 0.05 and 0.025 g·dL⁻¹) with a Ubbelohde viscometer using DMAc with 5% LiCl as the solvent at 25 °C ± 0.1 °C and extrapolating to zero concentration. The number average molecular weight (M_w) of the polyamides was measured using the Mark-Houwink-Sakurada equation, $[\eta] = k M_w^\alpha$, where the values of the constant k and α for polymer solutions in 5% LiCl DMAc at 25 °C are 0.00037 dL g⁻¹ and 0.74, respectively [25].

The food spoilage analysis carried out with the sensory label, the HPLC measurements, the microbiological assays and the volatile total basic nitrogen (TVB-N) were performed with 2 Kg of fish (*Trachurus trachurus*) bought in a local supermarket. The skin and bones were removed, and the fish were mixed and homogenized. For the sensorial analysis, two entire fish samples of *Trachurus Trachurus* were chosen and stored at room temperature while the study was performed.

The biogenic amines determination with the smart labels was carried out by taking a digital photo of the labels inside a closed vial containing biogenic amines or fish, in the presence of a colour reference (in our case a small piece of red tape). This reference was used to normalize

the colour response with a conventional image processing software, which reduces the errors associated with the different illumination conditions in different photos. The photographs were taken with a Samsung S8 smartphone and the B (blue) parameter of the RGB (red, green and blue) colour model was obtained with Photoshop Software to automatically average the data over an 11 x 11 (121) pixel area.

The HPLC results for the different samples were obtained using an HPLC VARIAN ProStar system, with a 150 x 4.6 mm Microsorb-MW 100-5 C18 column, and UV detection at 230 nm. Water (solvent A) and methanol (solvent B) were used as mobile phases. The solvent gradient started with 60% A-40% B, reaching 35% A-65% B at 6 min, 20% A-80% B at 7 min, 15% A-85% B at 12 min, and 50% A-50% B at 15 min, followed by the return to the initial conditions. Before the derivatization, the fish samples were shaken using a vortex mixer; VWR, centrifuged twice using a MEGAFUGE 16R Centrifuge, Thermo SCIENTIFIC and filtered with a filter paper Whatman® No.4 or a syringe filter (Puradisc™, Whatman™ 0.45 µm, VWR).

For the microbiological assay, 25 g of skinless and boneless fish (*Trachurus trachurus*) were aseptically taken and were homogenized with 225 mL of Ringer solution using a stomacher (STOMACHER 4000, LABORATORY BLENDER).

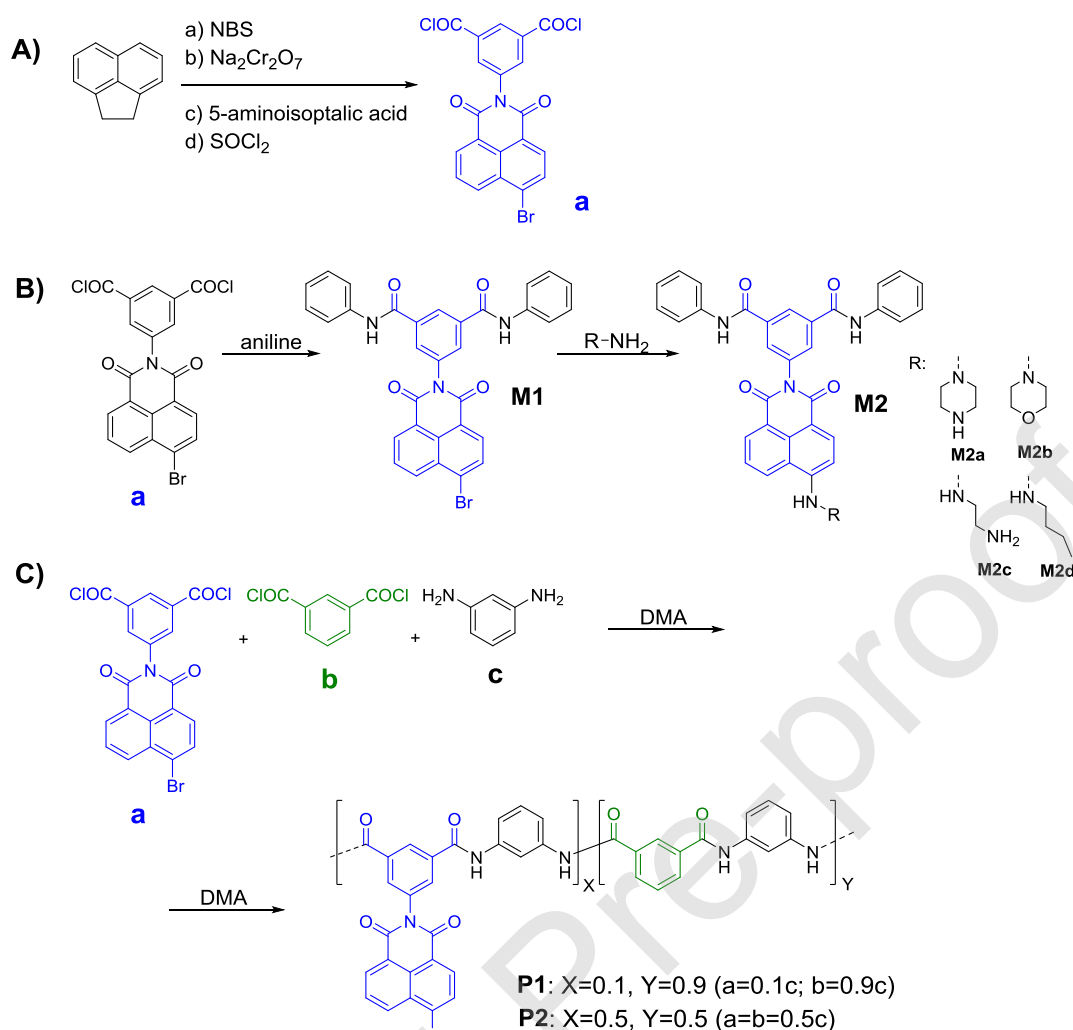
For the total volatile basic nitrogen (TVB-N) analysis, fish samples were homogenised by using a manual homogenizer and centrifugated using a MEGAFUGE 16R Centrifuge, Thermo SCIENTIFIC. A common steam distillation assembly was used.

In the analyses, 3-8 replicates were performed (except for HPLC that was just one measurement due to the time needed), and the errors were calculated once the dispersion of each series of data was determined. In the sensorial analysis were the measurements were performed by 14 people, the standard deviation or mean squared error was calculated.

2.3. Synthesis of sensory polymers

The sensory aromatic polyamides are prepared following the conventional way from two commercial monomers, *m*-phenylenediamine (**c**) and isophthaloyl dichloride (**b**), together with a synthesized aromatic diacid dichloride having the amine sensory motif (**a**) as pendant structure (See Scheme 1A and 1C, and Section S4 of the Supplementary information -SI-). The ratios of constitutional repeating units of polymer **P1** and **P2** were calculated with ¹H NMR (see SI, Section S4), and agreed with the monomer feed ratio, considering the error of the measuring technique (calculated X:Y ratio was 0.1:0.9 for **P1** and 0.45:0.55 for **P2**).

Scheme 1.



Scheme 1. Synthesis of: a) monomer; b) aromatic polyamide model and its general reaction with amines; and c) aromatic polyamides.

Before the preparation of polyamides, the viability of the polyamide synthesis was checked by previously preparing a polyamide model (**M1**) using polymerization conditions (SI, Section S2.). The characterization of **M1** allows us to discard by-products that could impair the preparation of the polymers. This step is important because aromatic polyamides are high-performance materials characterized by outstanding thermal and mechanical properties, and any by-reactions would impair these performances. Also, they are highly insoluble and not so easy to characterize. Moreover, **M1** also allows for the testing of the sensory mechanism. Thus, colourless organic solutions of **M1** react with amines rendering coloured arylamines by nucleophilic aromatic substitution of bromine (tested amines: piperazine, morpholine, ethylenediamine or 1-butylamine). The synthetic conditions and the analysis and properties of

monomers, model and polymers are reported in the supplementary information (SI, Section S3-S6).

From the viewpoint of the polymeric materials, the prepared aromatic polyamides are thermally resistant polymers with degradation temperatures, in terms of 5% and 10% weight loss calculated by thermogravimetry, of around 430 and 475 °C, respectively (SI, Section S6). They are soluble only in aprotic polar solvents, such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, *N,N*-dimethylformamide or dimethyl sulfoxide (SI, Sections S5). The average molecular mass of **P1** and **P2** was $M_w = 6.4 \times 10^4$ and $M_w = 4.5 \times 10^4$, respectively, and the intrinsic viscosities $[\eta] = 1.18 \text{ dL}\cdot\text{g}^{-1}$ and $[\eta] = 0.95 \text{ dL}\cdot\text{g}^{-1}$, respectively.

3. RESULTS AND DISCUSSION

3.1. Sensing of biogenic amines vapours

According to literature, bromonaphthalimides react with amines rendering coloured arylamines by nucleophilic aromatic substitution of the halide.^{26-27,28} Thus, the chemical reaction and the evolution of colour can be used to detect amines. Accordingly, we thought that polymers with bromonaphthalimides moieties could be worth to prepare sensory material and we designed aromatic polyamides containing these moieties. However, previous to the sensory polymer preparation we checked the validity of the idea by synthesizing a model molecule of the sensory polymer (**M1**), that renders the coloured arylamines, as anticipated, upon contact with amines (**M2**) (Scheme 1), thus validating the idea and the mechanism described in the literature. The reaction of **M1** with amines to render **M2** is observed immediately, even at room temperature, though it was carried out at higher temperature (SI, section S3) for obtaining high purity chemical for chemical characterization.

As expected by the behaviour of **M1**, the colourless sensory polymers **P1** and **P2** turned reddish in atmospheres containing ethylenediamine, putrescine and cadaverine, among other amines. Thus, we decided to prepare coated cotton fibres as sensory labels to amine vapours (**F_{P1}** and **F_{P2}** stand for the coated fibres prepared with polymers **P1** and **P2**, respectively) (see SI, Section S7, for preparation methodology). The coated fibres have advantages over sensory films. Thus, the thinner the coating the smaller the quantities of sensory polymers used and the lower response time of the sensor (because of the higher specific surface). In addition, migration tests were performed for **F_{P1}** and the results followed the restriction for the overall migration limit ($<10 \text{ mg}/\text{dm}^2$) as defined in Commission Regulation (EU) No 10/2011 for food

contact materials (See SI, Section S8). The response of the sensory material F_{P1} towards commercial biogenic amines is depicted in Figure 1. A photograph taken to the smart coated fibres allow for the individual titration of the amines, as shown as an example for putrescine in Figure 2, where it is shown the representation of B (blue component of the colour definition of the smart fibres) vs putrescine vapour concentration (titration curves for other amines are shown in SI, Section S9).

Figure 1.

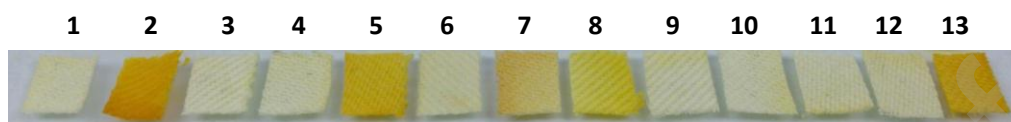


Figure 1. Response of coated fibre F_{P1} to the presence of amines (20 mg of amines in the bottom of a 14 ml sealed vial at 20 °C, the fibre on the top of the vial without contacting the amines): 1. Blank; 2. β -ethylenediamine; 3. Spermine, 4. Spermidine; 5. Cadaverine; 6. Histamine; 7. Trimethylamine; 8. Morpholine; 9. Piperazine; 10. Tryptamine; 11. Tyramine; 12. β -phenylenediamine; 13. Putrescine.

Figure 2.

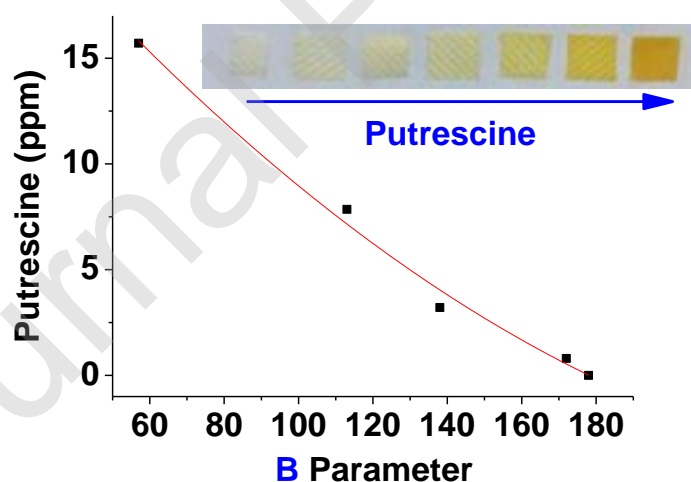


Figure 2. Response of coated fibre F_{P1} to the presence of putrescine (different amounts of putrescine in the bottom of a sealed vial at 20 °C with the fibre on the top of the vial without contacting the putrescine).

3.2. Sensing of biogenic amines vapours from fish spoilage

Once demonstrated that the smart coated fibres colorimetric sense the presence of amine vapours, and known that the spoilage of food, and specifically fish, is accompanied by the concomitant generation of biogenic amines [29], the deterioration of fish meat was followed with the colour development of the F_{P2} by two means: a) visually, and b) analysing the B component digital colour definition (RGB parameters) of pictures taken to the materials with smartphones. For this purpose, the fish Atlantic horse mackerel (*Trachurus trachurus*) was maintained at a constant temperature (20 °C) and samples were taken along time for 3 days (see Table 1). The methodology followed is described in SI, Section S10.

3.3. Comparison with conventional tests for fish quality control

The colour evolution, in terms of the digital definition of the colour of a picture taken with a smartphone (B parameter), was compared with well-established techniques [30-31,32,33], such as HPLC, microbiological assay, total volatile basic nitrogen (TVB-N), and sensory test (Figure 3). The concentration of amines (histamine, putrescine, cadaverine and tyramine) was determined by HPLC [34]. Similarly, the concentration amount of aerobic mesophilic microorganisms and the TVB-N were calculated [35]. Also, the subjective sensory test was performed [36]. These are conventional tests for fish quality control carried out systematically by highly-skilled personnel with expensive equipment or are time-consuming, or both. The methodology followed for HPLC calibration and measurements and for the other techniques is conventional and it is described in the SI (Sections S11-S14).

Thus, a simple picture taken to a smart label F_{P2} inside a package of fish, without contacting it, can be used to estimate the total amine concentration (treatment of the sample and HPLC), colony-forming unit (microbiological assays), total volatile basic nitrogen (TVB-N), and organoleptic test (sensory test). These are four relevant parameters usually measured for food control (see the correlation curves in SI, Sections S11-S11). Moreover, the colour can be used to visually predict the quality, in terms of the chemical parameters commented.

Each label has an estimated cost of production of 0.02 euros, so it can be considered inexpensive, especially compared to the cost of analysis of the microbiological assay, HPCL, or total volatile basic nitrogen. Also, it is interesting to consider that the analysis is carried out at a given time just taking a picture, without spending time and without the need of highly trained personnel.

Figure 3.

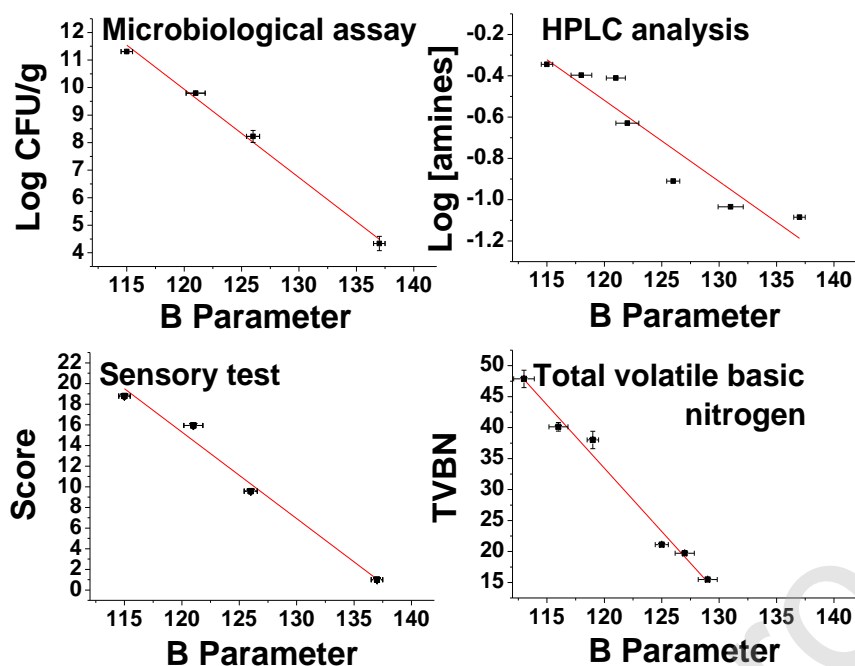


Figure 3. Correlation of the B parameter (blue component of the RGB parameters that define the digital colour) of pictures taken along time (3 days) to F_{P2} in an atmosphere containing fish meat with microbiological results, total amine content determined by HPLC, total volatile basic nitrogen and sensory test.

4. CONCLUSIONS

In summary, we have demonstrated that cotton fibres coated with high-performance sensory polymers can be used as costless colorimetric smart labels for the following of fish spoilage. The labels change their colour in the presence of biogenic amines in the atmosphere without being in contact with the fish meat (the amines are produced mainly by microorganisms along the spoilage process). This colour can be used to visually detect the freshness of the fish, or even the label can be photographed with a smartphone and its colour definition used to calculate within seconds relevant analytical data. Otherwise, this information could only be obtained by trained personnel with time-consuming and expensive techniques, such as total amine concentration (treatment of the sample and HPLC), colony-forming unit (microbiological assays), total volatile basic nitrogen (TVB-N), and organoleptic test (sensory test).

Declaration of Interest Statement

The authors declare no conflict of interest

Acknowledgements

The financial support provided by FEDER (Fondo Europeo de Desarrollo Regional), and both the Spanish Ministerio de Economía, Industria y Competitividad (MAT2017-84501-R) and the Consejería de Educación—Junta de Castilla y León (BU061U16) is gratefully acknowledged.

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Tables

Table 1. Evolution of F_{p2} sensory labels along time in a vial containing fish meat (Atlantic horse mackerel)

Time (minutes)	B parameter	Sensory label
0	137±0.50	
1520	121±0.83	
2960	118±0.90	
4400	108±0.87	