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Simplex optimization of the variables influencing the determination of pefloxacin by time-resolved chemiluminescence

José A. Murillo Pulgarín, Aurelia Alañón Molina *, Elisa Jiménez García

Department of Analytical Chemistry and Food Technology, University of Castilla-La Mancha, 13071 Ciudad Real, Spain

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ABSTRACT

A new chemiluminescence (CL) detection system combined with flow injection analysis (FIA) for the determination of Pefloxacin is proposed. The determination is based on an energy transfer from Pefloxacin to terbium (III). The metal ion enhances the weak CL signal produced by the $KMnO_4/H_2SO_3$/Pefloxacin system. A modified simplex method was used to optimize chemical and instrumental variables. The influence of the interaction of the permanganate, Tb (III), sodium sulphite and sulphuric acid concentrations, flow rate and injected sample volume was thoroughly investigated by using a modified simplex optimization procedure. The results revealed a strong direct relationship between flow rate and CL intensity throughout the studied range that was confirmed by a gamma test. The response factor for the CL emission intensity was used to assess performance in order to identify the optimum conditions for maximization of the response. Under such conditions, the CL response was proportional to the Pefloxacin concentration over a wide range. The detection limit as calculated according to Clayton's criterion 13.7 μg L^{-1}. The analyte was successfully determined in milk samples with an average recovery of 100.6 ± 9.8%.

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1. Introduction

Quinolones constitute a group of major antibacterials derived from the discovery by G. Lesher in 1962 that nalidixic acid was effective against gram-negative bacteria. The later inclusion of a fluorine atom at position six of the quinolone ring [1] yielded a sub-group called "fluoroquinolones" which exhibit even higher bactericidal activity than the original quinolones by effect of their inhibiting DNA-gyrase [2].

1-Ethyl-6-fluoro-7-(4-methylpiperazin-1-yl)-4-oxo-quinoline-3-carboxylic acid, commonly known as "Pefloxacin" (PEFLO), is one of the many antibiotics belonging to the fluoroquinolone group. PEFLO is a broad-spectrum antibiotic active against both gram-positive and gram-negative bacteria which has been used in the treatment of uncomplicated human gastrointestinal and genitourinary tract infections—this indication, however, is no longer effective owing to increasing bacterial resistance. PEFLO has also been increasingly used as a veterinary medicine to treat microbial infections. Resistant bacteria from animal sources can infect the human population, not only by direct contact, but also via food products of animal origin, and eventually transfer their resistant genes to other bacteria in the endogenous human flora [3].

These facts explain the growing interest in the determination of fluoroquinolones such as PEFLO in real samples. A variety of methods based in spectrophotometry [4–6], fluorimetry [7], chromatography [8–10] and capillary electrophoresis [11,12] are currently available for its determination in pharmaceuticals and biological fluids. Although these methods possess good sensitivity, they require using sophisticated, expensive equipment.

Chemiluminescence-based methods are not only highly sensitive, but also easier and faster to operate than most alternative methods. Most analytes exhibit very weak CL, so an additional fluorescent substance is typically used as a sensitizer. Such is the case with cerium, terbium, europium and dysprosium ions, which form metal chelates that give characteristic lanthanide line emission spectra upon excitation at the wavelengths typically absorbed by organic ligands [13].

The first CL method used to determine PEFLO [14] involved its reaction with *bis*(hydrogen periodate)–argentate(III) complex anion in an acid medium and afforded its determination in real samples. More recently, enoxacin, fleroxacin, pefloxacin and pipemidic acid were determined by dysprosium-sensitized CL [15]. The methodology used enabled the determination of residues of synthetic quinolone-based antibiotics in foods and biological samples (e.g., that of enrofloxacin, in eggs and veterinary drugs) [16].

The aim of this work was to develop a simple, fast, direct method for the determination of PEFLO based on the chemiluminescent reaction involving the oxidation of sulphite ion by permanganate ion to excited sulphur dioxide in the presence of a complex formed by the analyte and terbium (the sensitizer). The mutual dependence of the chemical and instrumental variables influencing the analytical signal led us to

* Corresponding author.
E-mail address: Aurelia.Alanon@uclm.es (A. Alañón Molina).

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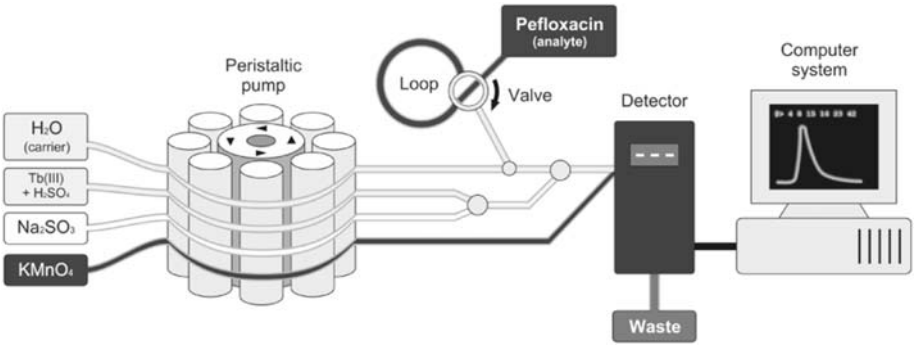

Fig. 1. Assembling FIA used.

use a simplex optimization procedure for increased efficiency and expeditiousness [17]. Nelder and Mead [18] devised a strategy known as the "modified simplex method" by which the shape and dimension of each simplex is adapted to the optimum experimental conditions. Subsequently, Ryan et al. [19] found a weighted modified simplex method to result in considerably improved performance. In this work, we used a combination of both methods as the fastest, easiest way [20,21] to simultaneously identify the optimum values for all mutually dependent instrumental variables. Based on the results, the proposed method is an effective choice for the determination of PEFLO in biological matrices such as milk. Also, it is simple and fast enough for use in routine analyses.

2. Experimental

2.1. Instrumentation

Fig. 1 depicts the manifold of the flow injection analysis and stopped flow system. The reactants were pumped through the three-line manifold by a computer-controlled Gilson Minipuls 3 peristaltic pump. The four streams were circulated through acid-resistant Tygon polytetrafluoroethylene tubes of 0.8 mm i.d. The sample (PEFLO) stream was mixed in sequence with sodium sulphite, the sensitizer [Tb (III) dissolved in H_2SO_4] and the oxidant ($KMnO_4$). Mixing with the permanganate took place in the flow cell, which was located right in front of the photomultiplier tube of the detector. This allowed the whole CL signal to be detected and recorded. After abruptly stopping the flow, the CL intensity of the mixture was measured by using a Camspec CL-2 chemiluminescence detector equipped with a Hamamatsu No. 00 photosensor module with spectral response from 500 to 900 nm and a 120 μL spiral-type flow cell from Sawson (Cambridge, UK). The detector was interfaced to a computer via an analogue-to-digital converter. This allowed the CL transient signal to be continuously monitored by using the software Chromatography Station for Windows CSW32 (Data Apex, Ltd., Prague, Czech Republic) in order to obtain CL intensity versus time plots that were processed by the authors. All measurements were made at room temperature (about 22 °C).

2.2. Reagents

A potassium permanganate ($KMnO_4$) stock solution (1 mmol L^{-1}) was prepared by dissolving 15.8 mg of the chemical in ultrapure water and making to 100 mL with more water in a calibrated flask. This coloured solution is photosensitive and should therefore be stored in the dark. A stock sodium sulphite (Na_2SO_3) solution (10 mmol L^{-1}) was made by dissolving 12.6 mg of the salt in ultrapure water and making to 100 mL with more water in a calibrated flask. Both stock solutions were prepared freshly on a daily basis and diluted as required.

A sulphuric acid working-strength solution (0.1 mol L^{-1}) was prepared by dilution to the volumetric mark of a volume of 5.6 mL of 96% H_2SO_4 in a 1000-mL calibrated flask.

A terbium (III) chloride hexahydrate working-strength solution (9 mmol L^{-1}) was made by adding 839.8 mg of the salt and 1.63 mL of the sulphuric acid solution (0.1 mol L^{-1}) to a 250-mL calibrated flask and then water to the mark.

A stock solution (100 mg L^{-1}) of PEFLO (Sigma Aldrich, St. Louis, USA) was obtained by dissolving 10 mg of the analyte in 100 mL of water. This solution remained stable for at least a fortnight if stored at 4 °C in the dark. PEFLO working-strength solutions were prepared in 25 mL volumetric flasks by dilution of appropriate aliquots of the stock solution to the mark with ultrapure water. These solutions were stable for at least 2 h.

All experiments were performed with analytical reagent-grade chemicals and pure solvents. Also, all solutions were prepared in ultrapure distilled water with a total organic carbon (TOC) content <5 μg L^{-1} obtained from a Milli-Q 185 plus system.

Sodium sulphite and sulphuric acid were supplied by Panreac Química, S.A. (Barcelona, Spain). Potassium permanganate was obtained from Merck (Darmstadt, Germany) and terbium (III) chloride hexahydrate from Sigma–Aldrich (St. Louis, MO, USA).

Whey was obtained by precipitating the casein protein fraction of milk at pH 4.6. To this end, a volume of 50 mL of semi-skimmed milk was placed in a 100 mL calibrated flask to which 45 mL of Milli-Q water at 40 °C and 1 mL of 10% *w/v* acetic acid solution were added. The flask contents were smoothly mixed and allowed to settle for 10 min. Then, 1 mL of 1 M sodium acetate buffer was added, followed by mixing and making to volume with water before allowing the flask to cool. Once the casein protein fraction precipitated, the soluble

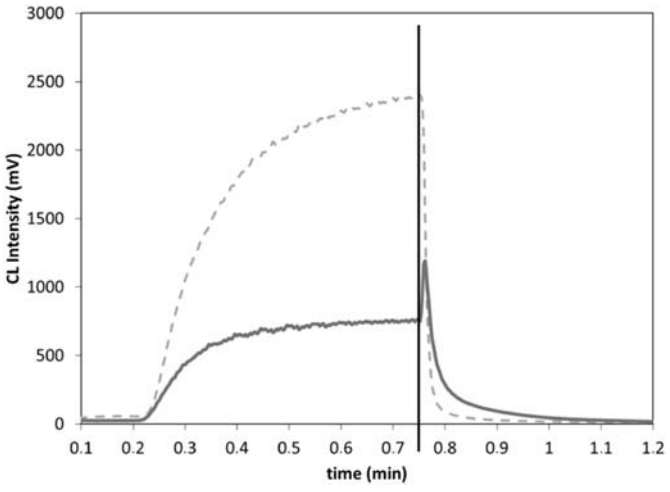

Fig. 2. Kinetics graph using stopped-flow. Dotted line: $[H_2SO_4] = 8{\cdot}10^{-4}$ M, $[KMnO_4] = 10^{-5}$ M, [Tb (III)] = $8{\cdot}10^{-3}$ M and $[Na_2SO_3] = 10^{-4}$ M, [PEFLO] = 100 μg L^{-1}. Continuous line: $[H_2SO_4] = 8{\cdot}10^{-4}$ M, $[KMnO_4] = 10^{-6}$ M, [Tb (III)] = $8{\cdot}10^{-3}$ M and $[Na_2SO_3] = 10^{-4}$ M, [PEFLO] = 100 μg L^{-1}.

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