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A multicommuted flow system for fast screening/sequential spectrophotometric determination of dichromate, salicylic acid, hydrogen peroxide and starch in milk samples

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ABSTRACT

In this work a multicommuted flow system for the sequential screening/determination of dichromate, salicylic acid, hydrogen peroxide and starch in milk samples was developed. The concept of multicommutation in flow injection analysis was chosen, resulting in an environmentally friendly system with minimal consumption of reagents and waste generation. The proposed approach is based on a simple binary DETECT or NO-DETECT response, thereby making it possible to determine analytes quickly, with high performance and easy operation. For dichromate determination, the proposed method was based on the reaction between Cr(VI) and 1,5-diphenylcarbazide, enabling a linear working range response, between 1.0 and 10.4 mg L^{-1}, ($R = 0.999$). In order to determine salicylic acid, the proposed method was based on a complexation reaction of Fe(III) and salicylic acid, with the linear working range response from 103.6 to 414.3 mg L^{-1} (7.5×10^{-4}–3.0×10^{-3} mol L^{-1}) ($R = 0.999$). The hydrogen peroxide determination was based on the oxidation reaction of hydrogen peroxide with vanadium oxide (V) in an acid environment, with a linear working range of 10.0–200.0 mg L^{-1} ($R = 0.996$). Starch determination was based on the complex reaction of starch and triiodide, with a linear working range of 12.5–150.0 mg L^{-1} ($R = 0.999$). The mean sampling rate for the four species was 83 determinations per hour. Performance curves were used to verify the quantity of false positives and false negatives. Addition and recovery tests were used for validation of the proposed procedures, resulting in variation between 90.1 and 108.7% for three different samples.

1. Introduction

Milk is a food consumed worldwide due to its widely known nutritional value and health benefits (Fox & McSweeney, 2009, chap. 4). Apart from being a source of nutrients essential for growth, development and maintenance of health, milk is a major source of protein in the diet of young animals and humans of all ages (Hurley, Coleman, Ireland, & Williams, 2006).

Recently, the occurrence of adulterations and frauds in liquid milk has increased. These adulterations have been practiced in a number of different ways, by the addition of an adultering agent to increase economic yield (Das, Sivaramakrishna, Biswas, & Goswami, 2011).

The addition of potassium dichromate, salicylic acid, hydrogen peroxide and starch in milk is not allowed in Brazil, in any concentration. Because of this, milk containing any of these substances is considered adulterated (Brasil, 2006). The adulteration of liquid milk by adding starch occurs with the intention of masking the extra addition of water. Adulteration using preservative substances such as dichromate, salicylic acid and hydrogen peroxide to milk have the objective of inhibiting or delaying the appearance of microorganisms in the liquid milk (Barbano, Wojciechowski, & Lynch, 2010; Borin, Ferrão, Mello, Maretto, & Poppi, 2006; Cerdán, Peris-Tortajada, & Maquieira, 1992; Souza et al., 2011).

Adulterations have increased because the consumption of milk has become more extensive and, in addition, the detection methods

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are difficult to implement in local production and packaging. The official procedures are time consuming, expensive and can provide false positive results, limiting their application in routine control (Kartheek, Smith, Muthu, & Manavalan, 2011).

Different analytical procedures have been proposed to detect dichromate in milk, such as titration with silver chloride (Brasil, 2006), and use of mid-infrared spectroscopy and molecular absorption spectrophotometry (Barbano et al., 2010; Cerdán et al., 1992).

The official methodology for salicylic acid determination in milk used in Brazil is based on the reaction of Fe^{3+} and salicylic acid in an acid medium (Brasil, 2006). Another analytical method based on amperometric biosensory methods has been reported for salicylic acid determination in milk (Zavar, Heydari, & Rounaghi, 2013).

Different methodologies for hydrogen peroxide determination in milk have been developed using colorimetric (Brasil, 2006) and electrochemical methods (Abbas, Luo, Zhu, Zou, & Tang, 2010; Campuzano, Pedrero, & Pingarrón, 2005; Shamsipur, Asgari, Maragheh, & Moosavi-Movahedi, 2012; Silva, Montes, Richter, & Munoz, 2012). One of the main methods for starch determination in milk involves the use of iodine titration with potentiometric or amperometric detection (Banks, Greenwood, & Muir, 1971). Another methodology was developed for starch determination in milk, using a spectroscopy technique such as Near-infrared (Borin et al., 2006). A complexation reaction of iodine with starch has been the official methodology used to determine starch in milk (Brasil, 2006).

It is important to develop analytical methodologies that are fast, less expensive and accurate for screening or quantification of adulterants in milk. The search for new analytical methodologies that reduce or replace materials harmful to human health and the environment, is becoming a key parameter in green chemistry research (Anastas, 1999; Vieira, Crispino, Perdigão, & Reis, 2013). Flow systems are excellent tools for dealing with solutions in wet chemical analysis (Rocha et al., 2002). The use micro-pumping in flow system analysis is a successful strategy, for the carrying, inserting and mixing of solutions in a flow analysis system (Lapa, Lima, Reis, Santos, & Zagatto, 2002). Another aspect of solenoid micro-pumping is that it allows implementation of a versatile and inexpensive flow system (Morales-Rubio, de la Guardia, & Reis, 2009). The multicommutation flow systems network, when designed by associating a solenoid valve, a solenoid pinch valve, and solenoid micro-pumps together with the concept of binary sampling is straightforward in operation, very versatile, robust, enables the development of green analytical methodologies and enables the use of automation (Lavorante, Pires, & Reis, 2006; Melchert, Reis, & Rocha, 2012).

Multicomponent flow analysis systems are efficient for the determination of multiple analytes. Most flow analysis systems deal with two analytes (c.a. 72%), three analytes (18% c.a.), four or five (c.a. 4%) analytes or six analytes (c.a. 2%) (Trojanwicz, 2008, chap. 1). In the literature there are some works that approach multidetermination employing different types of detectors. (Calvo, Durán, & Del Valle, 2007; Lavorante, Morales-Rubio, Guardia, & Reis, 2007; Rocha, Fatibello Filho, & Reis, 2003; Rocha, Martelli, & Reis, 2001). The development of these systems depends on a number of experimental circumstances, such as the number of components, the presence of interferences and the complexity of the sample matrix (Rocha, Reis, & Rohwedder, 2001; Silva, Nogueira, Souza, & Zagatto, 1998).

The Association of Official Analytical Chemists (AOAC) defines screening or qualitative methodologies of analysis as when the response is either the presence or the absence of the analyte detected in a specified test portion; a binary response may also be available to the analyst (Feldsine, Abeyta, & Andrews, 2002). Screening methodologies when associated with flow systems offer a fast answer when compared with quantitative methodologies (Amador-Hernández, Fernández-Romero, & Luque de Castro, 2001; Lima et al., 2004; Sainz-Gonzalo, Fernandez-Sanchez, & Fernandez-Gutierrez, 2011; Valcárcel, Cárdenas, & Gallego, 2002; Valcárcel, Gallego, Cárdenas, & Gambart, 1998).

This paper proposes a flow analysis screening system which is fast, simple and reliable for the sequential qualitative detection and determination of dichromate, salicylic acid, hydrogen peroxide and starch in milk. The methodology presented is based on the use of a multicommutation flow system based on binary sampling, with the use of pinch solenoid valves and solenoid micro-pumps. The methodology has been validated and applied to samples of liquid milk.

2. Experimental

2.1. Reagents, solutions and samples

All solutions were prepared with analytical grade chemicals. Purified water presenting conductivity less than 0.10 μS cm^{-1} was used throughout.

All stock solutions were stored away from light at 4 °C and remained for at least 15 days. A solution of 1381 mg L^{-1} (0.010 mol L^{-1}) salicylic acid (Vetec) was prepared by dissolving 0.1381 g in 10 mL of ethanol and subsequently, diluted to volume of 100 mL with deionized water. A solution of 1471 mg L^{-1} (0.010 mol L^{-1}) potassium dichromate (Vetec) was prepared by dissolving 0.1471 g in 100 mL deionized water. A solution of 3600 mg L^{-1} (0.106 mol L^{-1}) hydrogen peroxide (Vetec) was prepared by dissolving 658 μL in 100 mL deionized water. A solution of starch (Vetec) 400 mg L^{-1} was prepared by dissolving appropriate amounts of reagent to make up a volume of 100 mL.

Working reference solutions were prepared daily, by diluting stocks solutions with interval concentrations: 103.60–414.40 mg L^{-1} salicylic acid; 1.0–10.4 mg L^{-1} potassium dichromate; 10.0–200.0 mg L^{-1} hydrogen peroxide; and 12.5–150.0 mg L^{-1} starch.

The chromogenic reagents were prepared daily. For determination of salicylic acid, a solution concentration of 0.006 mol L^{-1} was prepared by diluting stock solution of 0.01 mol L^{-1}. A solution of $Fe_2(SO_4)_3$ 19.94 g L^{-1} (0.10 mol L^{-1}) (Vetec) was prepared by dissolving 1.9940 g in a 100 mL buffer HCl/KCl, pH 1.7, and another solution of $Fe_2(SO_4)_3$ with the same concentration in 100 mL buffer acetic acid/sodium acetate, pH 3.5. For potassium dichromate two solutions of 1.8×10^{-3} mol L^{-1} of 1,5-diphenylcarbazide (1,5-DFC), $C_{13}H_{14}N_4O$ (Sigma-Aldrich) were prepared by dissolving 0.0436 g in a 100 mL buffer HCl/KCl pH 1.2 and another 1,5-DFC solution at 100 mL buffer HCl/KCl pH 2.2. To determine of hydrogen peroxide, solutions of vanadium oxide, V_2O_5 (Sigma Aldrich) 1.8188 mg L^{-1} were prepared by dissolving 0.4547 g in 12% HCl (v/v) and 100 mL of V_2O_5 in same concentration dissolved in 6% HCl (v/v). For determination of starch, the reagent solution Lugol's iodine was prepared with 0.10 g of iodine (Vetec) that was first dissolved in 5 mL of ethanol P.A. (Vetec) then mixed with 0.20 g of potassium iodide KI dissolved in 250 mL of distilled water.

2.2. Apparatus

The following equipment was used: a multichannel spectrometer with linear array of diodes (USB4000, Ocean Optics), a flow cell with an optical path length of 10 mm (Hellma, Plainview, NY, USA) with an 80 μL internal volume. For the radiation source, a tungsten-halogen lamp (Ocean Optics, LS-1) was used to carry out spectrometric measurement. Fiber optic cable with 0.20 mm of diameter was used for transporting the radiation to the detection point.