

Subcritical-Water Extraction of Organics From Solid Matrices

An environmentally benign solvent is used in a simple extraction process.

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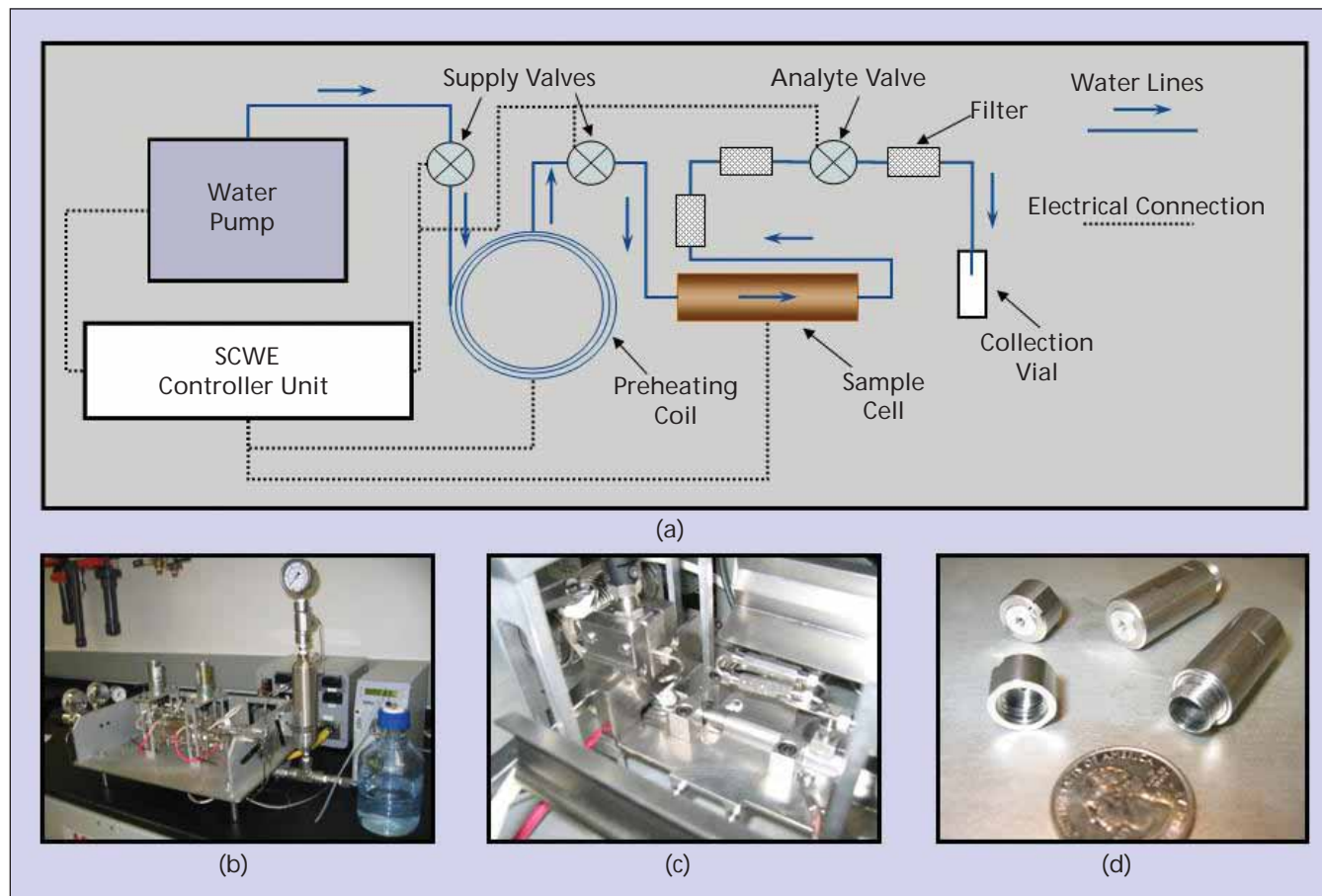
An apparatus for extracting organic compounds from soils, sands, and other solid matrix materials utilizes water at subcritical temperature and pressure as a solvent. The apparatus, called subcritical water extractor (SCWE), is a prototype of subsystems of future instrumentation systems to be used in searching for organic compounds as signs of past or present life on Mars. An aqueous solution generated by an apparatus like this one can be analyzed by any of a variety of established chromatographic or spectroscopic means to detect the dissolved organic compound(s). The apparatus can be used on Earth: indeed, in proof-of-concept experiments, SCWE was used to extract amino acids from soils of the Atacama Desert (Chile), which was chosen because the dryness and other relevant soil conditions there approximate those on Mars.

The design of the apparatus is based partly on the fact that the relative permit-

tivity (also known as the dielectric constant) of liquid water varies with temperature and pressure. At a temperature of 30 °C and a pressure of 0.1 MPa, the relative permittivity of water is 79.6, due to the strong dipole-dipole electrostatic interactions between individual molecular dipoles. As the temperature increases, increasing thermal energy causes increasing disorientation of molecular dipoles, with a consequent decrease in relative permittivity. For example, water at a temperature of 325 °C and pressure of 20 MPa has a relative permittivity of 17.5, which is similar to the relative permittivities of such nonpolar organic solvents as 1-butanol (17.8). In the operation of this apparatus, the temperature and pressure of water are adjusted so that the water can be used in place of commonly used organic solvents to extract compounds that have dissimilar physical and chemical properties.

Heretofore, laboratory extractions of organic compounds have involved the use, variously, of toxic organic solvents in Soxhlet extraction, strong acids in amino acid vapor-phase hydrolysis, or carbon dioxide as a solvent at supercritical temperature and pressure. Supercritical CO₂ is effective as a solvent for extracting lipids and other very nonpolar organic compounds because its relative permittivity is 1.4 and does not vary significantly with pressure in the range of 7 to 21 MPa or with temperature in the range of 25 to 200 °C. However, supercritical CO₂ is often inadequate as a solvent for extraction of other nonpolar and polar organics. Frequently, it is necessary to mix supercritical CO₂ with methanol or other more-polar organic solvents to obtain an extraction solvent having a greater relative permittivity.

The apparatus (see figure) includes a sample cell, into which a solid sample is



In this Subcritical-Water Extraction Apparatus, water at controlled pressure and temperature is pumped through a sample cell that contains a solid matrix material (e.g., a soil) from which organic compounds are to be extracted: (a) SCWE diagram, (b) portable SCWE apparatus, (c) close-up of the sample cell and filtration system, and (d) sample cell.

placed. During a typical extraction, water is pumped to the required high pressure through supply valves, a pre-heating coil, the sample cell, and an analyte valve into a collection vial. The filters, at various positions downstream of the sample cell, prevent contamination of analytical instruments by particles of the sample solid matrix.

Relative to prior methods and apparatuses used to extract organic compounds, the present apparatus and the

method of its operation offer several advantages:

- The solvent (water) is environmentally benign;
- The relative permittivity of the solvent can be adjusted to the values needed to selectively extract, with high efficiency, organic compounds that have different physical and chemical properties;
- The basic principle of operation is simple;
- The apparatus can be highly automated;

- Whereas Soxhlet and hydrolysis extractions often take many hours, an extraction by use of this apparatus takes only minutes.

This work was done by Xenia Amashukeli, Frank Grunthaler, Steven Patrick, James Kirby, Donald Bickler, Peter Willis, Christine Pelletier, and Charles Bryson of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1). NPO-44144

A Model for Predicting Thermoelectric Properties of Bi₂Te₃

A compromise between accuracy and computational efficiency is made.

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A parameterized orthogonal tight-binding mathematical model of the quantum electronic structure of the bismuth telluride molecule has been devised for use in conjunction with a semi-classical transport model in predicting the thermoelectric properties of doped bismuth telluride. This model is expected to be useful in designing and analyzing Bi₂Te₃ thermoelectric devices, including ones that contain such nanostructures as quantum wells and wires. In addition, the understanding gained in the use of this model can be expected to lead to the development of better models that could be useful for developing other thermoelectric materials and devices having enhanced thermoelectric

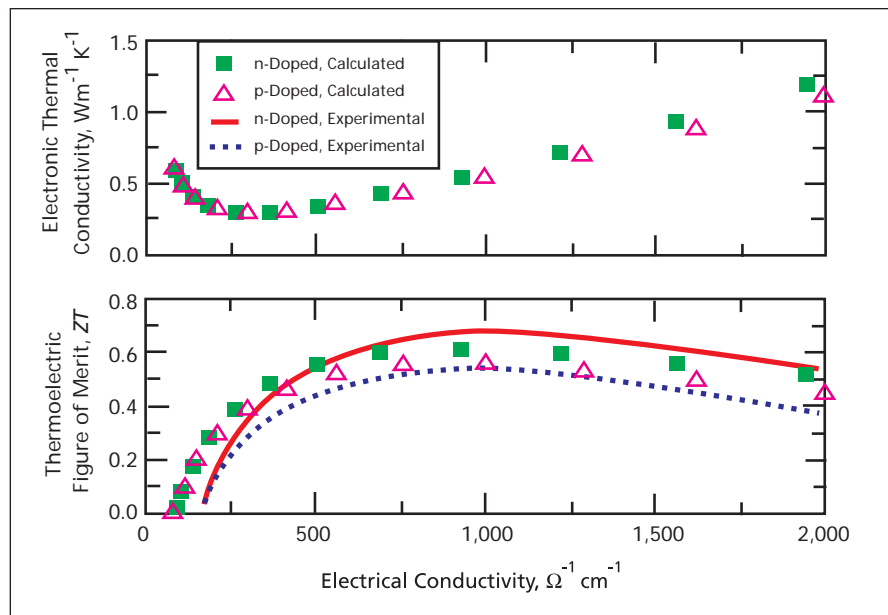
properties.

Bi₂Te₃ is one of the best bulk thermoelectric materials and is widely used in commercial thermoelectric devices. Most prior theoretical studies of the thermoelectric properties of Bi₂Te₃ have involved either continuum models or *ab-initio* models. Continuum models are computationally very efficient, but do not account for atomic-level effects. *Ab-initio* models are atomistic by definition, but do not scale well in that computation times increase excessively with increasing numbers of atoms. The present tight-binding model bridges the gap between the well-scalable but non-atomistic continuum models and the atomistic but poorly scalable *ab-initio* models:

The present tight-binding model is atomistic, yet also computationally efficient because of the reduced (relative to an *ab-initio* model) number of basis orbitals and flexible parameterization of the Hamiltonian.

The present tight-binding model includes atomistic descriptions of the Hamiltonian with sp³d⁵s* basis orbitals, nearest-neighbor interactions, and spin-orbit coupling. For the purposes of the model, within each primitive cell of Bi₂Te₃, two of the Te atoms are denoted Te^I and one is denoted Te^{II}. The difference between Te^I and Te^{II} is that the nearest neighbors of Te^I are three Te atoms and three Bi atoms, while those of Te^{II} are six Bi atoms. To capture the difference, separate tight-binding parameters are assigned to Te^I and Te^{II}.

Altogether, the tight-binding model incorporates 71 independent parameters, which are determined by fitting the computed band structure to a first-principles band structure obtained by use of a submodel based on a screened-exchange local-density approximation. The first-principles band structure predicts the energy gap, the degeneracy of the edges of the conduction and valence bands, and the effective masses of these two bands, in good agreement with experimental results. In the fitting process, a higher priority is given to the highest valence and the lowest conduction bands than to the rest of the band structure, inasmuch as these two bands are mainly responsible for the thermoelectric properties of lightly doped Bi₂Te₃. Moreover, the locations, energies, and effective masses of the two band edges are emphasized, as they largely determine the accuracy of the



Calculated and Experimental Values of the thermoelectric figure of merit and the electronic thermal conductivity of Bi₂Te₃ were found in fairly close agreement across a broad range of electrical conductivity.