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Photoacoustic measurements as a potential tool for assessment of primary production in aquatic ecosystems - the basics

Abstract

The light-energy absorbed by photosynthetic antenna pigments is

(i) chemically stored in form of energy-rich intermediates,
(ii) dissipated as heat and
(iii) re-emitted as fluorescence light.

The photoacoustic (PA) technique bears the potential for direct monitoring of photochemical energy storage and thermal dissipation. Analysis of the PA signals could provide the means for determination of the following parameters:

(1) absorbance of light-energy by photosynthetic organisms and all other substances in the sample;
(2) straightforward determination of the total and relative extent of photosynthetic light-energy usage (even for samples with a highly heterogeneous population of photosynthetic organisms);
(3) for excitation at various wavelengths, energy usage by the individual groups of photosynthetic organisms in the sample volume (green algae, cyanobacteria, ..).

Intrinsic and ambient acoustic noise are presently a significant obstacle to profitable *in-situ* measurements.

Measuring Principle

Absorption of the modulated light by a photosynthetically active sample (see Fig. 1) leads to two distinct contributions to the detectable

photoacoustic (PA) signal: the (i) thermal and the (ii) photobaric signal (BULTS et al. 1982; for reviews see BUSCHMANN 1990, FORK & HERBERT 1993, MALKIN & CANAANI 1994).

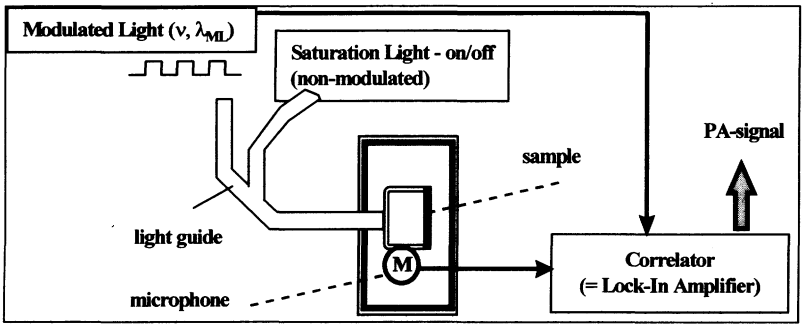

Fig. 1 Typical PA set-up. The modulated light (n = 1 Hz .. 10 kHz) is absorbed by an intact leaf (or macroalga), photosynthetic microorganisms on filter paper or by photosynthetic organisms in solution.

(i) Thermal signal.

The major part of the absorbed light-energy is converted into heat within a few milliseconds. The heat is transferred to a gas layer at the sample surface; the gas layer expands (according to the gas law: $P\ V = n\ R\ T$) and acts like a piston which compresses the air inside the closed measuring cell. This compression results in a pressure increase. Because the heat production is modulated with ν (frequency of the modulated light), the pressure changes with the same frequency. Consequently, these pressure changes are acoustically detectable by a microphone. The amplitude of this thermal photoacoustic signal, A_{th}, is proportional to the light-energy absorbed by the sample, but decreased due to reemission of fluorescence light and photochemical energy storage. Thus,

$$A_{th}(\nu) = \{1 - \psi_F - \psi_P(\nu)\}\ A_{th}^{max}(\nu) \qquad \text{(Eq. 1)}$$

where ψ_F and $\psi_P(\nu)$ are the fluorescence yield and the photochemical yield, respectively, in percent of the absorbed light energy (energy yields, but not quantum yields). The fluorescence yield, ψ_F, is relatively small in photosynthetic systems and therefore often neglected (but see also DAU

& HANSEN 1990). The photochemical yield, $\psi_P(\nu)$, is sometimes denoted as 'photochemical loss' or 'L'.

In photochemically inactive samples (e.g. inhibitor-treated samples) the thermal photoacoustic signal can be used as a measure of the absorption of the sample. Absorption measurements by PA-techniques can be advantageous in the case of highly scattering or non-transparent or optically inhomogenous samples.

Neglecting the contribution of fluorescence, the quantity A_{th}^{max} can be determined by application of non-modulated, saturating light. Because this 'background light' (BL) saturates the photochemical reactions, the yield of photochemistry approaches zero and the photoacoustic signal is approximately equal to A_{th}^{max}. Thus,

$$\psi_P(\nu) = L(\nu) \approx \{A_{th}^{max}(\nu) - A_{th}(\nu)\} \; / \; A_{th}^{max}(\nu) . \qquad \text{(Eq. 2)}$$

The A_{th}^{max} depends on the frequency of the modulated light because the involved heat-transfer processes are frequency dependent. Furthermore, the energy is dissipated in form of heat in different times after light absorption because the heat release is coupled to different steps in the chain of electron transfer reactions. Thus, also ψ_P is frequency dependent.

Analysis of the thermal PA signal could provide the means for determination of the following parameters:

(1) absorbance of light-energy by photosynthetic organisms and all other substances in the test-volume $A_{th}^{max}(\nu)$;
(2) straightforward determination of the total ($\psi_P A_{th}^{max}$) and relative (ψ_P) extent of photosynthetic light-energy usage even for samples with a highly heterogeneous population of photosynthetic organisms;
(3) for excitation at various wavelengths (various λ_{ML}), energy usage by the individual groups of photosynthetic organisms in the sample volume (green algae, cyanobacteria, ..). However, intrinsic and ambient acoustic noise are presently a significant obstacle to profitable *in-situ* measurements. Reasonable signal-to-noise ratios are only obtainable for extremely concentrated suspensions or by filtration and measurement on the filter containing the adsorbed photosynthetic organisms.

(ii) Superimposed photobaric contribution

The modulated light causes a modulation of the photosynthetic oxygen evolution resulting in pressure changes in the sample cell. Due to damping of the oxygen diffussion waves by the aequous medium, at modulation frequencies above 300 Hz the photobaric contribution to the PA signal is fully negligible. The oxgyen evolution contribution has been utilized for kinetic investigations on short-term light adaptation (e.g., DAU & HANSEN 1989).

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