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Luminescent determination of quinolones in milk samples by liquid chromatography/post-column derivatization with terbium oxide nanoparticles

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ABSTRACT

The usefulness of terbium oxide nanoparticles (Tb_4O_7NPs) as post-column derivatizing reagent for the liquid chromatographic determination of residues of quinolone antibiotics in milk samples has been studied. Seven quinolones of veterinary use have been chosen as model analytes to develop this method. The derivatization step is based on the formation of luminescent chelates of quinolones with Tb_4O_7NPs, which are monitored at λ_{ex} = 340 nm and λ_{em} = 545 nm. Another relevant feature of the method is that the use of a 10-cm column and a ternary mixture of methanol, acetonitrile and acetic acid as mobile phase in gradient elution mode allow the chromatographic separation of the quinolones in about 13 min, whereas previously described chromatographic methods require about 20 min.

The dynamic ranges of the calibration graphs and limits of detection are, respectively: 65–900 ng mL^{-1} and 35 ng mL^{-1} for marbofloxacin, 7.2–900 ng mL^{-1} and 2.5 ng mL^{-1} for ciprofloxacin, 6–900 ng mL^{-1} and 2 ng mL^{-1} for danofloxacin, 50–900 ng mL^{-1} and 20 ng mL^{-1} for enrofloxacin, 35–900 ng mL^{-1} and 12 ng mL^{-1} for sarafloxacin, 5–900 ng mL^{-1} and 2 ng mL^{-1} for oxolinic acid, and 7–900 ng mL^{-1} and 2.5 ng mL^{-1} for flumequine. The precision, established at two concentration levels of each analyte and expressed as the percentage of the relative standard deviation is in the range of 1.9–8.1% using standards, and of 3.4–10.7% in the presence of milk samples. The method has been satisfactorily applied to the analysis of skimmed, semi-skimmed and whole milk samples, with recoveries ranging from 89.0 to 106.5%.

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1. Introduction

Lanthanide-sensitized luminescence (LSL) technique, which involves the formation of chelates between an organic ligand and a lanthanide ion, such as europium(III) and terbium(III), has found interesting analytical applications owing to the features of these chelates: (1) a large Stokes shift, (2) a relatively long emission wavelength, (3) narrow emission bands (1–20 nm half width), and (4) a relatively long-lived luminescence, up to milliseconds order. The first three features provide these chelates with a good spectral selectivity, whereas the fourth one allows the temporal discrimination of the analytical signal when the time-resolved mode of the instrument is used [1–4]. The luminescent behavior of these chelates has given rise to the development of sensitive and selective analytical methods in which lanthanide ions are used for the direct determination of organic compounds [2,5–13], as labels in bioassays [1,2] and as derivatizing reagents in separation techniques [2,14–16].

Nowadays, the special features of nanomaterials have made them attractive as analytical reagents [17]. In the case of nanomaterials based on lanthanide ions, they have found some applications as labels in bioassays [18], but their use for the direct determination of organic compounds has been scarcely described up to date. A recent method for the determination of fluoroquinolones is based on the quenching effect caused by these antibiotics on the luminescence of Eu(III)-thenoyltrifluoroacetone complexes inside polymeric capsules prepared using a layer-by-layer method [19]. Lanthanide oxide nanoparticles (NPs) are another type of nanomaterials that have shown their usefulness as analytical reagents. Thus, Tb_4O_7NPs and Eu_2O_3NPs have been used for the determination of lasalocid in eggs, water and premixes samples [20] and tetracyclines in calf urine and honey samples [21], respectively, providing satisfactory

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results in both instances. Also, Tb_4O_7NPs have been described as activators of laccase enzyme, which has been applied to the determination of polyphenols in wine samples [22]. However, to the best of our knowledge, the use of these NPs as derivatizing reagents in liquid chromatography (LC) with photoluminescence detection has not been reported up to date. Nanotechnology has been previously applied to LC for the determination of small biothiols in biological matrices using gold nanoparticles (AuNPs) as post-column derivatizing reagents [23,24]. Thus, aggregation of the AuNPs in the presence of thiols led to a change in the surface plasmon resonance band of AuNPs, measured at 680 nm [23], whereas a decrease in the chemiluminescence of the luminol–AuNPs system in the presence of thiols allowed the determination of these compounds [24].

The work presented here is aimed to prove the usefulness of Tb_4O_7NPs as post-column derivatizing reagent for the determination of quinolones in milk samples by LC. These antibiotics have become an integral part of livestock production and play an important role in maintaining animal welfare. The presence of their residues in foods can cause in consumers some undesirable effects, such as allergic hypersensitivity reactions, toxic effects and, also, the development of resistance to antibiotics, which constitutes a major threat to public health. Several analytical methods have been reported for the determination of quinolones using capillary electrophoresis (CE) with UV detection [25] and, mainly, LC with UV [26–28], fluorometry [14–16,28–30] and mass spectrometry [26,28,31,32] detection systems. The low MRLs defined for quinolones in milk samples, which are in the range of 30–100 $\mu g\,kg^{-1}$ [28,33], make it necessary the use of liquid–liquid extraction procedures and, in some instances, the additional use of a solid-phase extraction step [25,27,28,30] to obtain suitable recoveries and to clean-up samples by removing co-extracted compounds from sample matrix, like lipids, carbohydrates, proteins and vitamins.

Terbium-sensitized luminescence (TSL), based on the use of Tb(III) ions in solution as reagent, has been previously reported as a sensitive and selective detection system for the chromatographic determination of quinolones in food samples, using only a simple deproteinization step for sample treatment [14,15]. In this instance, the capability of commercial Tb_4O_7NPs to react with quinolones and to act as an alternative derivatizing reagent is investigated in the study described here. For this purpose, seven quinolones, namely marbofloxacin (MAR), ciprofloxacin (CIP), danofloxacin (DAN), enrofloxacin (ENR), sarafloxacin (SAR), oxolinic acid (OXO) and flumequine (FLU), which are intended for veterinary use, have been chosen as model analytes. Also, the chromatographic experimental variables have been optimized to improve the separation of the analytes, shortening the duration of the chromatogram. Thus, a relatively high number of chromatographic methods for quinolone determination require about 20 min to obtain the chromatogram [14,26,27,29,30], whereas the new method allows their separation in about 13 min. The practical usefulness of the method has been demonstrated by its application to the analysis of different kinds of milk samples, obtaining satisfactory recovery values.

2. Experimental

2.1. Instrumentation

An SLM AMINCO (Urbana, Illinois, USA) Model 8100, luminescence spectrometer provided with a 450 W xenon lamp was used for monitoring fluorescence spectra for the preliminary studies at batch measurements, using a conventional 1 cm path-length quartz cell. The detector high voltage was set at 900 V with gain 1. All measurements were obtained using 16-nm bandwidth for both excitation and emission slits.

The chromatographic separation was performed on a modular liquid chromatograph consisting of a Jasco PU-2089 Plus (Jasco, Tokyo, Japan) high pressure quaternary gradient pump, a 7725 Rheodyne (Cotati, CA) high-pressure manual injection valve with a 20 μL injection loop, and a Halo C_{18} column of 100 mm × 4.6 mm i.d., 2.7 μm used as analytical column. A Gilson (Villiers-le-Bel, France) Minipuls-3 low pressure peristaltic pump and Omnifit (Cambridge, UK) Teflon tubing of 0.5 mm i.d. were used to build up the post-column derivatization manifold. The same spectrofluorometer was used as detection system in LC, using a 176-052-QS Hellma (Hellma Hispania, Barcelona, Spain) flow cell with an inner volume of 18 μL.

2.2. Reagents

All chemicals used were of analytical reagent grade. Stock solutions were prepared by dissolving standards in deionized water, obtained using a Millipore (Bedford, MA) Milli-Q system. Stock solutions (1000 $mg\,L^{-1}$) of ciprofloxacin hydrochloride (Lesvi Laboratories, Barcelona, Spain) and marbofloxacin (Fluka, Buchs, Switzerland) were prepared using deionized water. Enrofloxacin (Fluka, Buchs, Switzerland), danofloxacin (Fluka, Buchs, Switzerland), flumequine (Sigma–Aldrich, Seelze Germany), sarafloxacin hydrochloride (Fluka, Buchs, Switzerland) and oxolinic acid (Sigma–Aldrich, Seelze Germany) were prepared at the same concentration, adding a minimum volume of 0.1 M sodium hydroxide and then, raised up to mark with deionized water. These solutions were stored at 4 °C for a month, and further dilutions were performed in deionized water to obtain working solutions. Commercial Tb_4O_7 nanopowder (<100 nm, 99.5%) was obtained from Aldrich (St. Louis, MO, USA). A 1.34 mM Tb_4O_7 stock solution was prepared in 2-propanol (Pareac Quimica, S.A., Barcelona, Spain). A 1 mM tri n-octyl phosphine oxide (TOPO) solution was prepared by dissolving the appropriate amount of TOPO (99%, Aldrich, St. Louis, MO, USA) in a minimum volume of ethanol and then, adding water dropwise until mark. Stock solutions of the surfactants cetyltrimethylammonium bromide (CTAB) (10 mM), Triton X-100 (1%) (Fluka, Buchs, Switzerland), and sodium dodecylsulfate (SDS) (0.2 M) (Sigma–Aldrich, Seelze Germany) were prepared in distilled water. Also a 1 M hexamethylenetetramine solution (Hexamine) (Merck, Schuchardt, Germany) was prepared in distilled water. A 1 M buffer solution of hydroxymethyl-aminomethane (TRIS) (Merck, Schuchardt, Germany) was prepared by dissolving the appropriate amount in water and adjusting the pH with nitric acid (Merck, Schuchardt, Germany). A 3 M sodium acetate solution was prepared by dissolving the appropriate amount of this salt (Aldrich, St. Louis, MO, USA) in distilled water and used for the sample treatment.

The mobile phase was constituted by solvents A [HPLC-grade methanol (MetOH) Fluka, Buchs, Switzerland], B [far UV/gradient quality acetonitrile (ACN)] Romil Pure Chemistry, Lameira, UK] and C [acetic acid (10 mM, pH adjusted to 2.6 using HCl), Panreac Quimica, S.A., Barcelona, Spain]. The ternary mobile phase was mixed by operating in the gradient mode during the chromatographic separation.

2.3. Procedures

2.3.1. Batch measurements

Individual solutions containing a quinolone (CIP, DAN, ENR, FLU, MAR, SAR and OXO (0.5 $mg\,L^{-1}$), Tb_4O_7 NPs (30 μM), TOPO (40 μM), SDS (10 mM), TRIS (15 mM) and hexamine (5 mM) were prepared in 10-mL volumetric flasks. The luminescence intensity was measured at the characteristic excitation wavelength of each quinolone and at the maximum emission wavelength of Tb_4O_7NPs, which is 545 nm.

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