

Solid-liquid-liquid extraction as an approach to the sensitive detection of a hydrophobic pollutant through surface-enhanced Raman spectroscopy



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ABSTRACT

Surface-enhanced Raman scattering (SERS) spectra of thiram (tetramethylthiuram disulfide), a dimethyl dithiocarbamate fungicide, were recorded after the adsorption on plasmonic silver nanowires from a system of water, organic solvent and nanoparticles. As organic solvents dichloromethane and 1-octanol were involved. A method for measuring the adsorption constant of thiram as a model molecule to the silver surface by studying its partition phenomena in a binary solvent system is presented. The method is based on the extraction of a hydrophobic molecule from an organic solvent by an aqueous suspension of silver anisotropic nanoparticles. The obtained results demonstrate the effectiveness of SERS methodology for the sensitive analysis of compounds with low aqueous solubility, and a reliable SERS spectrum of thiram was obtained with excellent signal/noise ratio at low concentrations. In addition, for vibrational assignments, Density Functional Theory (DFT) was used for the simulation of the Raman and SERS spectra of thiram and its complexes with silver considering the following two models: a single silver atom and an Ag₂₀ cluster.

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1. Introduction

Partition coefficients are important properties for environmentally relevant compounds, and strongly influence their fate and distribution between the available compartments of the environment, such as soil, water, and air. Partition coefficients of hydrophobic organic compounds are also important physicochemical data used as indicators and/or predictors of bioaccumulation of a wide variety of species, and are therefore often used as the most important physicochemical parameters in environmental risk assessment, fate and transport models, and in the study of the potential environmental impact of many compounds. The most widely used and reported partition coefficient is for the octanol–water system (K_{ow}), although the literature reports concerns about the quality of these fundamental physicochemical data by questioning them with the consequences of undermining many environmental models and assessments [1,2].

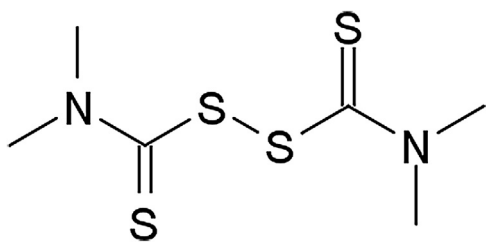
Given the demand for trace analysis of pollutants from environmental samples, which are typically very complex, a highly sensitive and selective analytical approach is of great demand [3]. The capability of both detecting molecules in trace amounts and giving structural information about intricate materials such as soil's humic substances and plant tissues including their interaction with organic pollutants, and the possibility to detect and quantitatively analyze important herbicides [4] for example, makes SERS a suitable and interesting technique for environmental analysis and monitoring [5,6].

Thiram (C₆H₁₂N₂S₄), represented in Scheme 1, is a commercial fungicide and animal repellent. The first reports on surface enhanced Raman spectra of thiram and other thiocarbamate pesticides were published few months after a leakage of huge amounts of metam-sodium (another thiocarbamate) to the Sacramento River (California, USA) was made public after the derailling of a train in 1992 [7]. However, it took several years before new studies on the SERS spectrum of thiram were published [8,9], and, more recently, thiram has been shown to be a suitable probe molecule for environmental SERS [10–13].

In the present work, thiram was used as a probe molecule to propose a method based on the extraction of hydrophobic pollutants from organic media (in which most pesticides are

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Scheme 1. Molecular structure of thiram (tetramethylthiuram disulfide, $C_6H_{12}N_2S_4$).

better soluble) using a suspension of silver nanoparticles. It was possible to detect reliable spectra of thiram at low concentrations through SERS and to determine its adsorption constant to the silver surface, which is the basis for the study of partition phenomena. Moreover, the vibrational band assignment for the Raman and SERS spectra of thiram was achieved by comparing the latter with the simulated Raman spectra of the isolated molecules, and thiram attached to a single silver atom or an Ag_{20} cluster, respectively, as calculated by Density Functional Theory (DFT). It is important to mention that, to the best of our knowledge, the complete band assignment for thiram has not been published in previous literature.

2. Experimental

2.1. Substrate synthesis and characterization

Silver nanowires were synthesized by a polyol method [14]. Briefly, 3 mL of a 0.1 mol L^{-1} silver nitrate solution in ethylene glycol were transferred through a peristaltic pump to a 10 mL synthesis flask containing 50 mg of polyvinylpyrrolidone (average molecular mass of 40,000) and 200 μL of a 0.01 mol L^{-1} NaCl solution dissolved in 7 mL of ethylene glycol, preheated to 160°C . After 1 h of reaction, the resulting material was washed with ethanol and water. SEM images were obtained with a JEOL JSM 5330F microscope, and UV–vis spectra recorded by a Shimadzu UV-31010PC spectrometer.

2.2. Raman and SERS measurements

The first partition test was performed with 1 mL of a thiram solution at a concentration of $10^{-3} \text{ mol L}^{-1}$ in dichloromethane and 1 mL of silver nanowire suspension in water, forming a biphasic system in an Eppendorf tube. Then, tests with thiram in 1-octanol were performed in order to compare with registered partition data. These tests used a wider range of concentrations (5×10^{-3} , 5×10^{-4} and $5 \times 10^{-5} \text{ mol L}^{-1}$) and the pesticide was also extracted from 1 mL of the prepared solution with 1 mL of the nanowire suspension. In all cases, flasks were gently shaken for ten times,

similarly to standard shake-flask procedures, after the addition of the nanowire suspension, and SERS spectra were obtained from a dried drop of this suspension onto a glass microscope slide after 4 h of first preparation. All spectra (solid thiram and SERS) were obtained by a Renishaw InVia Raman microscope, with 633 nm excitation wavelength.

2.3. Partition coefficient determination

Partition coefficients of thiram in 1-octanol/nanoparticle aqueous suspension systems were determined through high performance liquid chromatography (HPLC). 10 μL of the organic phase were injected and eluted in a silica C18 analytical column, with an eluent flux of 0.3 mL min^{-1} . The mobile phase was isocratic, containing 70% of acetonitrile and 30% of 0.1% formic acid buffer solution. This method was based on the work of Irth et al. [15].

3. DFT calculations

All the calculations were performed using the *Gaussian 09W* software [16], where the ground state geometries and the vibrational frequencies were calculated employing density functional theory (DFT) [17,18] using the B3LYP hybrid functional [19] (Becke's gradient-corrected exchange correlation [20] in conjunction with the Lee-Yang-Parr correlation functional with three parameters [21]). The basis set considered for thiram calculations was 6-311G++(3df,3pd) (scaling factor of 0.9679 according to the literature [22]). The calculations of the fragment of thiram attached to a single silver atom and to a Ag_{20} cluster were performed [23–25] using the keyword “gen” with 6-311G++(3df,3pd) basis set for C; H; N; S atoms and LANL2DZ for the Ag atom(s); considering a pseudopotential for the inner shell electrons. The assignment of the vibrational wavenumbers was carried out using *Gaussview 05*.

4. Results and discussion

The polyol synthesis of silver nanoparticles results in anisotropic morphologies like nanowires and, less commonly, nanocubes and pyramids. Fig. 1(a) shows a typical SEM micrograph of the nanoparticles, composed mainly by nanowires with an average cross-section of 68 nm, while some nanocubes are also present. Although the cross-section of silver nanowires is the nanoscale for two of their dimensions, they typically reach a length of 6–8 μm , what makes them visible through optical microscopy (Fig. 1(b)). The typical extinction spectra of the plasmonic sample in aqueous suspension consist of two main bands arising from localized surface plasmon resonances (LSPR), one of them at 385 nm, which can be assigned to plasmon dipoles, and a second higher energy band at ca. 351 nm, assigned to a quadrupolar resonance mode [26]. The presence of

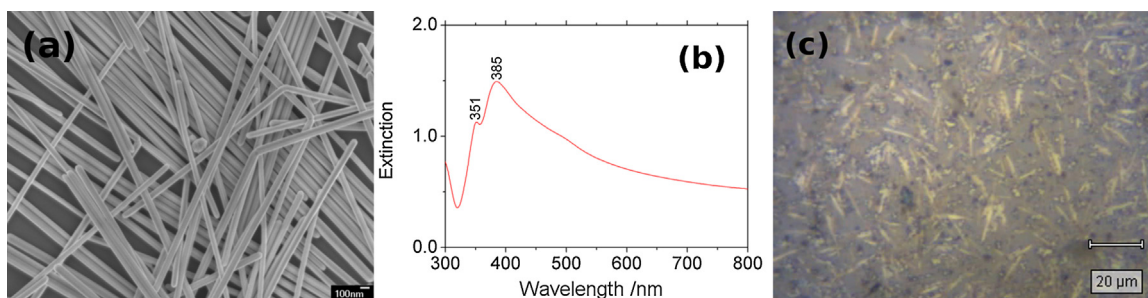


Fig. 1. (a) SEM micrograph of the silver nanoparticles obtained with a 30,000 \times magnification, (b) extinction spectra of silver nanoparticles suspension in water, (c) optical micrograph of silver nanoparticles sample, collected with a 50 \times magnification.

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