8 Conclusions

The main purpose of the use of nanoparticles in analytical chemistry is to exploit their peculiar properties in order to improve well-established analytical methods or to develop methods for new analytes and for the analysis of different matrices. In this context, one of the most promising nanomaterials are the semiconductor nanoparticles (quantum dots), which have been used in the present work as photoluminescent nanoprobes for the sensing of diverse chemical species.

The present work focused on the synthesis of thioglycolic acid (TGA) and 2-mercapoprionic acid (2MPA) modified CdTe nanoparticles and cysteine modified ZnS nanoparticles via colloid aqueous phase route. These nanomaterials were characterized using different approaches and techniques aiming to access their quality and to evaluate their potential as selective optical probes for determination of captopril, histamine, kanamycin and thyroxine.

The aqueous dispersion of 2MPA-CdTe nanoparticles have been applied as novel photoluminescent probe for the determination of captopril. The presence of captopril in non-buffered aqueous media causes the quenching of the photoluminescence measured from 2MPA-CdTe nanoparticles, on the other hand, in a buffered aqueous system, captopril effectively enhances the photoluminescence of quantum dots. The photoluminescence enhancement approach is analytically favoured due to its selectivity as compared to the quenching approaches, therefore, it was used for the determination of captopril. Under optimum conditions, the enhancement in photoluminescence of 2MPA-CdT quantum dots dispersion fits to a Langmuir model (as a calibration model). The applications of probe for determination of captopril in fortified human serum and pharmaceutical formulation were demonstrated. The proposed photoluminescent probe enabled sensitive determination with selectivity towards captopril in the presence of many concomitant substances commonly present in pharmaceutical formulations and in biological matrices. The simplicity of the

approach makes the proposed probe very competitive compared to the ones reported in the literature.

The photoluminescence of TGA-CdTe nanoparticles was quenched by histamine in a concentration dependent manner (Stern-Volmer model). The solid phase extraction with cation exchange resins and its combination with the sensitive TGA-CdTe sensing provide a very simple and easy approach for the determination of histamine in complex samples. The method has been tested in the determination of histamine in the flesh of fresh and canned tuna fish samples. The application is not only limited to fish and fish products but may also be applied for histamine sensing in red wines and cheese.

The presence of aminoglycosides enhanced the photoluminescence of the TGA-CdTe nanoparticles (following a Langmuir binding isotherm model). Kanamycin was used as a model aminoglycoside in order to study its effect on the photoluminescence enhancement of TGA-CdTe quantum dots dispersed in aqueous solution. Binding constants were calculated for several aminoglycosides from Langmuir binding isotherm indicating strong interactions between surface of nanoparticles and aminoglycosides. This approach was successfully applied for determination of kanamycin fortified milk and in stream water samples after solid phase extraction using a molecular imprinted polymer produced using a kanamycin template. The LOD value achieved (at the ng mL^{-1} level) and the simplicity makes the method a strong candidate for screening aminoglycosides contamination in food and environmental samples (water).

The photoluminescence intensity from the cysteine-ZnS nanoparticles aqueous dispersion containing cetyltrimethyl ammonium bromide (CTAB) is quenched by thyroxine. The overall quenching followed a Stern-Volmer model. The presented results are relevant since there are only a few methods for the determination of thyroxine available because of the poor optical properties of this substance. The aqueous dispersion of cysteine-ZnS was used as optical probe for the determination of thyroxine in pharmaceutical formulations and in analyte fortified human saliva.

All of the above proposed methods take advantage of the strong photoluminescence from the nanomaterials avoiding the use of complex chemical derivatization procedures and enabling simple and sensitive quantifications.

However, experimental conditions must be carefully optimized in order to achieve stable signal and repetitive measurements.