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Cotton swabs supported in-situ assay for quaternary ammonium compounds residues in effluents and surfaces

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ABSTRACT

Cellulose paper and cotton swabs have been tested as sampling, reaction and measurement media for quaternary ammonium compounds (QACs) using the reagent Chromo Azurol S in the presence of aluminum cations (CAS-Al). On the basis of the results obtained a new method is proposed for the analysis of QACs in water samples which only entails the successive immersion of swabs into 1 mL of the samples, 1 mL of a solution of CAS-Al for the formation of a ternary blue complex, and 1 mL of water to remove the excess of reagent. The method can be used for the visual on site detection of QACs in effluents, as well as for their quantification within the 3.62–36.2 mg/L range through the direct measurement of the reflectance diffuse of the cotton tips. The proposed approach has been validated for the identification and quantification of QACs in water, and applied to effluents generated by the dairy industry. Moreover, the proposed methodology can be also adapted to the on-site detection of residues of QACs in surfaces at sub μg/cm^2 levels.

1. Introduction

Quaternary ammonium compounds (QACs) are cationic surfactants widely used in the production of cleaning agents, fabrics, cosmetics, disinfectants and other industrial products. The most widely used QAC is benzalkonium chloride (BAC), a mixture of *n*-alkylbenzyldimethyl ammonium chloride homologues with *n* in the 8–18 range, and the C_{12}, C_{14} and C_{16} homologues as the predominant compounds. Other QACs widely produced are dialkyldimethylammonium compounds, being didecyldimethylammonium chloride (DDAC) the most representative member of this group.

Due to their widespread use large amounts of QACs enter the environment compartments through wastewater (Clara, Scharf, Scheffknecht, & Gans, 2007; Zhang et al., 2015). The presence of QACs in the environment is of major concern because of their toxicity to aquatic organisms. For this reason, several efforts have been paid to develop analytical methods for their determination in environmental matrices such as waters, effluents, sludge and sediments (Olkowska, Polkowska, & Namieśnik, 2012; Prieto-Blanco, López-Mahía, & Campíns-Falcó, 2009, 2013, 2016). Due to their biocidal effects some QACs are also increasingly used in the food industry for the disinfection of production equipment. However, as these compounds can have negative effects on human health mainly associated with asthma and skin allergy, their presence in foods has to be controlled. For example, in the European Union BAC and DDAC are allowed in the food industry, but a residual maximum amount of 0.1 mg/kg has been set (Commission Regulation EU 1119/2014), and similar regulations have been adopted by other countries.

Liquid chromatography (LC) is generally used for the analysis of QACs, although due to the lack of chromophores in some of them (i.e. DDAC) mass spectrometry (MS) detection is required. Several LC-MS methods have been described for the identification and quantification of QACs in environmental (Olkowska et al., 2012; Prieto-Blanco et al., 2013) and food matrices (Bertuzzi & Pietri, 2014; Xian et al., 2016; Cao et al., 2014). However, this technique may be unsuitable for on-site applications or when a rapid action must be taken. Examples are the on-site detection of QACs residues in tools and equipment utilized in food industries, or the control of QACs in the effluents generated during cleaning and maintenance processes. Other methodologies typically used for QACs such as two-phase titration methods (Tsubouchi, Mitsushio, & Yamasaki, 1991) and colorimetric methods based on the formation of ionic-

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pairs followed by their extraction into an organic solvent (Idouhar & Tazerouti, 2008), as well as methods which involve extensive data treatment (Plesha, Wie, Mullin, & Kidwell, 2006) may be also impractical for on-site applications.

The colorimetric determination of QACs in aqueous samples has been reported using different reagents. These assays are typically based on the modification of the color of the reagent (or a complex formed in the presence of metallic cation) due to the interaction with QACs. For example, Idouhar and Tazerouti proposed a method based on the reaction of QACs with patent blue V (Idouhar & Tazerouti, 2008). Aliquots of the samples (100 mL) were treated with aliquots of reagent and buffer; the mixture was stirred for 15 min with 15 mL of chloroform in order to extract the ionic pair formed. The organic phase was then separated and washed with water; once purified, the absorbance of the organic phase was measured for the quantification of the analyte (cetyltrimethylammonium bromide, CTAB). Ensafi et al. used eriochrome black T (EBT) to form colored derivatives with different QACs using a flow injection manifold (Ensafi, Hemmateenejad, & Barzegar, 2009). The reagent Chromo Azurol S (CAS) was utilized for Afkhami et al. for the determination of CTAB, cetylpiridinium bromide (CPB) and dodecyltrimethylammonim bromide (DTAB) through the formation of a ternary complex with Be(II) or with Al(III) (Afkhami, Nematollahi, Madrakian, & Hajihadi, 2011). The formation of the complex entailed the treatment of the sample with aliquots of the individual CAS, aluminum cation, acetate buffer (pH 5.4) and Triton X-100 solutions. Semiquantitative colorimetric assays for QACs have been described by Zheng et al. based on the employment of nanoparticles (NPs) (Zheng, Yu, Xu, & Chen, 2014a, 2014b). The authors found that the color of Ag NPs and Au NPs solutions changed in the presence of QACs, which was exploited for their identification with limits of detection (LODs) in the 0.17–1.54 mg/L range; the assay with AgNPs was also used for the semiquantitative analysis of BAC (Zheng et al., 2014a). Mousavi et al. proposed a procedure for the detection of QACs residues on stainless steels surfaces based on the formation of a colored ion pair with Eosin-Y in the presence of Triton X-100 (Mousavi, Butler, & Danaher, 2013). QACs residues were removed from the surfaces with swabs, and then extracted into a borate buffer by sonication; the collected extracts were treated with the reagent for the formation of the colored derivative.

It can be concluded that there are several alternatives for QACs determination suitable for laboratory processing. However, most of the proposed methods are not suitable for in-situ tests because they involve the manipulation of several solutions; in some cases organic solvents or specific instrumentation (such as the flow-injection-based method) are also required. The assays with NPs proposed by Zheng et al. were adequate for the visual on-site detection of QACs but they have not been validated for quantitative purposes. In addition, according to the authors, the aggregation of the NPs was strongly affected by the presence of common anions such as chloride or nitrate, among others, which are frequently found in industrial effluents. Therefore, simple and rapid tests for the detection and quantification of QACs are still needed.

In colorimetric assays sample handling can be substantially reduced if the analyte is extracted from the sample matrix, made to react and naked-eye detected and/or measured in the same media, i. e. in a solid support. This scheme is increasingly used for the development of optical sensors and microfluidic devices (Dungchai, Chailapakul, & Henry, 2010; Sicard et al., 2015; Pla-Tolós et al., 2016). In the present work we have evaluated the possibility of integrating sampling and the formation of a colored derivative for the rapid visual detection of QACs. Two cellulose-based supports, paper trips and cotton swabs, have been selected for this purpose as they are very cheap, widely available and well suited for on-site assays. The reagent selected was CAS; owing to the toxicity of Be (II), the cation selected was Al(III) (Afkhami et al., 2011). For method development DDAC was selected as model compound because, as stated earlier, this QAC is widely used and cannot be detected by spectrophotometry. The adsorption and derivatization of DDAC and its CAS-Al derivative on cellulose surfaces has been studied. On the basis of the results obtained, a new procedure is proposed based on the employment of swabs for the visual detection and/or quantification of QACs. To the best of our knowledge, this is the first assay in which the colored derivative is formed in a solid support. The main novelty of the proposed approach over previous colorimetric assays for QACs is that the same support is used for sampling, reaction and absorbance measurement, which simplifies the analytical protocol and reduces the manipulation of solutions. Therefore, the developed strategy is better suited for the on-site tests.

2. Materials and methods

2.1. Reagents and solutions

Chromazurol S (CAS) and sodium acetate trihydrate were obtained from Merck (Darmstadt, Germany). Aluminium and potassium sulphate dodecahydrate, sodium chloride and acetic acid (99.8%) were purchased from Scharlab (Sentmenat, Spain). Sodium dodecyl sulphate (SDS) and nitric acid (69%) were purchased from Panreac (Barcelona, Spain). Solutions of 50% DDAC and dioctyldimethylammonium chloride (m/v) both prepared in a mixture water:ethanol (1:1, v/v), and solutions of 80% BAC (m/v) prepared in a mixture of water:2-propanol (3:2, v/v) were supplied by Betelgeux (Gandía, España). The BAC reagent was a mixture of homologues C_{10} (2%), C_{12} (57%), C_{14} (23%), C_{16} (11%) and C_{18} (7%). Sodium hydroxide (J.T. Baker, Deventer, Holland) and sacarose (Guinama, Alboraya, Spain) were also used.

Working solutions of the QACs were prepared by dissolving the bulk products in nanopure water. Stock solutions of CAS at a concentration of 0.01 M were prepared by dissolving the pure compound in nanopure water. Solutions of aluminum at a concentration of 100 mg/L were prepared by dissolving aluminium and potassium sulphate dodecahydrate in water. Acetate buffer solutions of pH 5.4 at a concentration 1 M were prepared by dissolving the appropriate amount of sodium acetate trihydrate in water; then, the pH was adjusted to the required value with acetic acid.

The CAS-Al solutions containing 10^{-4} M CAS and 1 mg/L Al(III) in 0.01 M acetate buffer were prepared by mixing the appropriate amounts of the 0.01 M CAS, 100 mg/L Al (III) and 1 M acetate buffer solutions using nanopure water to adjust the volume.

Ultrapure water was obtained using Nanopure II system (Barnstead, United States).

2.2. Apparatus and methods

Spectrophotometric measurements of solutions were carried out using a UV–vis Agilent 8453 diode-array UV spectrophotometer (Agilent Technologies, Waldbronn, Germany). Aliquots of 1 mL of the Al-CAS reagent were placed in a quartz cuvette, and then mixed with 1 mL of water (blank) or with the standard solutions of DDAC. The absorbances of the resulting mixtures were registered between 400 and 800 nm.

When the colored product was formed on paper strips or on cotton swabs, measurements were carried out using a Cary 60 Fiber Optic UV–Vis spectrophotometer (Agilent Technologies), fitted with a remote fiber optic diffuse reflectance accessory from Harrick Scientific Products (Mulgrave, Victoria, Australia). The absorbance spectra were registered in diffuse reflectance mode. Data were