Environment Protection Engineering

Vol. 13 1987 No. 1

RYSZARD CZAJKA**, STANISŁAW SZUBA**, JERZY RAUŁUSZKIEWICZ***

APPLICATION OF THE INELASTIC ELECTRON TUNNELING SPECTROSCOPY TO THE INVESTIGATION OF NATURAL ENVIRONMENT POLLUTIONS*

Inelastic Electron Tunneling Spectroscopy (IETS) may be applied to the investigations of natural environment pollutions, especially of water environment. This technique is characterized by extremely high sensitivity and very good resolution. IETS is suitable for the detection of very small amounts of trace substances (on the level of 10^{10} molecules) in the studied substances of subnanogram amounts. The application of IETS is exemplified by study of the decay of m-cresol in water solutions under the influence of ozonation, which was investigated in the Institute of Physics of the Poznań Technical University.

1. INTRODUCTION

The Inelastic Electron Tunneling Spectroscopy (IETS) is one of the youngest spectroscopic techniques existing since the sixties [1]. It is based on the quantum tunneling of electrons through a very thin (in the range of 2–5 nm) insulating barrier in the metal/insulator/metal (M/I/M) junctions. Most of electrons (about 99%) tunnel without any loss of their energy. The remaining (about 1%) falls to inelastic tunneling with the dissipation of energy. In this process the collective excitations like phonons, magnons or plasmons can be excited in electrodes or in the barrier and, which is the most important for our purposes, the oscillation modes of molecules introduced into the barriers of tunnel junctions generated.

The observation and recording of vibrational and rotational modes of molecules excited by the inelastically tunneling electrons in the tunnel junctions is called the Inelastic Electron Tunneling Spectroscopy (IETS).

---

*The work was carried out under project CPBP 01.08.C24.

**Institute of Physics, Poznań Technical University, ul. Piotrowo 3, 60-965 Poznań.

***Institute of Physics, Polish Academy of Sciences, al. Lotników 32, 02-668 Warszawa.

The advantages of this prism-less spectroscopy are:

1. Extremely high sensitivity of order of 10^{10} molecules which corresponds to 1 atom of deuterium per 1500 Å^2 of the surface of junction.

2. High spectroscopic resolution. In some special cases its range, being 3–0.25 cm^{-1}, is comparable with the high quality optical instruments.

3. The possibility of observation of molecular excitations at very low energies which correspond to the far and very far infrared regions of optical spectra [2].

The main disadvantages of IETS are:

1) the fact that measurements must be performed at liquid helium temperatures,

2) a lack of a good theory, which would interrelate the intensity of the lines observed and the amounts of substances introduced into a junction.

The usefulness of IETS in the investigation and control of environment pollutions is due to the following facts:

1) IETS junctions can be easily doped with the investigated substances from liquid phases [3], [4],

2) the oscillation spectra of molecules as well as low energy electronic excitations can be investigated without masking water absorption, which is very disturbing in IR optical measurements or in the fluorescence of solvents or substrates in Raman measurements [5],

3) IETS is able to detect the nano- and picogram quantities of substances dissolved in water or in other solvents [6].

2. PREPARATION OF SAMPLES AND MEASUREMENTS

Each tunneling junction consists of two metallic electrodes separated by a very thin (2–5 nm) film of an insulator. It is fabricated in the following processes:

1. Evaporation of a metallic base electrode of Al or Mg in the form of a strip, about 1 mm wide [7], [8], on an insulating substrate (glass, alundum and so on).

2. Oxidation of the base electrode to form on its surface an insulating layer of the required thickness.

3. Doping the oxide layer with the investigated substance. It can be done either by putting on the oxide surface a small drop of examined substance and centrifuging off its excess [9]–[11], or by oxiding base electrode in the presence of vapours of the investigated substances or, finally, by the process of infusion. The latter consists in putting one drop of substance on the top electrode of completed junction. The substance penetrates through the cracks and slits in top electrode up to the insulator layer.

4. Evaporation of the outer electrode, also in the form of a narrow strip, but perpendicular to the base electrode. Usually, the outer electrode is made of lead, which is superconductor in liquid helium, and its very well known properties are used for testing the quality of tunneling junctions.

In fig. 1 the processes described above are presented schematically.

Recording of IETS spectra consists in the measurements of current–voltage (I–V) characteristics and their first (dI/dV) and second (d^2I/dV^2) derivatives. As an example, the slope of I–V characteristic of a junction with possible single excitation (fig. 2) suddenly increases the energy $eV = h\omega$. This increase is very small (below 1%) and is hidden in the monotonic change of the background. Therefore, in order to obtain the IETS structures, it is necessary to record the first and second derivatives of the I–V characteristic. The excitations of molecules inside the barrier, or of the phonon modes of the barrier itself, appear as peaks similar to peaks recorded in infrared or Raman spectroscopy.

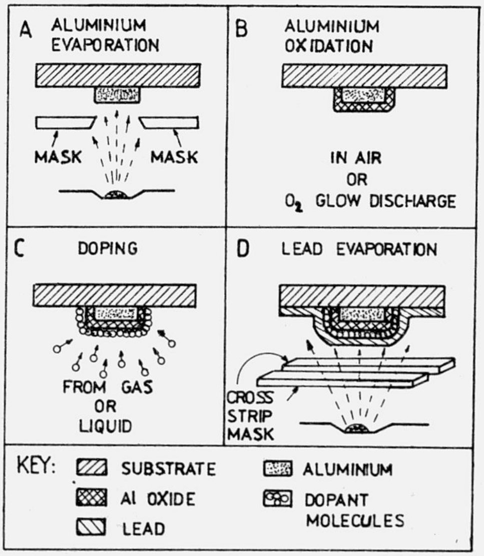

Fig. 1. Schematic view of the four steps involved in a conventional crossed film junction for tunneling spectroscopy [2]

For the measurements of the first and the second derivatives of the I–V characteristics the harmonic detection is the most often used. This method consists in applying a very low alternating voltage (so-called modulating voltage) of the order of some mV on a *dc* voltage biasing the tunnel junction. Subsequently, the voltage across the junction is measured by a lock-in amplifier. As the tunnel junction is the only passive element in the circuit, then, keeping the amplitude of modulating current at a constant level, the voltage across the junction can be expanded in a Taylor series as:

$$V(I) = V(I_0) + \left(\frac{dV}{dI}\right)_{I_0} \delta \cos \omega t + \frac{1}{4}\left(\frac{d^2V}{dI2}\right)_{I_0} (1 + \delta^2 \cos 2\omega t).$$

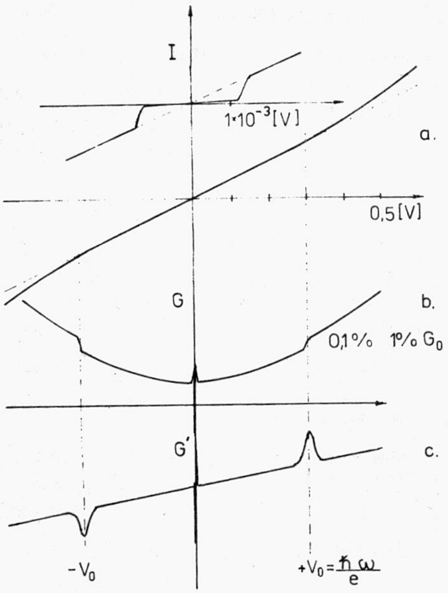

Fig. 2. Tunnel characteristics with structures created by inelastic transition: on I–V characteristic (a), dV/dI (b) and d^2V/dI^2 (c). The upper inset represents a superconduction gap structure on I–V characteristic near zero voltage bias, it is a test of good quality of tunnel junction

From the above expansion it can be seen that the voltage of the frequency ω is proportional to dV/dI and the voltage of the frequency 2ω is proportional to d^2I/dI^2 where δ is the amplitude of modulating current. Figures 3a and 3b present schematically flow diagram of the set-up for measurements of the IETS spectra constructed in the Institute of Physics of the Poznań Technical University [14]. The measured signals are on the level of 10^{-7} V, therefore the apparatus must fulfil high requirements of electrostatic screening and the purity of modulation voltage, i.e., of frequency ω without harmonics.

3. EXAMPLES OF APPLICATIONS

The investigations of KLEIN et al. [15] on the air pollutions in Paris and the works by WALACHOWA [16] on the tabacco smoke in the air were the first applications of IETS to the problems of natural environment protection. However, the above problems could be solved more easily and reliably with the aid of IR or Raman spectroscopy. But the advantages of IETS are visible in the investigations of water environments. As it has just been mentioned, a doping of tunneling junctions with water solutions does not introduce any inconvenience – the great amount of water does not mask the presence of investigated substances, which because of very high sensitivity of the measuring technique of the order of 10^{10} mol/cm^2 allows the detection of some substances at the concentrations of nano- and picomol/cm^3 in water solution.

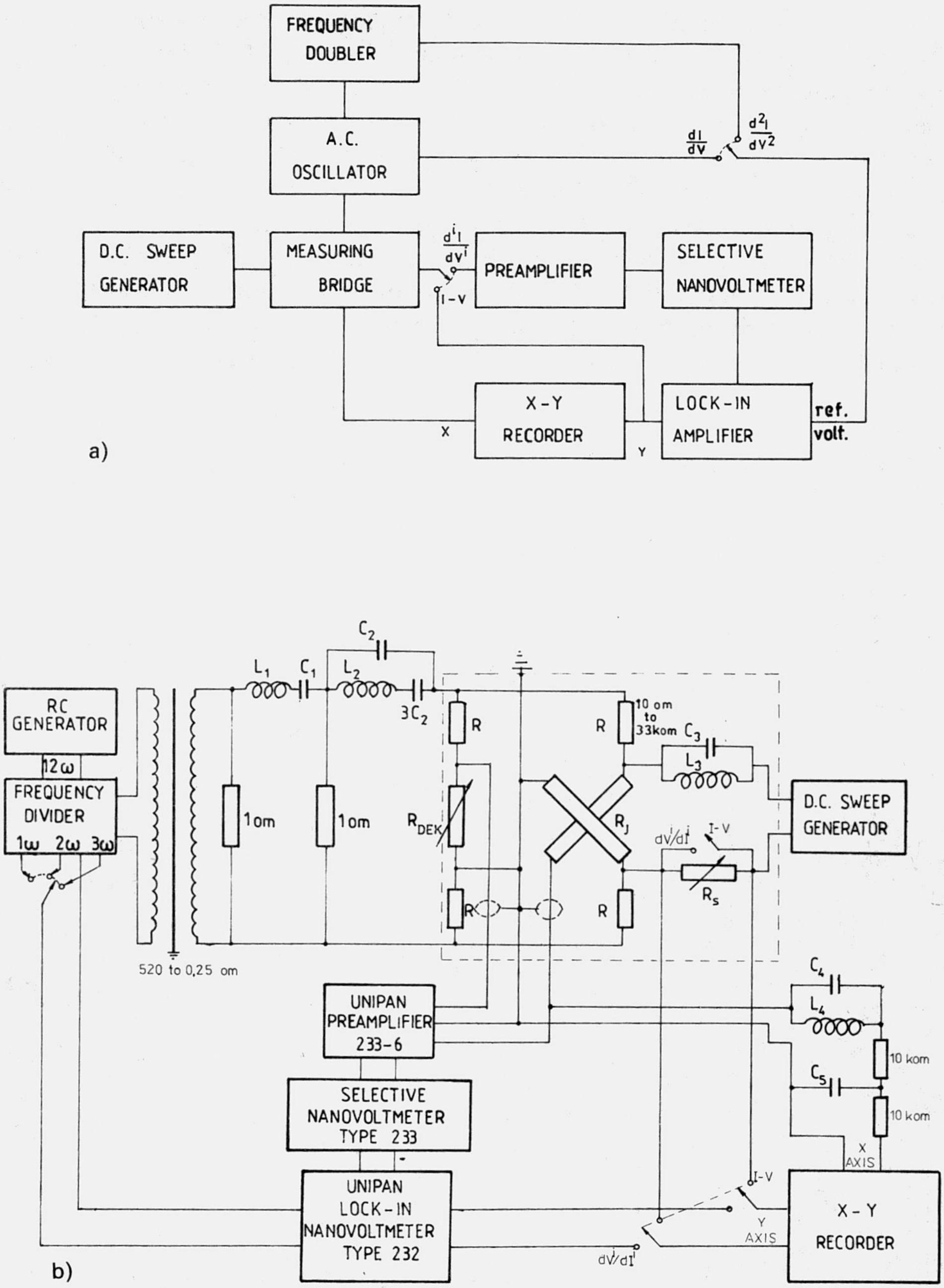

Fig. 3. (a) Block diagram of tunnel spectrometer, (b) Hybrid block-circuit diagram of tunnel spectrometer constructed in the Institute of Physics of the Poznań Technical University

The first applications of IETS to the studies on the pollutions in water environment were performed by Prof. YELON and his group [17]. He applied IETS to detect the presence of phenol in water and the decay of phenol under the influence of ozonation. He has stated that phenol can be detected in water in the ppm concentrations and that the ozonation process leads to decomposition of phenol, the glyoxylic acid being intermediate product. These experiments were the first proof of this particular decomposition of phenol in the process of ozonation.

Similar studies on the decay of m-cresol in water under influence of ozonation were carried out by the authors. The IETS spectra were studied using the tunneling junctions, fabricated according to the procedure described above, and above mentioned doping methods. In figure 4 the tunneling spectra d^2V/dI^2 vs. V of

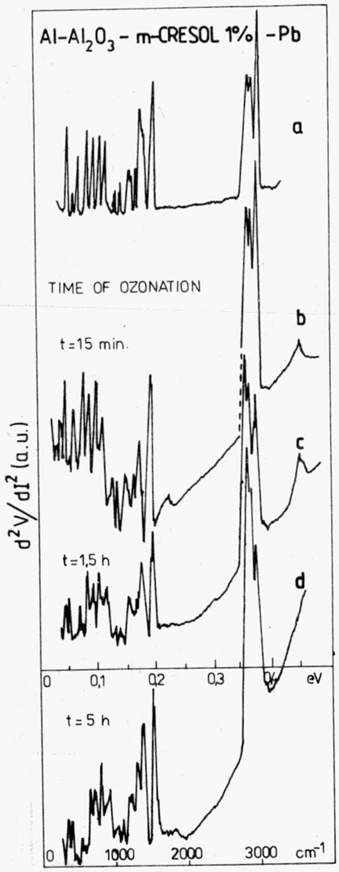

Fig. 4. Tunneling spectra for junctions doped with 1% aqueous solution of m-cresol ozonated for 0 min. (a), 15 min. (b), 1.5 h (c) and 5 h (d)

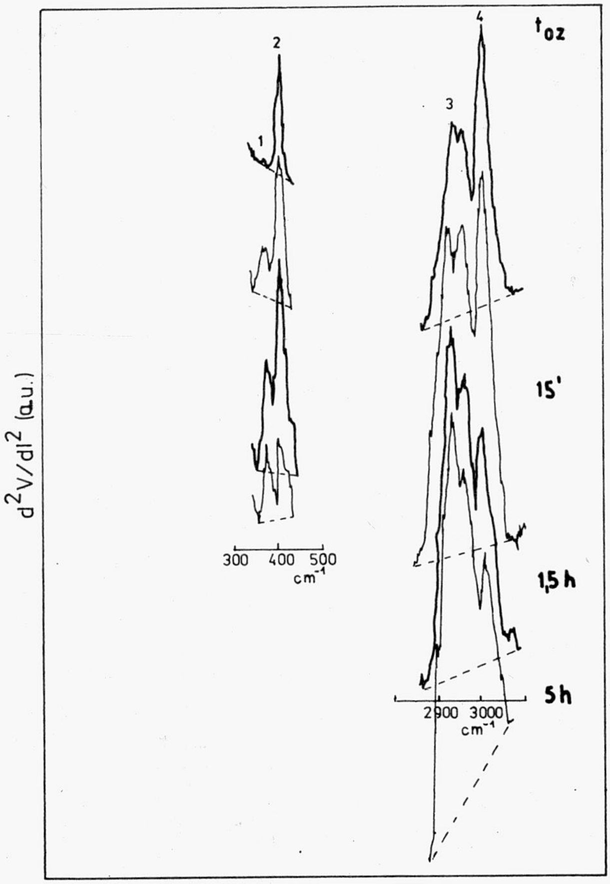

Fig. 5. Two chosen groups of lines: about 400 cm^{-1} and 3000 cm^{-1} representing decay of m-cresol due to ozonation process (line no. 4) and appearance of COO$^-$ group as one of ozonation products (line no. 1)

junctions doped with 1% solution of m-cresol and with the same solution after 15 min, 1.5 h and 5 h of ozonation are presented. The ozonation process was performed by means of the ozonator constructed in the Institute of Environment Protection Engineering of the Poznań Technical University. This apparatus was based on the LO-20-S tubes of the efficiency of 40–60 mg of ozon/h, the intensity of air flow being about 20 dm^3/h [18].

The spectra presented in fig. 4 are different for each time of ozonation. The most important differences which can be found in fig. 4 are distinguished and clearly presented in fig. 5. It shows the lines of excitations C–H at about 3000 cm^{-1} and two lines in the vicinity of 400 cm^{-1}. These results can be interpreted as follows: the cleavage of benzen ring of m-cresol during the ozonation results in the decay of characteristic of m-cresol vibrations mode C–H at 3007 cm^{-1} as compared to lines connected with C–H mode in methyl group CH_3 or C–H stretching modes characteristic of simpler organic compounds, e.g., carboxylic acids. Similarly the increasing intensity of line 384 cm^{-1} can be assigned to the out-of-plane twisting modes for group COO^- [19], suggesting the gradual formation of simple carboxylic acids which are the expected products of phenol compound ozonation in water. The results discussed above concern the relatively high (about 1%) concentrations of m-cresol in water. The application of oilless vacuum systems and air purity control in laboratory may, however, increase the sensitivity of measurements by several orders of magnitude (YELON [5] and HANSMA [6]).

4. APPLICATION OF IETS TO DETECTION OF TRACE AMOUNTS OF SUBSTANCES

As it was mentioned above, the IETS is a relatively young and new analytical technique of very high sensitivity, allowing us to detect the trace amounts (some molecules per cm^2) of investigated substances. The substance can be identified comparing unknown IETS spectrum with the Raman or infrared standard spectra.

The disadvantage of this technique is the lack of simple theory which would relate the intensity of a IETS line to the amount of substance adsorbed on the surface of base electrode, or to concentration of solution used for doping a junction. Nevertheless, with the aid of other methods, mainly radioactive traces method, it has been proved that the C–H line at 2903 cm^{-1}, typical of many organic acids, should be observed in concentration below 1 ppm, and the line C≡N at 2258 cm^{-1} at 10 ppm. It is illustrated in fig. 6 where the dependence of line intensity on the concentration of cyanoacetic acid ($CNCH_2COOH$) in water solution is presented.

Recent investigations of HANSMA et al. [6] prove the possibility of tracing some substances on the concentration level of 10^{-10} amounts of solution needed for doping the junction being of nl order. Figure 7 presents the IETS spectra of junctions doped with (7+2) nl drops of aqueous solution of benzoic acid in

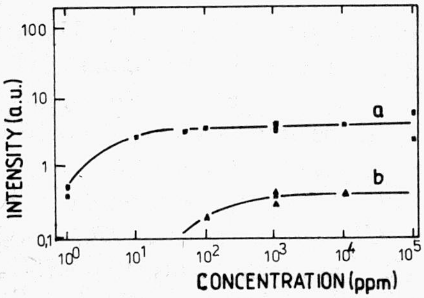

Fig. 6. Plot of intensity versus solution concentration for $CNCH_2COOH$ doped junctions: (a) C–H peak at 360 meV, (b) C≡N peak at 280 meV [11]

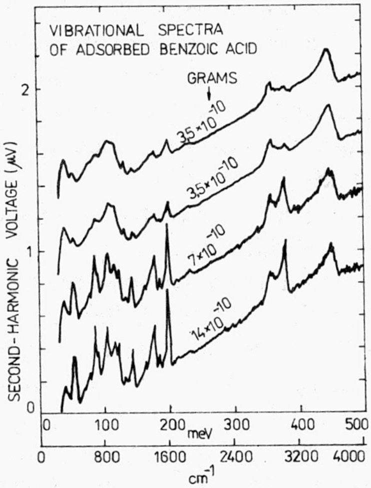

Fig. 7. Vibrational spectra of adsorbed benzoic acid from 7 nl drops of 0.05, 0.05, 0.1 and 0.2 g/dm^3 solutions of benzoic acids in water to tunnel junctions

concentrations of 0.005, 0.05, 0.1 and 0.2 g/dm^3. The top two spectra were measured on different junctions to illustrate the good reproducibility of technique. The next two spectra illustrate the saturation for higher concentrations. As it has been proved that 1% concentration can be detected, the lower limit of detectability of investigated substance was estimated as 10 pg.

Because of the need of application of specific apparatus to the detection of IETS spectra, as well as of some experimental difficulties connected with the application of liquid helium temperatures, and with the lack of collection of standardized IETS spectra, this technique is rarely applied to pollution control of natural environment, especially to water environment. Nevertheless, the dynamic development of IETS and its application can be expected in very near future.

ACKNOWLEDGMENT

Authors thank Dr. Cichosz–Raczyk and management of the Institute of Environment Engineering of Poznań Technical University for the offered facilities to ozonate the m-cresol solutions.

We would like to acknowledge mgr Andrzej Reich for his help in the preparation of this manuscript.

REFERENCES

[1] Jaklevic R. C., Lambe J., Phys. Rev. Lett., 17, 1139 (1966).

[2] Hansma P. K., [in:] *Tunneling Spectroscopy*, ed. P. K. Hansma, p. 1, Plenum Press, New York and London 1982.

[3] Jaklevic R. C., Gaertner M. R., Appl. Surf. Sci., 1, 479 (1978).
[4] Jaklevic R. C., Gaertner M. R., Appl. Phys. Lett., 30, 646 (1977).
[5] Yelon A., [in:] *Inelastic Electron Tunneling Spectroscopy*, ed. T. Wolfram, p. 61, Springer Verlag, New York 1978.
[6] Hansma P. K., Hansma H. G., [in:] *Tunneling Spectroscopy*, ed. P. K. Hansma, p. 475, Plenum Press, New York and London 1982.
[7] Miles J. L., Smith P. H., J. Electrochem. Soc., 111, 1240 (1978).
[8] Magno R., Adler J. G., Phys. Rev., B13, 2262 (1976).
[9] Simonsen M. G., Coleman R. V., Hansma P. K., J. Chem. Phys., 61, 3789 (1974).
[10] Hansma P. K., Coleman R. V., Science, 184, 1369 (1974).
[11] Skarlatos Y., Barker R. C., Haller G. L., Yelon A., Surf. Sci., 43, 353 (1974).
[12] Adler J. G., Jackson J. E., Rev. Sci. Instrum., 37, 1049 (1965).
[13] Thomas D. E., Rowell J. E., Rev. Sci. Instrum., 36, 1301 (1965).
[14] Czajka R., Susła B., Rauluszkiewicz J., Szuba S., Electron Technology, 17, 47 (1985).
[15] Klein J., Leger A., (cited).
[16] Valachova J., [in:] *Prace 3rd Konf. Cesk. Fyz. Pr.*, ed. M. Matyas, p. 154, Academia, Prague 1974.
[17] Skarlatos Y., Barker R. C., Haller G. L., Yelon A., Phys. Chem., 79, 2587 (1975).
[18] Cichosz–Raczyk N., Ph.D thesis, 1981.
[19] Brown N. M. D., Nelson W. J., Walmsley D. G., J. Chem. Soc. Faraday Trans., II 75, 32 (1979).

ZASTOSOWANIE SPEKTROSKOPII TUNELOWEJ DO BADANIA ZANIECZYSZCZEŃ ŚRODOWISKA PRZYRODNICZEGO

Spektroskopia nieelastycznego tunelowania elektronów (SNTE) może być stosowana do badania zanieczyszczeń środowiska przyrodniczego, a w szczególności środowiska wodnego. Technika ta charakteryzuje się bardzo dużą czułością i dobrą zdolnością rozdzielczą. Stosuje się ją między innymi do detekcji śladowych ilości substancji na poziomie 10^{10} cząsteczek przy subnanogramowych ilościach badanych roztworów. Zastosowanie SNTE opisano na przykładzie badań rozkładu m-krezolu w roztworach wodnych pod wpływem ozonowania, które przeprowadzono w Instytucie Fizyki Politechniki Poznańskiej.

ПРИМЕНЕНИЕ ТУННЕЛЬНОЙ СПЕКТРОСКОПИИ ДЛЯ ИССЛЕДОВАНИЯ ЗАГРЯЗНЕНИЙ ОКРУЖАЮЩЕЙ СРЕДЫ

Спектроскопия неэластичного туннельного перехода электронов (SNTE) может быть использована для исследования загрязнений окружающей среды, а в частности водной среды. Эта техника характеризуется большой чувствительностью и хорошей разделительной способностью. Её применяют между прочем для детектирования минимального количества веществ на уровне 10^{10} частиц при субнанограммовом количестве исследуемых растворов. Применение SNTE описано на примере исследований распределения м-крезола в водных растворах нод давлением озонирования, которое проведено в Институте Физики Познанского политехнического института.