VIBRATIONAL CHARACTERIZATION AND SURFACE-ENHANCED RAMAN SCATTERING DETECTION OF BETA-AGONISTS USED IN SPORT DOPING

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Clenbuterol (CB), salbutamol (SB) and terbutaline (TB) (Fig. 1) are phenylethanolamine drugs which act as activators of β2 adrenoreceptors[1]. These receptors are distributed throughout the body and their activation provokes responses such as bronchodilation, increased heart rate and vasodilatation. Effects seen in the skeletal muscle include increased growth and speed of contraction[2]. They are therapeutically employed for the treatment of asthma in some countries because of their bronchodilator activity. In addition, these drugs can also be illicitly employed by sportsmen to improve performance or for their anabolic effects[3]. The use of these drugs is regulated or even prohibited, in the case of CB, by the World Anti-Doping Agency[4].

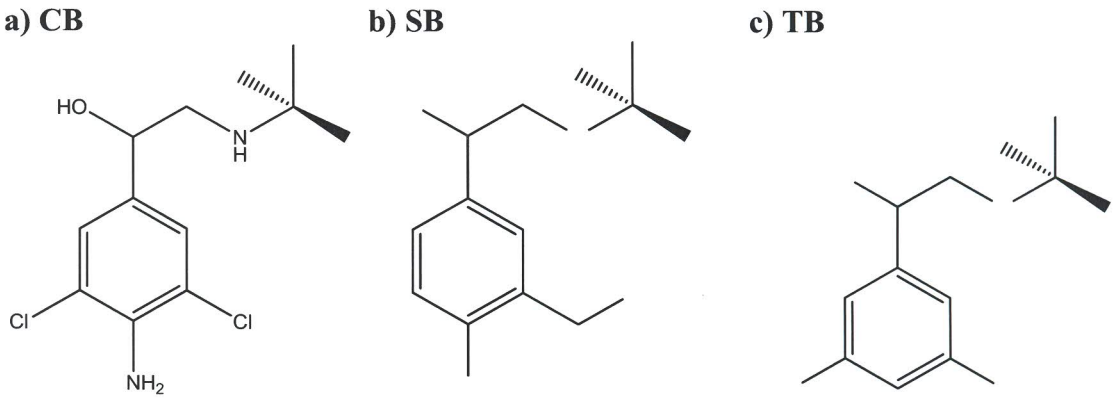

Figure 1. Structure of Clenbuterol (a), salbutamol (b) and terbutaline (c).

In this work Raman and IR spectroscopy are used for the first time to characterize these compounds. Additionally, Surface-enhanced Raman Scattering (SERS) was employed in the trace detection of these important drugs. A previous study implying the effect of different experimental conditions such as the pH and the concentration was done in order to find the optimal conditions to carry out their detection by SERS. In this case, these compounds are able to directly interact with the metal, so that no previous functionalization of the metal was needed.

These compounds presented substrate selectivity, as they were SERS-active only on Au nanoparticles (Au NPs). The amino groups existing in these molecules are the responsible for the adsorption on the metal surface. CB being an interesting case for it includes two amino groups on its structure which lead to two possible orientations of the molecule controllable by the pH of the medium.

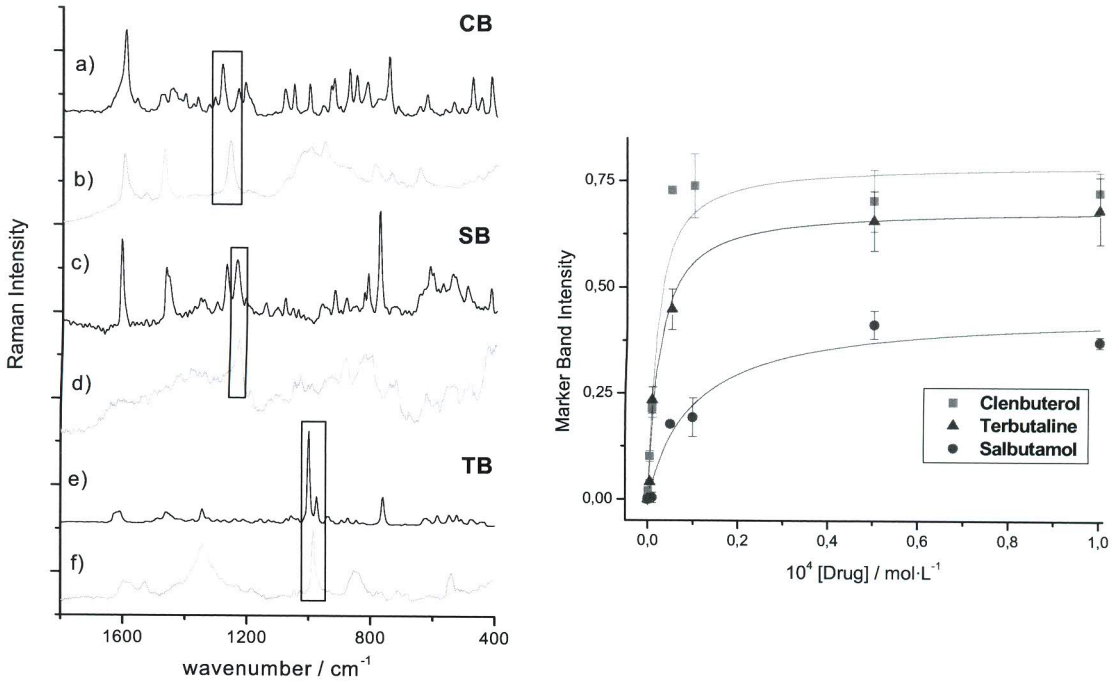

Figure 2. Left: Raman of solid (a,c,e) and SERS on Au NPs (10^{-5} M) (b, d,f) of Clenbuterol (a,b), salbutamol (c,d) and terbutaline (e,f). Right: Plot of the SERS intensity of the marker squared bands vs. the drug concentration showing a Langmuir adsorption model. Excitation at 785 nm (SERS) and 1064 nm (solid samples).

Fig. 2, left panel, shows the SERS spectra of CB, SB and TB obtained at the optimal conditions (acidic pH, the first, and alkaline the two latter drugs). This Figure shows the squared marker bands employed for the detection in each case. Fig. 2, right panel, shows the dependence of the SERS intensity of the latter bands at different concentration. The adsorption of these drugs on Au NPs followed a Langmuir model. The analysis of the SERS intensity of characteristic bands versus the compound concentration allowed the calculation of the adsorption constants on Au NPs and the limits of detection of each drug.

This work is a first step towards real sample analysis, showing that SERS is a promising technique to be applied in the field of sportive doping drug detection.

ACKNOWLEDGMENTS

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