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Raman fingerprints for unambiguous identification of organotin compounds

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ABSTRACT

Raman spectra of the different ecotoxicants such as perfluorooctane sulfonate acid, organotin compounds of different families tributyl-, and triphenyl-, as well as chemically close compounds belonging to the same family – such as mono-, di-, and tributyl organotin compounds were analyzed. The comprehensive Raman spectra analysis allowed suggesting the identification scheme for clear recognition of the toxins family and the following intra-group specification. Possibility of unambiguous toxins detection and identification was demonstrated also for complex mixtures of various toxins on a base of control of characteristic peak groups, which can be considered as Raman fingerprints of the listed environmentally hazardous substances.

1. Introduction

The ecological safety is largely dependent on the type and concentration of hazardous substances in natural samples that requires the regular monitoring of environmental objects. This is especially important for the pollutions connected with human activity and the elevating effect to the environment in recent decades. A significant group of environmentally hazardous substances is organotin compounds which have entered various ecosystems due to the wide industrial and commercial use. Organotin compounds (OTCs) are the class of organometallic substances, containing at least one C-Sn bond [1]. Virtually all the known OTCs are formed by tetravalent tin, and include fully substituted compounds R_4Sn or compounds of the type R_3SnX, R_2SnX_2 and $RSnX_3$, where R is the same or different organic radicals and usually it is a butyl, octyl, or phenyl group; X is halogen or hydrogen. The organotin compounds are widely used in industry, agriculture and technology [2–4]. Trisubstituted organotin compounds (R_3SnX) demonstrate pronounced biocidal properties that are strongly influenced by the R-groups. The most important of these compounds are the tributyl-, triphenyl-, and tricyclohexyltin, which are used as agricultural and general fungicides, bactericides, herbicides, insecticides, nematocides, ovicides, rodent repellents [5, 6]. Also, trisubstituted organotin compounds are widely used as fungicide for wood preservation (R = Bu, Ph,). In chemical industry the OTCs are used for copolymerization with many organic substances and for the production of a number of film-forming materials, epoxy resins, varnishes, paints, enamels, and other organic synthesis products [7, 8]. For many years, tributyl- and triphenyltin were used as the main component of antifouling agents for ship bottoms and fishery, but now they are prohibited due to the high toxicity [9]. Also, the OTCs are used in the light industry for impregnation of textiles materials – protection of stone, leather, paper as fungicide, algicide, bactericide (Bu_2SnX_2, Bu_3SnX, Ph_3SnX).

The underside of wide industrial application of the organotin compounds is the OTCs accumulation in nature resulting in the strong environment poisoning. The main toxicity of the OTCs is connected with cell apoptosis, thymus atrophy (immune system), pancreatic damage, mutagenic effects, etc. [10, 11].

It is important to note that the members of the OTCs family demonstrate different degree of the systemic effects – the mono- and di-organotin compounds demonstrate less toxicity than the triorganotin compounds, which are considered to be the most hazardous of all tin compounds [11–13]. That is why not only the detection but also the reliable identification of the OTCs in the environment such as biological samples, ocean and river sediments, and industrial waste are the urgent ecological problem. To date, various methods are used for the identifying of the organotin compounds – chromatography, including gas chromatography (GC), high-performance liquid chromatography (HPLC), capillary electrophoresis, colorimetric methods and others [14, 15]. However, the reliable methods have still to be developed for the detection and identification of the individual OTC species in the complex natural objects such as biological tissues, industrial effluents, and river sediments containing the multicomponent mixtures of the inorganic tin (IV) and organotin compounds. The main problem of the current analytical approaches is the multistep procedure requiring the preliminary sample preparation and involving the extraction, derivative's formation,

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separation, detection and quantification stages. Together with the need to use the stationary bulk setups and toxins' standards, it makes the analysis procedure complex and lengthy.

An alternative way can be analysis of the multicomponent samples with Raman spectroscopy that is rather sensitive technique as allows fine distinguishing signals from different components and does not require the preliminary sample preparation procedure; moreover the modern Raman spectrometers can be used as portable units in the mobile laboratories for express monitoring [16–18]. The main problems that can be foreseen for Raman spectroscopy in the case of analysis of the multicomponent complex media, and especially natural samples are the overlapping of characteristic bands from different components of the analyte and poor detectability for the low concentrated samples. The latter difficulty can be overcome with surface-enhanced Raman spectroscopy (SERS) based on the local electric field enhancement by metallic nanoparticles and allowing investigation of highly diluted solutions down to single molecule detection [17, 19–23]. The problem of clear Raman-based identification of the components for the complex mixtures can be solved by means of the ascertainment of the groups of the characteristic bands that can be considered as Raman fingerprints for unambiguous identification of the OTCs family members. Here, we present the detailed and comparative analysis of the organotin compounds Raman spectra that can be used for confident identification of the analyte components even for mixtures containing chemically close compounds belonging to the same family – such as mono-, di-, and tributyl chloride (MBT, DBT, TBT).

2. Materials and Methods

MBT, DBT, TBT, triphenyltin chloride (TPhT), perfluorooctane sulfonate acid (PFOS) (Sigma-Aldrich, 95%) were dissolved in methanol to get 1.0 mg/ml solutions of individual toxins. Dual solutions of MBT + PFOS, MBT + TPhT and MBT + TBT were prepared with 1:4, 1:1 and 1:1 volume ratios, respectively. A drop of prepared solution (10 μl) was placed on the subject glass and then was dried under ambient conditions for 10 min for the subsequent Raman measurements. Raman spectra were measured on Raman spectrometer Senterra (Bruker) with an excitation wavelength of 532 nm, laser power 2–10 mW under long-distance 50× objective (NA 0.5). All spectra were acquired from several randomly selected spots. In order to avoid substrate contribution, confocal mode was applied with 50 μm iris aperture. The spectra were pre-treated by baseline correction using the OriginLab software to subtract luminescence signal.

Vibrational modes of a single molecule toxin were calculated using Gaussian 09 W. Among the DFT methods Becke's three parameter hybrids function combined with the Lee-Yang-Parr correlation function (B3LYP) was chosen using 3-21G basis set for organotin toxins and 6–311++G(d,p) for PFOS. The phonon frequency calculations were preceded by geometry optimization of the toxin molecules. The scaling factors which is defined as $\omega_{experimental}/\omega_{calculated}$ for MBT was 0.947, for DBT was 0.943, for TBT was 0.943, for TPT was 0.947, for PFOS was 0.995.

3. Results and Discussion

The choice of the toxins set for Raman measurements was determined with high probability of several OTC compounds presence (including compounds with the same kind of radicals) in real natural samples or tissues, especially river or ocean sediments, industrial wastewater, etc. That is why the organotin compounds of the butyl family, containing different number of butyl groups: MBT, DBT, TBT, as well as the OTCs with triphenyl group, and PFOS which belongs to other group of toxins but also is known as a carcinogen with a strong toxic effect were chosen for Raman measurements. The molecular structures of the toxins under consideration are presented in Fig. 1. One can see that the chosen organotin compounds contain one tin atom surrounded with chlorine atoms or bytil/phenyl radicals, while PFOS belongs to the group of fluorinated compounds with shared feature of hydrogen to fluorine substitution in the carbon chain bonded to the sulphonate group.

Fig. 2 presents Raman spectra for the listed toxins. One can see that the Raman spectra are characterized by a large number of specific peaks, but nevertheless each compound can be distinguished via consistent analysis and “key peaks” control.

Raman bands of PFOS (Fig. 2a) are localized in the spectral range below 1400 cm^{-1}, the most intense peaks are 302 cm^{-1} ω(-CF_2), 386 cm^{-1} δ(-CF_2), 728 cm^{-1} ν(C—C) and δ(C—C) - coupling of bending and stretching modes in carbon skelet, CF_2 and CF_3 groups, 809 cm^{-1} (carbon skeletal C—C vibrations), 1374 cm^{-1} (ν_{ax}(C—F) – neighbor

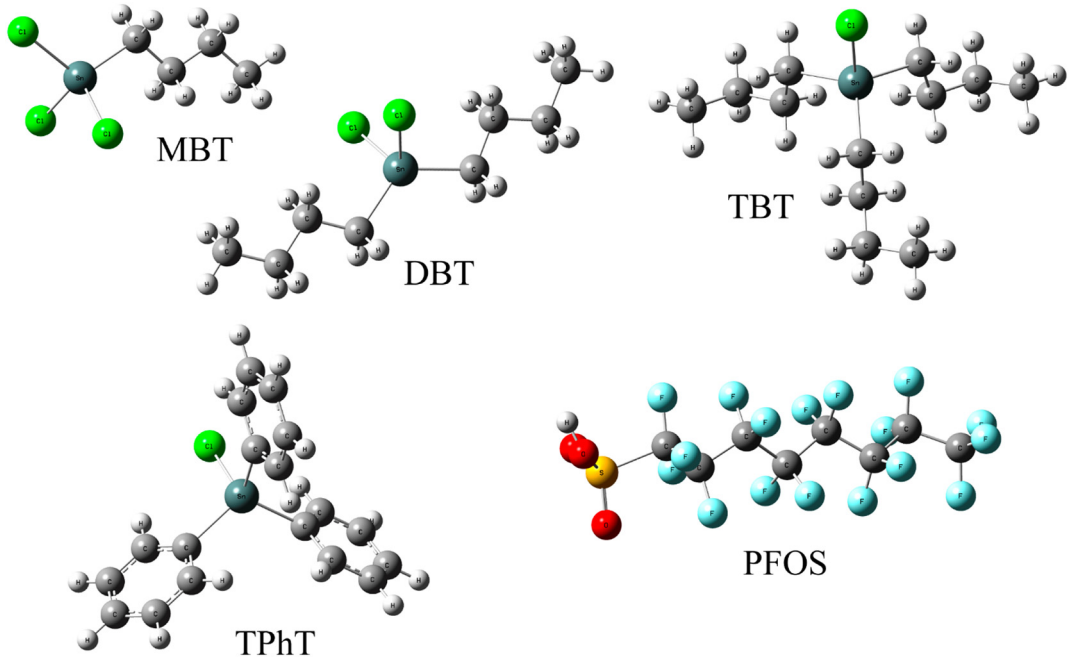

Fig. 1. Geometrically optimized molecular structures of MBT, DBT, TBT, TPhT and PFOS toxins.