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PHOTOACOUSTIC RESPONSE OF RED FRUIT PYRACANTHA COCCINEA

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Abstract: The photoacoustic (PA) spectra of the red fruit Pyracantha Coccinea sample, prepared in a thick film form were investigated and analysed. Several absorption peaks were registered in the visible range of electromagnetic radiation while the most intense was at 548 nm. The obtained photoacoustic spectra were compared with the spectra of leaves, sea creatures and the human skin. There are significant similarities which confirm that similar bioorganic compounds are present in any living system. In particular, the obtained results confirm experimentally that the red fruits of Pyracantha Coccinea intensively absorbed UV solar rays and had several additional absorption bands in the visible and near infrared regions, i.e. in that part of the solar spectrum for which water is almost transparent.

Key words: Photoacoustic spectroscopy, Pyracantha Coccinea, Electronic transitions

Introduction

Photoacoustic (PA) spectroscopy (PAS) is one of the most useful techniques both for research purposes and application, especially for materials related to the living matter, e.g. [1-11]. PAS allows light-induced heat production to be detected due to the non-radiative deactivation of light excitation. It is very useful in photosynthesis research to measure energy conversion and storage, and in molecular structure and interaction studies as well as oxygen evolution in photosynthetic systems [12]. PAS is also used to detect and monitor ethylene concentrations emitted by urban public transport which is essential for human health [13]. A recent application of this technique is PA imaging which is a hybrid technology that images the internal distribution of the optical energy deposition in biological tissues [14-16]. One of the more interesting areas of the PAS research is the study of radiation in the 540 to 580 nm range which, in many cases, gives for instance the red color of blood, the color of leaves and fruits. The human blood produces the PA peak at about 550 nm [1] and the red leaf at 544 nm [11]. It is well known that human blood contains complexes with many transition ions, for example, with iron (transferrin) and copper (ceruloplasmine). The electron paramagnetic resonance study of ceruloplasmene has shown that the disease cancer has an impact on the electronic structure of copper complexes in the blood [17]. The question is whether the above transition group ions complexes do not occur in the case of red leaves and fruits. In our previous work we have proposed the existence of a channel selector mechanism [18, 19]. This is because the wave functions of 3d ions extend over the entire molecule; there is one shape in the ground state and another in the excited state. This could have far-reaching consequences on pathological changes of living beings and their development.

The aim of this report is to investigate the tissues of the red fruit of Pyracantha Coccinea in the visible ranges of electromagnetic radiation by PAS and comparison with corresponding data obtained for tissues of red Ficus Benjamina leaves, Pyracantha Coccinea, Asterias Rubens, Trunculariopsis Trunculus, spermidine, and the human skin.

Experimental

The red fruit of Pyracantha Coccinea was collected in November 2013 at the University of Athens campus. The PA spectra were measured using a thick film sample of the

Pyracantha Coccinea tissue at room temperature using conventional equipment and methodology, as described in [7, 20].

Results and Discussion

Fig. 1 presents a Pyracantha Coccinea plant with red fruits within its green leaves. The obtained PA spectrum of the red fruit of Pyracantha Coccinea is presented in Fig. 2. Similarly as for the red leaf, very intense PA lines due to n→p* and n→n* transitions connected with charge transfer are dominating the spectrum below 350 nm [11]. In the visible range the peaks near 369, 399, 412, 432, 506, 548, 574, 631 and 664 nm are visible where the most intense peak is at 548 nm. The absorption band at 664 nm could be related to photosynthesis [21], analogous as for red Ficus Benjamina leaves [11]. The effects of visible light on the skin produced peaks at the following wavelengths: 405 nm, 410 nm, 504 nm, 538 nm, 576 nm and 630 nm [22]. Absorption in this region of electromagnetic radiation was also observed in blood [23]. Table 1 shows PAS peaks observed in samples from different plant and animal organisms and (for comparison) from human skin. The PA absorption attributed to photosynthesis is not observed in animal organisms.

Fig. 1: The Pyracantha Coccinea plant at Athens University Campus

Inside the sample, radiative and non-radiative processes related to electron transitions on molecular levels can create phonons. Electronic excited states are unstable and the excess energy is transferred to other excited states and to the vibrating environment after this. It could cause thermal processes which are very important in complex molecules in the living matter. As transition metal complexes, e.g. containing copper(II), iron(II) or iron(III), are present in the living matter and play a crucial role there, they are studied intensively. The wavelength values, λ, corresponding

Table 1: PAS peaks observed in samples from different plant and animal organisms and (for comparison) in human skin

Sample	Peaks [nm]						Reference
The skin	405	410	504	538	576	630	[22]
Ficus Benjamina	398	414	504	544	578	635	[10]
Asterias Rubens	397	415	508	548	570	620	[24]
Truncularіopsis Trunculus	397	413	507	547	570	635	[6]
Sea Urchin	399	420	508	547	570	632	[25]
Pyracantha	399	412	506	548	574	631	this paper

to the differences in energy ΔE between the excited states are equal to $\lambda = \frac{hc}{\Delta E}$, where h is the Planck constant and c is the speed of light. The difference between the energies corresponding to the peaks at 412 nm and 506 nm gave the wavelength λ of about 2000 nm. This value corresponds to the intense absorption observed for the blood by IR spectroscopy [23]. If we consider the wavelengths of 369 nm and of 399 nm, the energy difference corresponds to 1400 nm. An intense absorption in the same energy region was also observed in the blood [23].

In the case of living matter containing large concentrations of water molecules and subjected to the direct action of solar radiation, similar mechanisms for collection and use of this energy should have emerged during evolution. The transitions n→n* are responsible for the creation and destruction of the most complex molecules and a PA spectrum is several orders of magnitude more intense than that observed in the visible and infrared part of electromagnetic radiation. Ion complexes of the 3d transition group (commonly copper and iron ions) with their so-called d-d transitions are generally observed in the visible range. This means that the absorption of solar electromagnetic radiation in the visible range should be focused on electron transitions [22, 26-29]. The role in processes related to the living matter of most of the observed electronic transitions in the visible range is not known. A photoacoustic study of polyamines has shown the presence of the same range of electronic transitions [18, 19, 30-33]. In the paper [33] a mechanism for the occurrence of the so-called „channel selector" has been proposed. Complexes of copper ions and iron have extended wave functions and electrons could be propagated throughout the whole molecule. This distribution is different in the excited state in comparison to the ground state. This fact may play an important role in the regulation of many processes in the living matter. This is particularly evident in the area of production of food, wine and generally in human life. PA spectra in the visible spectrum are more intense in living organisms and fruits than in leaves. This is understandable because the fruit is formed at the beginning of a living organism [6, 7, 10, 11].

It should be noted that between the red leaf and the fruit there are very big differences in the intensity of transitions that are responsible for the process of photosynthesis and in the visible range [11]. Another very important fact is the great concentration of molecular water in living systems. Molecular concentration of water is a very important factor leading to an increase in bioorganic complexes of metal involved in the photoacustic process. Water is transparent to longer wavelengths of electromagnetic radiation. This was demonstrated experimentally in hydrated and dehydrated tissues. In the latter case less intense photoacustic spectrum was recorded [6, 7].

It is obvious that the processes associated with heat play a very important role in the living system. It was shown that the intensities of the photoacustic absorption are different in different organisms. Thus, the photoacoustic spectroscopy gives us additional information about the thermal processes that can occur in the living organism and especially provides information about their intensities. In the future much more attention should be paid to the investigations on relative intensities of the d-d transitions being detected by the photoacoustic spectroscopy.

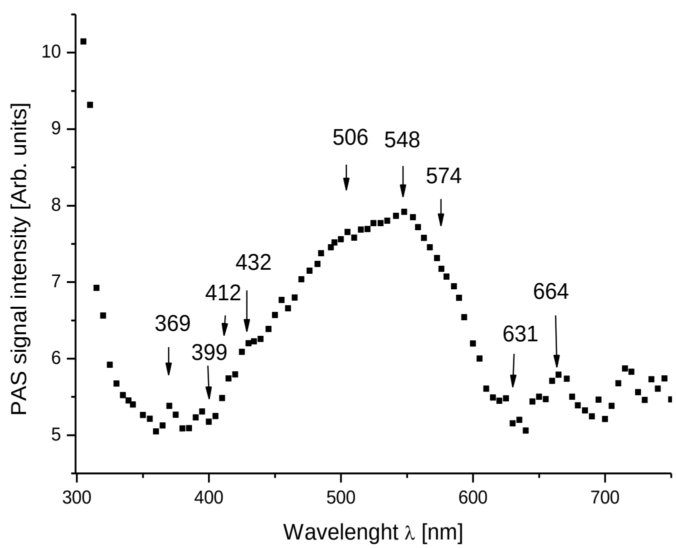

Fig. 2: PA spectrum of the red fruit of Pyracantha Coccinea

Conclusions

The measurements of photoacoustic spectroscopy on the red fruit of Pyracantha Coccinea showed the presence of electronic transitions similar as in the cases of Ficus Benjamina, Asterias Rubens, Trunculariopsis Trunculus, Sea Urchin, human skin and blood obtained by UV spectroscopy. Living matter, plants, animals and humans have similar basic ingredients necessary for life. Thus, it could be suggested that solar radiation plays an important role in the regulating mechanisms in the same biological processes connected with the life.

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