

# Near infrared emission spectroscopy induced by ultrasonic irradiation

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## Abstract

Near infrared emission caused by ultrasonic excitation is demonstrated for the first time in this work. The instrument is constituted of an acousto-optical tunable filter-based spectrometer, an ultrasonic processor connected to a titanium alloy ultrasonic probe and a cylindrical borosilicate flask containing the sample to be excited. The radiation emitted by the sample is collected by a concave mirror and sent to the spectrometer. The effects of the position of the probe extremity in relation to a lateral entrance of the borosilicate flask and of the ultrasonic power on the emission signal were studied. The best results were obtained by positioning the probe extremity up to 2 mm from the reflexive body (lateral entrance) using 30% of the full ultrasonic incident power and acquiring spectra after 5 min of sonication. The NIR emission spectra resulting from the ultrasonic excitation were in agreement with that obtained by thermal excitation. The proposed technique was utilized to study different poly(dimethylsiloxane) samples having different viscosities.

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## 1. Introduction

Recently, a growing interest in near infrared (NIR) spectroscopy has arisen due to improvements in instrumentation and in data analysis. The spectral NIR region, which covers the range between ca. 4000 and 12,800  $\text{cm}^{-1}$  (corresponding to 0.780–2.5  $\mu\text{m}$ ), contains absorption bands corresponding to overtones and combinations of fundamental vibrations from C–H, O–H and N–H bonds, because of the large anharmonicity of the vibrations involving the light hydrogen atoms. As the overtones and combination bands are much weaker than the fundamental absorption bands, NIR spectroscopy allows the analysis of samples up to several millimeters thick. The speed, simplicity of sample preparation and non-destructive nature of the technique have

been established as the principal advantages offered by NIR absorption spectroscopy [1,2]. NIR technology has undergone a remarkable increase in its applications to real-life analytical problems and has recently been reviewed in most of its historical, fundamental and applications aspects [3–5]. However, there are still only a few papers dealing with near infrared emission spectroscopy (NIRES) or on its exploitation for analytical purposes [6,7].

On the other hand, mid infrared emission spectroscopy (MIREs) has been the subject of numerous papers [8–12] and has a good review of the research developed in this area [8]. In these studies, a sample is thermally excited to higher vibrational energy levels and the radiant relaxation process is monitored by a spectrometer. A molecular emission spectrum is recorded whose emission maxima agree with the absorption maxima of the conventional absorbance spectra of the same samples in terms of wavelength position and relative intensities. Due to the nature of near and mid infrared regions, MIREs presents the disadvantage of being less tolerant of sample thickness (only a few

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examples can be found where thicknesses above 100  $\mu\text{m}$  have been employed [9–11]), but MIREs presents the advantage of needing lower excitation temperatures to obtain measurable emission signals (one paper reports emission from a sample at room temperature [12]). A recent paper on NIREs provides a good description of the emission phenomena related to both NIREs and MIREs [13].

High-intensity ultrasonic fields in liquids furnish a rare condition for chemical reactions [14]. The chemical effects from ultrasound originate from stable and mainly transient acoustic cavitation bubbles, which attain extremely high temperatures and pressures [15,16]. Several studies have demonstrated that ultrasonic irradiation can produce sonoluminescence from cavitation bubbles [17] and induce chemiluminescence [18]. The energy necessary to perform chemi- or sonoluminescent process are higher than those related to infrared radiation emission. Therefore, emissions in the infrared range should occur for transient stable bubbles.

In this paper, the potential for molecular emission in the NIR region induced by acoustic cavitation is demonstrated. This new technique is called near infrared emission spectroscopy induced by ultrasonic irradiation—NIRESIUS.

## 2. Experimental

### 2.1. Equipments and instrumentation

A 20 kHz 130 W ultrasonic processor, VibraCell model VC130, from Sonics Instruments (Newtown, CT, USA) was employed to induce emission in the NIR range. Probes of 2 and 6 mm diameter fabricated from titanium alloy (TI-6AL-4V) were adequately attached to the ultrasonic processor in order to attain the maximum transduction of energy.

The spectrometer developed to collect and analyse the radiation emitted by the samples is based on an acousto-optical tunable filter (AOTF). The AOTF is made with a  $\text{TeO}_2$  crystal, manufactured by Brimrose (TEAF\_1.5–3.0) to operate in the spectral region from 1500 to 3000 nm with nominal spectral resolution varying from 9 to 37 nm as the selected wavelength increases in its useful range. The optical aperture of the device is a square window having 7 mm sides. The AOTF was driven by a radio frequency (rf) signal generated by a digital synthesizer (Analog Devices—AD 9852), assembled to be controlled by a parallel interface (ICP-DAS A8111) placed in a microcomputer running a customized software written in Visual Basic 5.0. Under computer control, the synthesizer board generates an rf signal in the range of 68–34 MHz, necessary to select the wavelength emitted by the sample in the 1500–3000 nm range. The rf signal is modulated with a TTL level signal at 167 Hz and amplified by a rf amplifier (RF Gain, BBM2C4AJT, 8 W, 10–1000 MHz) to produce a 3.0 W signal applied to the AOTF. Therefore, radiation of selected

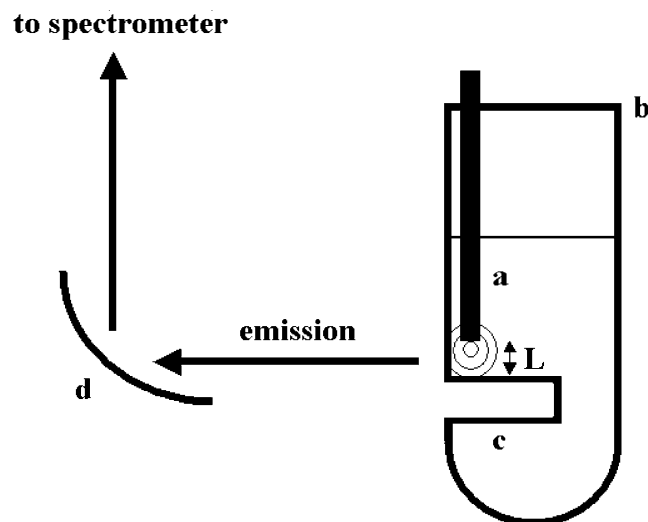


Fig. 1. Schematic representation for the ultrasonic excitation system. (a) Ultrasonic probe; (b) borosilicate cylindrical flask; (c) lateral entrance (reflexive body); (d) concave mirror; ( $L$ ) distance between the ultrasonic probe extremity and the reflexive body.

wavelengths is also modulated at this frequency. This spectrometer has been more fully described in an earlier paper using thermal excitation of samples through an electrical heater [13]. Here, the electrical heater was substituted by a concave mirror and a cylindrical borosilicate flask containing the probe for ultrasonic excitation. The probe extremity was positioned toward to the concave mirror and closed to the sonoreactor wall, without having contact with the wall. The borosilicate cylindrical flask contains a lateral entrance serving as a reflexive body to permit the reflection of the ultrasonic waves (concentrating the acoustic energy) and to induce NIR radiation emission toward the concave mirror. The general diagram of the ultrasonic excitation system is depicted in Fig. 1.

### 2.2. Procedures

Poly(dimethylsiloxane) oil samples with viscosities from 1000 to 60,000 cSt were used to demonstrate the potential of NIRESIUS. Seven milliliter of these fluids were placed in the sonoreactor and emission spectra were obtained from 2000 to 3000 nm with nominal resolutions of 5 nm. The effect of ultrasonic wave amplitude on the emission signal was investigated and distances “ $L$ ” between the probe extremity and the reflexive body, depicted in Fig. 1, from 1 to 12 mm were also evaluated.

The acoustic power dissipated into the 5000 cSt poly(dimethylsiloxane) oil sample was calculated by the calorimetric method [19], employing Eq. (1):

$$\text{Power (W)} = \left( \frac{dT}{dt} \right) \times c_p \times m, \quad (1)$$

where  $c_p$  is the heat capacity of the 5000 cSt poly(dimethylsiloxane) oil sample ( $\text{J g}^{-1}$ ),  $m$  is the mass of water

(g) and  $(dT/dt)$  is the temperature rise per second which was obtained with optimal experimental conditions.

### 3. Results and discussion

Fig. 2 shows a comparison between the emission signals generated by thermal (Fig. 2A) and ultrasonic excitation (Fig. 2B) of a poly(dimethylsiloxane) oil sample when the excitation is interrupted (by turning off the heater or the ultrasonic processor, respectively). The experiment with thermal excitation was made through an electrical heater in an early arrangement of the instrument [13]. In both experiments, the spectra were continuously obtained (48 s for each spectrum) and the interruption of the excitation was made between two subsequent spectra. The upper spectra shown in Fig. 2A and B were acquired immediately before the interruption of the excitation. Although heating is produced in the bulk of the media submitted to ultrasonic irradiation (the whole sonoreactor achieves a uniform temperature of 170 °C), there is an abrupt and instantaneous decrease in the amplitude of emission bands when ultrasonic excitation is interrupted, much faster than the decrease observed after interruption of thermal excita-

tion. This confirms that the near infrared emission was induced by the ultrasonic cavitation process and not by bulk heating. Probably the bulk heating produced by cavitation was not sufficient to overcome the self-absorption phenomena, enhanced by the large volume of the ultrasonic irradiation cell and, consequently, the higher sample thickness in comparison with other papers describing infrared emission spectroscopy.

All spectra obtained with thermal excitation (Fig. 2A) show two emission band maxima (2700 and 2800 nm) related to the poly(dimethylsiloxane) oil sample, since there is no window between the sample and the spectrometer as there is with the borosilicate cell in the ultrasonic excitation. For emission spectra obtained under ultrasonic irradiation, the borosilicate cell absorbs radiation in the NIR range emitted from poly(dimethylsiloxane) between 2600 and 2900 nm (Fig. 2B). This effect was confirmed by the spectrum of a borosilicate disk warmed to 200 °C, where an intense emission band between 2600 and 2900 nm was observed. So, if the borosilicate presents an intense emission in this region, it also presents an intense absorption as well. Therefore, during the assays carried out with ultrasound, the borosilicate reactor was cooler than the poly(dimethylsiloxane) and the irradiation from 2600 to 2900 nm was absorbed by the cell material, causing a cutoff in the emission signal from 2600 nm (Fig. 2B).

Despite the high sample volume (7 mL), the maximum sample thickness was restricted and is defined by the maximum extent of the ultrasonic waves. The better spectral resolutions were obtained with the presence of the lateral entrance in the sonoreactor (Fig. 1), which restricts the reach of the ultrasonic waves and concentrates the acoustic energy. The distance between this entrance (reflexive body) and the ultrasonic probe extremity was evaluated to determine the optimum ultrasonic irradiation conditions to maximize the NIR emission from the sonicated material. Distances between the ultrasonic probe extremity and the reflexive body from 1 to 12 mm were evaluated and these spectra can be seen in Fig. 3A. For distances from 4 mm, the spectral intensity and the spectral resolution decrease, due to losses in the incident acoustic energy (higher scattering of the acoustic waves), and the contribution of blackbody emission from bulk heating increases. The contribution of blackbody emission was proven by comparison with the profile of a blackbody emission spectrum (Fig. 3B) obtained through an experimental blackbody constituted by the same poly(dimethylsiloxane) oil sample mixed into a graphite powder (resulting in an opaque suspension). The blackbody emission is intense enough to overcome the absorption of the borosilicate cell and explains the shoulders at about 2700 nm in Fig. 3A. The ultrasonic blackbody spectrum has the same profile as the blackbody spectrum obtained with thermal excitation [13]. So, the best condition was obtained for distances between 1 and 2 mm. For the remainder of this investigation, a distance of 1 mm was maintained.

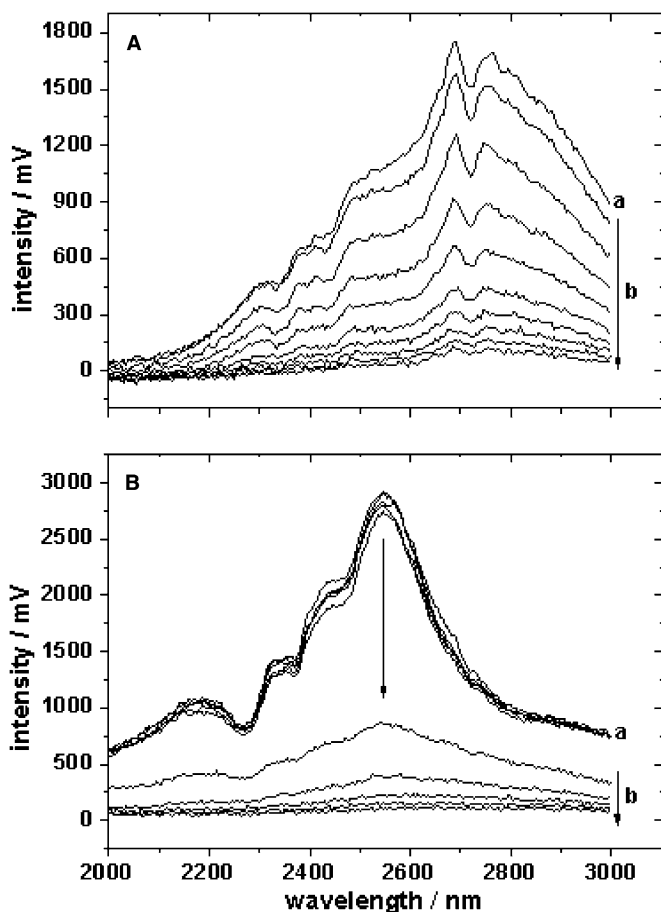


Fig. 2. Near infrared emission spectra for a poly(dimethylsiloxane) oil sample with thermal (A) or ultrasonic excitation (B) for constant external excitation (a) and by interrupting the excitation source (b).

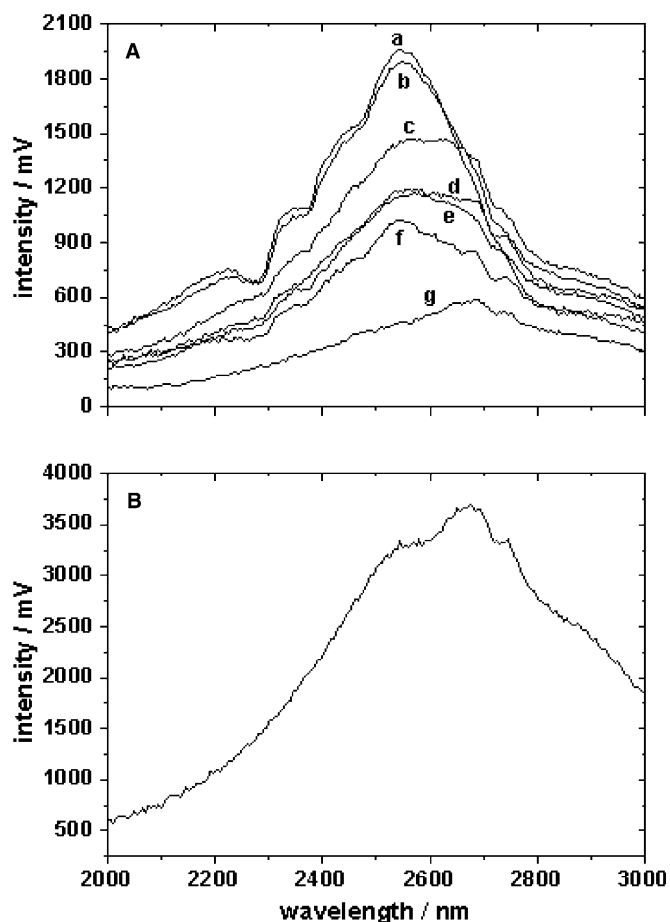


Fig. 3. Effect of the distance  $L$  between the ultrasonic probe extremity and the reflexive body on the NIR emission spectra (A) and blackbody emission spectrum of poly(dimethylsiloxane) with graphite powder (B).  $L$  values: (a) 1 mm; (b) 2 mm; (c) 4 mm; (d) 6 mm; (e) 8 mm; (f) 10 mm; (g) 12 mm.

The effect of ultrasonic intensity on the emission signal was also considered. Ultrasonic irradiation was carried out using a Vibracell which is nominally 130 W at 20 kHz, operating from 5% to 40% of its full intensity. The ultrasonic intensity from 5% to 30% of its full intensity corresponds to a power of 1.4–2.8 W dissipated into the 5000 cSt poly(dimethylsiloxane) oil sample. It was observed that the emission intensity in the evaluated NIR region increased with the increase in the ultrasonic wave intensity, as shown in Fig. 4. Moreover, the emission intensity increased exponentially with the increase of the ultrasonic power dissipated into the sample. Probably, the power increases cause an exponential increase in the fraction of excited species in relation to the species in the fundamental state, as predicted by the Boltzman equation. A similar result was obtained by increasing the sample temperature in thermal excitation [13]. However, since the highly effective ultrasonic intensity causes an evident temperature increase and acoustic transfer variations, 30% of the incident ultrasonic intensity (power of 2.8 W dissipated into the sample) was selected throughout. For higher incident ultrasonic intensities, the NIRESIUS spectra also

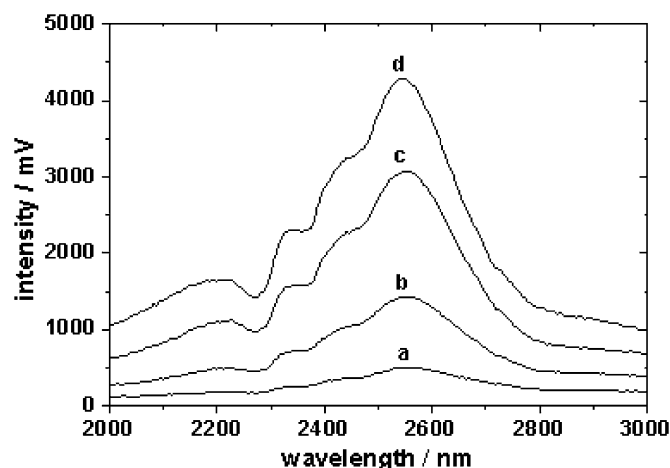


Fig. 4. Effect of ultrasonic power dissipated into the 5000 cSt poly(dimethylsiloxane) oil sample on the NIR emission spectra. (a) 1.4 W; (b) 2.5 W; (c) 2.6 W; (d) 2.8 W.

showed significant noise. It was also observed that repetitive emission intensities for the same sample can only be obtained after 5 min of sonication.

The proposed technique using optimized conditions was applied to differentiate poly(dimethylsiloxane) oil samples having different viscosities (60,000, 5000 and 1000 cSt) using their NIRESIUS spectra, as depicted in Fig. 5. As the excitation is made through a mechanical wave (acoustic waves), for very low or very high viscosities (1000 and 60,000 cSt), the energy transfer from the ultrasonic probe extremity to the sample through the cavitation process is decreased, also decreasing the emission intensity. The 5000 cSt poly(dimethylsiloxane) oil sample presents a more favorable medium for acoustic energy transfer, and the spectrum shows a higher emission intensity. For the 1000 cSt poly(dimethylsiloxane) oil sample and in comparison with the 5000 cSt poly(dimethylsiloxane) oil sample, the energy transfer through the cavitation process is less intense, resulting in an emission spectrum with a similar

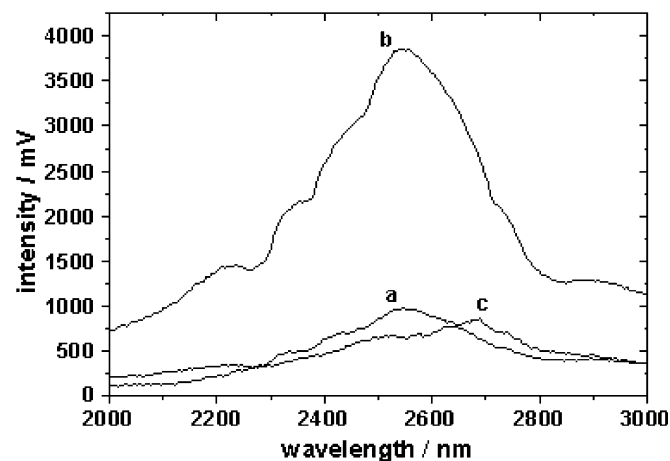


Fig. 5. Emission spectra for poly(dimethylsiloxane) oil samples with different viscosities. (a) 1000 cSt; (b) 5000 cSt; (c) 60,000 cSt.

profile but with lower intensity. For the 60,000 cSt poly(dimethylsiloxane) oil sample, the sonication process is unstable (formation of a lot of bubbles), resulting in only thermal excitation through frictional forces between the ultrasonic probe and the sample. This led to an emission spectrum with lower intensity and some contribution of blackbody emission from bulk heating (spectral profile similar to that shown in Fig. 3B).

#### 4. Conclusion

Near infrared emission spectroscopy induced by ultrasonic excitation (NIRESIUS) has been successfully demonstrated. The instrument was developed by substituting the electrical heater of an emission spectrometer by an ultrasonic probe immersed in a sample holder. The comparison between the emission signal behaviors immediately after interruption of thermal and ultrasonic excitation proved the effectiveness of ultrasonic excitation. The ultrasonic excitation was also proven by exponential increases caused in the emission signal due to increases in the ultrasonic power applied to the sample, as predicted by the Boltzmann equation. As ultrasound is a mechanical wave, the energy transfer efficiency between the ultrasonic probe and the sample depends on the physical characteristics of the sample, such as viscosity. This allowed the application of the NIRESIUS to differentiate poly(dimethylsiloxane) oil samples through their different viscosities. The higher sample volume (7 mL), in comparison with other infrared emission spectroscopy procedures and the locally restricted excitation (only close to the ultrasonic probe extremity) made by the ultrasonic cavitation process demonstrates the advantage of NIRESIUS over NIRES and mainly over MIRES, in relation to tolerating higher sample thicknesses. The portability of the ultrasonic probe and its easy utilization as an excitation source (a simple immersion into a sample close to a NIR detector preceded by a NIR wavelength selector) permits predicting the application of NIRESIUS in manufacturing processes.

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#### References

- [1] J.J. Workman, *Appl. Spectrosc. Rev.* 31 (1996) 251–320.
- [2] P. Williams, K. Norris, *Near-Infrared Technology*, second ed., American Association of Cereal Chemistry, St. Paul, 2001.
- [3] C. Pasquini, *J. Brazil. Chem. Soc.* 14 (2003) 198–219.
- [4] M. Blanco, I. Villarroya, *Trend. Anal. Chem.* 21 (2002) 240–250.
- [5] W.F. MacClure, *J. Near Infrared Spectrosc.* 11 (2003) 487–518.
- [6] B.A. Nelson-Avery, D.C. Tilotta, *Appl. Spectrosc.* 48 (1994) 1461–1467.
- [7] V.S. Ovechko, A.M. Dmytruk, O.V. Fursenko, T.P. Lepeshkina, *Vacuum* 61 (2001) 123–128.
- [8] D.H. Sullivan, W.C. Conner, M.P. Harold, *Appl. Spectrosc.* 46 (1992) 811–818.
- [9] L.T. Lin, D.D. Archibald, D.E. Honigs, *Appl. Spectrosc.* 42 (1988) 477–483.
- [10] R.J. Pell, B.C. Erickson, R.W. Hannah, J.B. Callis, B.R. Kowalski, *Anal. Chem.* 60 (1988) 2824–2827.
- [11] M. Celina, D.K. Ottesen, K.T. Gillen, R.L. Clough, *Polym. Degrad. Stab.* 58 (1997) 15–31.
- [12] D.L. Allara, D. Teicher, J.F. Durana, *Chem. Phys. Lett.* 84 (1981) 20–24.
- [13] F.B. Gonzaga, C. Pasquini, *Anal. Chem.* 77 (2005) 1046–1074.
- [14] K.S. Suslick, *Science* 247 (1990) 1439–1445.
- [15] W.B. McNamara, Y.T. Didenko, K.S. Suslick, *Nature* 401 (1999) 772–775.
- [16] T.G. Leighton, A.J. Walton, J.E. Field, *Ultrasonics* 27 (1989) 370–373.
- [17] M.A. Margulis, I.M. Margulis, *Ultrason. Sonochem.* 9 (2002) 1–10.
- [18] T. Tuziuti, S. Hatanaka, K. Yasui, T. Kozuka, H. Mitome, *Ultrasonics* 40 (2002) 651–654.
- [19] S. Koda, T. Kimura, T. Kondo, H. Mitome, *Ultrason. Sonochem.* 10 (2003) 149–156.