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## Room temperature phosphorimetric determination of bromate in flour based on energy transfer



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### ABSTRACT

Determination of bromate ions in contaminated flour samples by using a room temperature phosphorescence (RTP) optosensor is described. The optosensor is based on the non-radiative energy transfer from  $\alpha$ -bromonaphthalene (a phosphorescent molecule insensitive to the presence of the analyte) acting as donor, to an energy acceptor bromate-sensitive molecule (trifluoperazine hydrochloride). The RTP emission of the selected donor greatly overlaps with the absorption spectrum of the acceptor, resulting in a decrease of the measured signal as the concentration of bromate ions increases.

A simple and general procedure is proposed to carry out the incorporation of both the donor and acceptor molecules in an appropriate solid material (sensing phase) through the co-immobilization of the species in a sol-gel inorganic matrix. The optimum amounts of the sol-gel precursors, including silica precursors, type of catalysis, and concentrations of donor and acceptor molecules, have been evaluated in order to obtain the best analytical features of the proposed optosensor for bromate determination. The highly stable developed sensing phase shows a selective and reversible response towards bromate even in presence of dissolved oxygen (a well-known quencher of the RTP). The calibration graphs were linear up to  $200 \text{ mg L}^{-1}$ , with a detection limit for bromate dissolved in aqueous medium of  $0.2 \text{ mg L}^{-1}$ . Sample throughput of the proposed optosensor was about  $18 \text{ measurements h}^{-1}$ . Application of the developed sensing phase was successfully proved for the detection of bromate ions in commercial flours, obtaining good recoveries.

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### 1. Introduction

It is widely known that the bread making quality of freshly milled flour improves after two months storage. However, this process can be carried out faster through the addition of chemical substances called improvers [1]. Among these improvers, potassium bromate is commonly added because it is a slow-acting oxidizer that contributes to its functionality throughout the mixing, fermentation and proofing stages. Moreover, it presents an important residual action during the early stages of baking, resulting in strengthen dough and allowing for greater oven spring and higher rising in the oven [2].

However, there is a concern regarding the use of bromates in baking due to its possible relation to the development of tumors in laboratory animals, and therefore, European, American and Chinese regulations have limited its use. In this sense, the Code of Federal Regulations of the U.S. Food and Drug Administration has

restricted the amount of potassium bromate added in a quantity not exceeding 50 parts to each million parts of the finished bromated flour, and is added only to flours whose baking qualities are improved by such addition [3]. For this reason, the development or improvement of analytical methods for the determination of bromate ions at such levels in flours is a matter of great interest. A large number of analytical methods have been published exploiting ion chromatography coupled with accelerated solvent extraction [4], high performance liquid chromatography-inductively coupled plasma mass spectrometry [5], or ion chromatography with a conductivity detector [6]. However, those methodologies present some disadvantages such as the need for extraction of the bromate ions at high temperatures [4], sophisticated instrumentation not affordable for many laboratories [5], or time consuming analytical strategies [6].

Room temperature phosphorescence (RTP) offers interesting advantages over fluorimetric-based methods that makes it attractive for analytical applications [7]. For instance, the phosphorescence signal is a low-noise emission because it is measured after any short-lived background luminescence or scattered light has ceased, allowing lower detection limits (DLs). Besides, the long emission wavelength of the phosphorescence phenomena facilitates

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the design of robust and inexpensive instrumentation based on decay time measurements [8]. Nevertheless, despite those benefits, there is a lack of known RTP emitters whose spectroscopic characteristics change when there are bromate ions present in the medium. This limitation might be overcome by resorting to energy transfer (ET) from a RTP emitter (donor) insensitive to bromate ions to a suitable acceptor which is sensitive to bromate. This methodology is based on the transfer of energy from the donor to the absorber and, then, the absorber dissipates this energy through nonradiative processes [9–12].

Moreover, in order to develop an ET-RTP sensor it is necessary to immobilize the appropriate reagents in solid supports to fabricate “active” solid phases [13]. In this sense, sol–gel processing has gained an increasing importance in the incorporation of luminescence indicators into a structured media. This is mainly due to the simplicity of its preparation, chemical inertness, tunable porosity, optical transparency, mechanical stability and negligible swelling behavior [14]. Herein, donor and acceptor molecules are randomly mixed in close packed sol–gels. In this way, it is expected to demonstrate a very simple and general procedure for the co-immobilization of donor and acceptor molecules in a solid support, maintaining their optical properties and ensuring that they are close enough in proximity to allow the transfer phenomena to take place.

In this context, a simple, fast and selective ET-RTP sol–gel sensing phase for bromate determination in flour samples is here proposed. The method is based on the interaction of the donor molecule  $\alpha$ -bromonaphthalene (BrN), which emits a very stable RTP that it is not affected by the presence of dissolved oxygen [12] nor by the presence of bromate ions, and it was matched with another molecule acting as acceptor whose spectroscopic characteristics change in the presence of bromate ions.

## 2. Experimental

### 2.1. Reagents

The reagents used for the preparation of the standards and solutions were of analytical reagent grade. All standards and solutions were prepared with ultrapure deionised Milli Q water (Milli-Q2 system, Millipore, UK).

A stock solution of  $1.00 \times 10^{-4}$  M of  $\alpha$ -bromonaphthalene (Riedel-deHäen, Seelze, Germany) was prepared in a  $1.00 \times 10^{-2}$  M solution of  $\beta$ -cyclodextrin (Aldrich, Milwaukee, WIS, USA) and stored in the darkness. The mixture is left to stand in an ultrasonic bath for 30 min before added to the sol–gel precursors mixture. Stock solutions  $1.00 \times 10^{-3}$  M of trifluoperazine hydrochloride (Sigma-Aldrich) or phenothiazine (Sigma-Aldrich) were prepared by dissolving the appropriate amount of reagent with deionized Milli-Q water. Sol–gel silicate precursors, tetramethoxysilane (TMOS) and methyltrimethoxysilane (MTMOS) were obtained from Fluka Chemie (Steinheim, Germany). A stock standard solution of  $100 \text{ mg L}^{-1}$  of bromate was prepared in milli-Q water from potassium bromate (Merck, Darmstadt, Germany), dried at  $105^\circ\text{C}$  for 30 min. The stock solution is stable at least one week stored at  $4^\circ\text{C}$ . Ethanol and hydrochloric acid were purchased from Prolabo (Spain). Sodium nitrate, sodium sulfate, sodium chloride, sodium acetate, sodium phosphate, potassium nitrate, magnesium sulfate, copper (II) sulfate, zinc sulfate heptahydrate, iron (III) chloride, sodium hydrogen carbonate and calcium chloride, (all of them from Sigma-Aldrich) were used for the study of the potential interferences.

For real sample applications, four wheat flours commercialized for different purposes (2 regular flours, 1 special type for frying and 1 special type for pastymaking) have been used.

### 2.2. Instrumentation

Spectrophotometric measurements were performed with a Lambda 20 UV–vis spectrophotometer (Perkin Elmer, Norwalk, CT, USA) equipped with 10 mm quartz cells. Slits were fixed at 2 nm.

Phosphorescence measurements were performed on a Varian Cary Eclipse Luminescence spectrometer (Madrid, Spain), equipped with a discharge lamp. Unless stated otherwise, excitation and emission slits were fixed at 10 nm. A delay time of 0.1 ms and a gate time of 1.2 ms were typically used for RTP intensity measurements. The excitation and emission wavelengths were set at 220 nm and 540 nm, respectively, and the PMT voltage was adjusted to 775 V. In order to measure the solid sensing phase, sol–gel matrices were packed into a conventional Hellma luminescence flow-through cell made of quartz (Model 176.052-QS, Mullheim, Germany) of 1.5 mm of light path was employed in all the experiments. A peristaltic pump (model Minipuls 2, Scharlab, Barcelona, Spain) was used to generate the flow of the carrier solution through the system. 0.8 mm i.d. PTFE tubes were used throughout the flow system. The pH measurements were made with a pH-meter (Mod. MicroPH 2000 from Crison, Barcelona, Spain). All the analytical measurements were carried out at room temperature ( $20 \pm 3^\circ\text{C}$ ).

### 2.3. Synthesis of the sensing phase

The preparation of the sol–gel sensing phase providing the best analytical features was as follows. Briefly, 2.5 mL of ethanol, 0.5 mL of stock solution of  $10^{-4}$  M of BrN prepared in a  $10^{-2}$  M solution of  $\beta$ -cyclodextrin, 0.05 mL of trifluoperazine hydrochloride  $10^{-3}$  M and 0.25 mL of 0.1 M HCl, and 1.1 mL of Milli-Q  $\text{H}_2\text{O}$  were mixed and stirred. Afterwards, 0.6 mL of TMOS and 0.4 mL of MTMOS were added. After homogenization of the mixture, the polymerization process takes place and the mixture was left to dry for two weeks in the absence of light, until a constant weight is achieved. The dry xerogel was crunched and fragmented in an agate mortar and particle sizes of diameters between 80 and  $160 \mu\text{m}$  were selected by sieving for further experiments.

### 2.4. General procedure

The two carriers employed in order to make the sample pass through the sensing phase were 3 M HCl and  $\text{H}_2\text{O}$ , at a flow rate of  $1 \text{ mL min}^{-1}$ . For the preparation of the calibration graphs, 1 mL of bromate standard (or sample) was injected into the flow system via an injection valve located in the  $\text{H}_2\text{O}$  carrier channel (see Fig. 1). After injection, the standard is mixed with 3 M HCl by using a “Y” type connector. Finally, the mixture passed through the

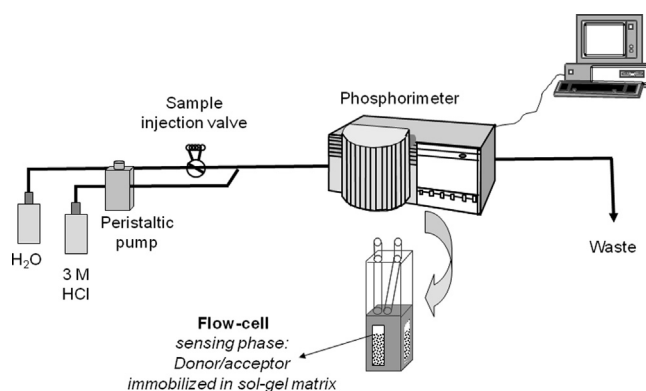


Fig. 1. Experimental set up used for the ET-RTP measurements.

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