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Photometric determination of thioglycolic acid in cosmetics by using a stopped-flow reverse flow-injection system and the formation of gold nanoparticles

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ABSTRACT

The positive effect of thiol compounds as reducing agents in the synthesis of gold nanoparticles in the presence of a micellar medium of Triton X-100 has been photometrically studied using a reverse flow-injection system which operates in the stopped-flow mode (SF-rFIA). The analytical usefulness of this new system has been assessed by its application to the determination of thioglycolic acid (TGA), which was chosen as the analyte model. The dynamic range of the calibration graph was 5.97–80 μmol L^{-1}, and the detection limit was 1.73 μmol L^{-1}. The behaviour of other thiol compounds on the system has been also studied. The precision of the method, expressed as relative standard deviation, ranged between 1.5 and 2.3%. The method was applied to the determination of TGA in several cosmetic samples with acceptable recoveries in all instances, which ranged between 90.32 and 101.46%.

1. Introduction

A general trend in the development of new analytical methods is the use of nanomaterials as alternative reagents to conventional organic ones, due to their special properties that are not shown by the bulk material. Among the different nanomaterials described for this purpose, gold nanoparticles (AuNPs) are probably the most widely used [1]. The optical and electrochemical properties of these NPs have been widely explored in a large number of photometric, fluorimetric, scattering, surface plasmon resonance, potentiometric, amperometric and voltammetric methods, among others. Photometric methods are usually based on the bright colour of AuNPs, which is due to the presence of a plasmon-absorption band that appears at 520–560 nm and is not present in the spectrum of the bulk metal. This band is a result of the resonance of the incident photon frequency with the collective excitation of the conductive electrons of the particle.

The formation of AuNPs is generally carried out by reducing tetrachloroauric acid with a suitable reagent such as citrate [2], ascorbic acid [2,3], cysteine [4] or sodium borohydride [5]. The appropriate selection of the different experimental variables such as pH and concentration of reducing reagent allows the control of the size and shape of the NPs obtained. When cysteine is used, it may undergo dimerization to form cystine via the oxidation of two thiol groups, which chemically adsorb on the surface of the AuNPs, allowing their stabilization [4]. The synthesis was carried out by mixing cysteine and tetrachloroauric acid and the solution was left undisturbed at room temperature for 6 h. UV-photoactivation for the reduction of tetrachloroauric acid in the presence of the surfactant Triton X-100 (TX-100) has been also described to obtain AuNPs [6] or AuSe nanoalloys [7]. In these instances, TX-100 acts as both a reducing agent and a stabilizer.

Although most methods for the synthesis of AuNPs involve the use of batch formats, there are some examples of the use of flow systems for this purpose [3,5,8]. For instance, a continuous method involving the use of a helical quartz coil, UV irradiation, and citric acid and poly (vinylpyrrolidone) (PVP) as photosensitive and protector agents, respectively, has been proposed [8]. The shape and size of the NPs obtained were very dependent on the experimental conditions, such as the flow rate and the PVP concentration.

In the present work, the synthesis of AuNPs and the direct measurement of the absorbance of the resonance plasmon band have been used for the first time to develop a flow-injection (FI) method for the determination of thiols and related compounds. The method is based on the capability of these compounds to reduce tetrachloroauric acid in the presence of a TX-100 micellar medium. The flow system operated in a reverse stopped-flow mode, involving the injection of the reagent to minimize its consumption, and the stop of the system to allow the formation of the NPs. The usefulness of the proposed method has been shown by its application to the determination of thioglycolic acid (TGA), also named mercaptoacetic acid, in cosmetic samples. TGA and its calcium, ammonium and sodium salts are widely used in permanent waving and depilatory products as reducing agents on the hair keratin fibers, giving rise to the disconnection of the –SS- groups. This reduction mechanism has been studied using FT-Raman spectroscopy [9]. TGA is also used in several industrial applications such as the synthesis of polyvinylchloride stabilizers, as a corrosion

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inhibitor in oil field industry, in shrink resistant treatment of wool and in leather processing.

Two HPLC methods with photometric detection have been developed for the determination of TGA in cosmetic samples using pre-column derivatization to convert TGA into a yellow-coloured nitrobenzooxadioazole derivative [10] or to form a thiol adduct by reaction with the ethacrynic acid [11]. Another HPLC method applied to the determination of TGA in hair-waving products involves the coupling of a disposable electrochemical sensor based on the use of a preanodized screen-printed carbon electrode [12]. Differential pulse voltammetry has been also described for the detection of TGA in similar samples [13]. A comparative study of the response of glassy carbon, carbon paste and ceramic–carbon composite electrodes, showed that the latter facilitates the electrooxidation process, obtaining better results. Also, two kinetic photometric methods have been recently described for the determination of TGA based on its inhibitory effect in two reactions catalized by Hg(II) [14,15]. However, the practical usefulness of these methods by their application to the analysis of real samples has not been described.

2. Experimental

2.1. Apparatus and instruments

A Perkin-Elmer Lambda 35 UV/VIS spectrometer (Beaconsfield, UK) equipped with a 10 mm light path and 100 μL inner volume Helma flow-cell (176.051-QS) (Helma Hispania, Barcelona, Spain) was used. The instrument was controlled through a personal computer (PC). A four-channel peristaltic pump with rate selector (Gilson Minipuls-3, Vilier le Bel, France), a low pressure injection valve and a switching valve (both from Reodyne, Tecnokroma, Barcelona Spain), and Omnifit (Cambridge,UK) Teflon tubing of 0.5 mm I.D. were used for the construction of the hydrodynamic manifold. The temperature of the experimental setup was kept constant at 90 ± 0.1 °C using a Precisterm thermostatic bath from Selecta (Barcelona, Spain). The characterization of the NPs was performed by Transmission Electron Microscopy (TEM), using a CM-10 Philips Microscope with 0.5 × 0.34 nm resolution and equipped with a digital megaview III camera. Copper grids (200C-FC) coated with a Formvar® carbon film 200 mesh supplied by Aname (Madrid, Spain) were used as support in TEM experiments.

2.2. Reagents

All chemicals used were of analytical grade. Stock solutions of 1.0% w/v tetrachloroauric acid trihydrate (Sigma), 0.1 mmol L^{-1} nitric acid (Merck), 10% w/v Triton X-100 (Fluka), and 10 mmol L^{-1} TGA (Sigma) were prepared using deionized water purified with a Milli-Q system (Millipore, Bedford, Ma, USA), and stored at 4 °C until use. The cleaning solution (CS) of the flow system consisted on a mixture of $HCl:HNO_3:H_2O$ (30:10:60). Other reagents used were sodium dodecylsulphate (SDS, Sigma), cetyltrimethyl ammonium bromide (CTAB, Aldrich), L-cysteine (Fluka), homocysteine (Sigma), homocystine (Sigma), N-acetylcysteine (Sigma), glutathione (Sigma), and methionine (Sigma).

2.3. Procedures

2.3.1. Determination of thioglycolic acid

Fig. 1, depicts a scheme of the stopped-flow reverse FI system used. This configuration minimizes the tetrachloroauric acid consumption and also provides an effective AuNP growth. The flow system consists on a peristaltic pump (P) which propels the carrier (C) stream (0.1 mmol L^{-1}) through the system, in which a 0.015% tetrachloroauric solution (400 μL) was inserted as reverse FI mode. Then the reagent plug merges downstream with a previous formed mixture of

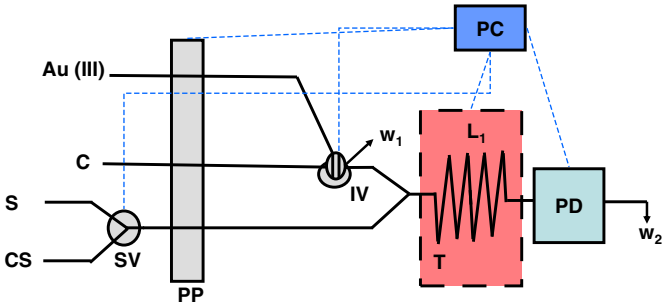

Fig. 1. Flow-injection manifold for the AuNP formation and TGA determination. Au(III): $HAuCl_4 \cdot 3\ H_2O$ (0.015%); C: HNO_3 (0.1 mmol L^{-1} M); S: Sample + TX-100 (0.1%); CS: Cleaning solution ($HCl:HNO_3:H_2O$ 30:10:60); PP: peristaltic pump; SV: switching valve; IV: injection valve; T: thermostatic bath; L_1: open reactor; PD: photometric detector; PC: personal computer; w_1 and w_2: wastes.

0.1% TX-100 and the analyte solution. The mixer reaction bolus reaches a thermostated reactor L_1 (250 cm) heated at 90 °C, in which the AuNPs are synthesized. In order to increase the AuNP formation, the flow system is stopped for 4 min. The flow system started again and the reaction mixture reaches the detector in which the plasmon band is monitored at λ = 540 nm. A switching valve (SV) allows the alternative selection of the sample (S) or the cleaning solution (CS), which provides a cleaning cycle between each injection. Each standard or sample solution was assayed in triplicate. The linear calibration graphs were obtained by plotting each analytical signal versus the TGA concentration. The concentration of TGA in the samples was determined by interpolation of these calibration graphs.

Fig. 2 depicts the typical peak profile of the flow system used. As can be seen, five sequential time increments are defined for each injection. After injection, the flow takes 50 s (Δt_1) from the injection of $HAuCl_4$ until the reaction mixture reaches the thermostatic bath, in which the flow is stopped for 4 min (Δt_2). The residence time (Δt_3) corresponds to the time over which the reaction mixture passes through the detector. The cleaning time ($\Delta t_4 = 10$ s) is the time in which the switching valve changes its position, allowing that the cleaning solution (CS) passes through the reactor and the detector. Finally, a recovery time ($\Delta t_5 = 90$ s) is necessary to re-start the reagent stream before a new injection.

2.3.2. Analysis of cosmetic samples

Four waving lotions and depilatory creams were processed to determine the TGA concentration. About 0.5 g of each sample was accurately weighed and dissolved in 100 mL of deionized water. In order to fit the linear range of the calibration graph, each sample solution was diluted 1:250, and treated as described above.

The results obtained were compared with those achieved using the iodometric titration established as the official method for the

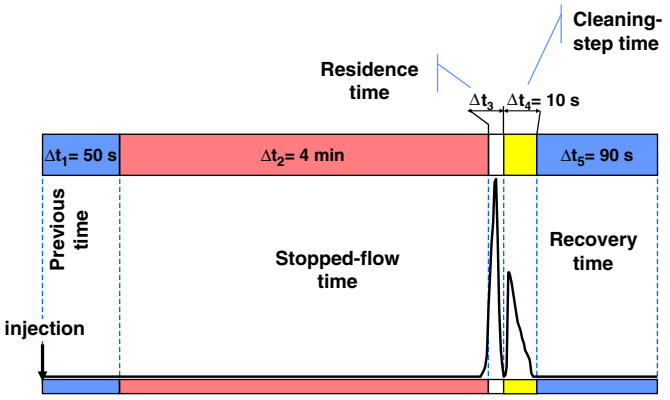

Fig. 2. Absorbance–time recorder and sequential times involved in the process.