Summary

Tip-enhanced Raman spectroscopy (TERS) is a surface measurement technique which, combining surface-enhanced Raman spectroscopy (SERS) and scanning probe microscopy (SPM), is capable of topographic and chemical imaging simultaneously, each with nanometric lateral resolution, and can achieve single-molecule Raman detection. The Raman community is currently lacking reference samples, standardised procedures for enhancement factor evaluation, and even common definitions which are essential for the harmonisation and comparability of results. This work tackled some of the most pressing metrological needs of TERS while also exploring innovative approaches for the improvement of the efficiency of the technique, its accuracy, and the evaluation of its uncertainty.

TERS requires specific probes with strict parameters in terms of shape, dimensions and material for plasmon resonance with a specific excitation wavelength. The first part of the thesis was dedicated to manufacture highly enhancing TERS probes; for uniformity and comparability of Raman intensity of single spectra and spatial resolution of multispectral images, high reproducibility of these tips was sought. Optimised and reproducible STM-TERS tips were produced by devising and constructing an electronic control circuit for the electrochemical etching of silver wire. Tips with apices radii of (40 ± 10) nm were achieved. Best parameters for the fabrication of AFM-TERS gold-coated tips by sputtering were also determined by conceiving and exploring a novel configuration for TERS, the “isolated tip”, to improve spectral intensity reproducibility.

A candidate reference sample for assessing the spatial capabilities of TERS was designed, manufactured and measured with STM-TERS. Compounds able to form ordered self-assembled monolayers (SAMs) were employed for this. Surfaces were produced with SAMs of two different organic molecules, and analysed after an optimisation study on their manufacturing steps. After topographic and chemical mapping by STM-TERS, a suitable substrate production process was identified.

The subject of TERS intensity reproducibility was also studied. The isolated tip mode was compared to measurements carried out with the most common methodology. The novel procedure reduced data dispersion by more than 40%.

A new concept was also conceived and achieved: "tip dimers". This new configuration, consisting in the contact of two TERS tips, conceptually equal to the commonly occurring SERS nanoparticle dimers, was sought to improve the sensitivity of the technique. A convenient substrate for the realisation of tip dimers was produced. Spectral intensities up to three times higher than those arising from the standard technique were measured.

Thiram, a law-regulated pesticide, was analysed, furtherly opening up TERS for much needed real-world applications. Traces of this chemical agent (in the order of magnitude of 1000 molecules) were successfully detected with tip dimers with high signal to noise ratio, suggesting a much lower limit of detection.

The accurate quantification of enhancement factor is an open issue in SERS and TERS. In this thesis, a study was conducted to face this problem, executing novel operating procedures: a measurement for the estimation of non-enhanced Raman intensity of an analyte with the same instrumental conditions as its amplified counterpart was performed by employing a liquid solution of the analyte in a solvent; furthermore, the number of molecules investigated by non-amplified Raman was quantified by a precise estimation of the focal volume of the microscope by probing it with monolayer graphene sheets, measuring their Raman intensity while scanning them in the three dimensions. Enhancement factors were calculated with their uncertainties for the three TERS configurations explored in this thesis for three analytes. It was found that thiram yielded higher enhancement factors with respect to commonly employed TERS analytes.