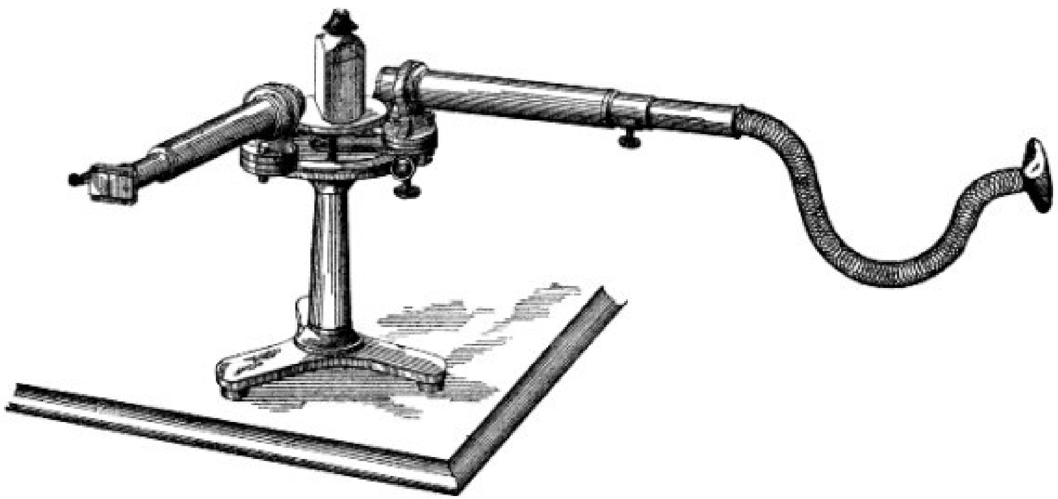
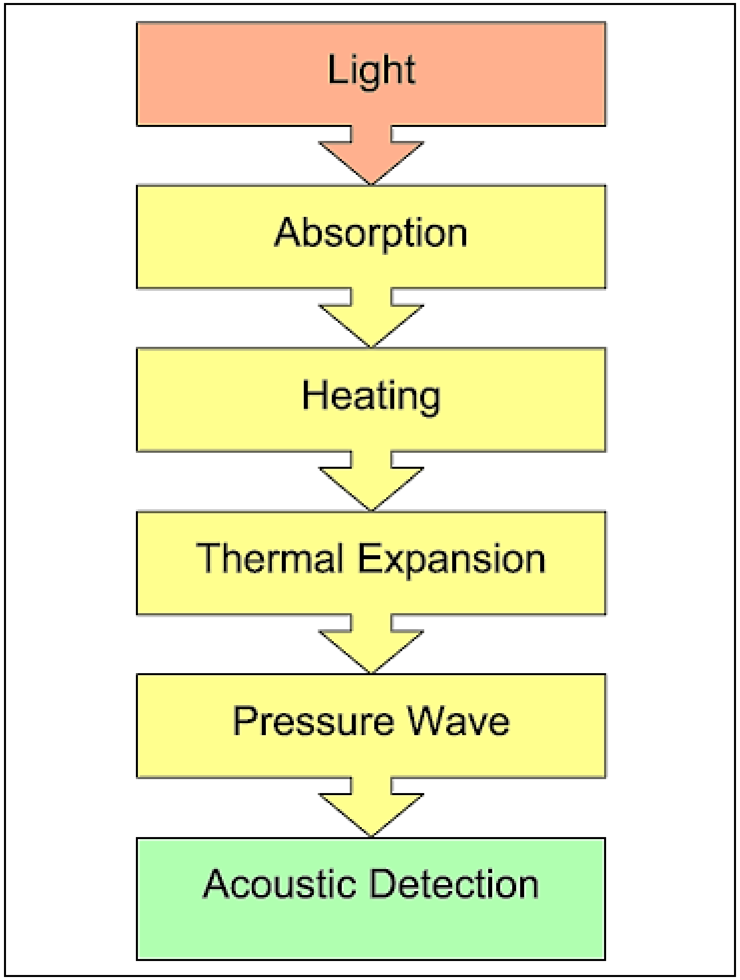
PHOTOACOUSTIC

Vítězslav Otruba

The spectrophone

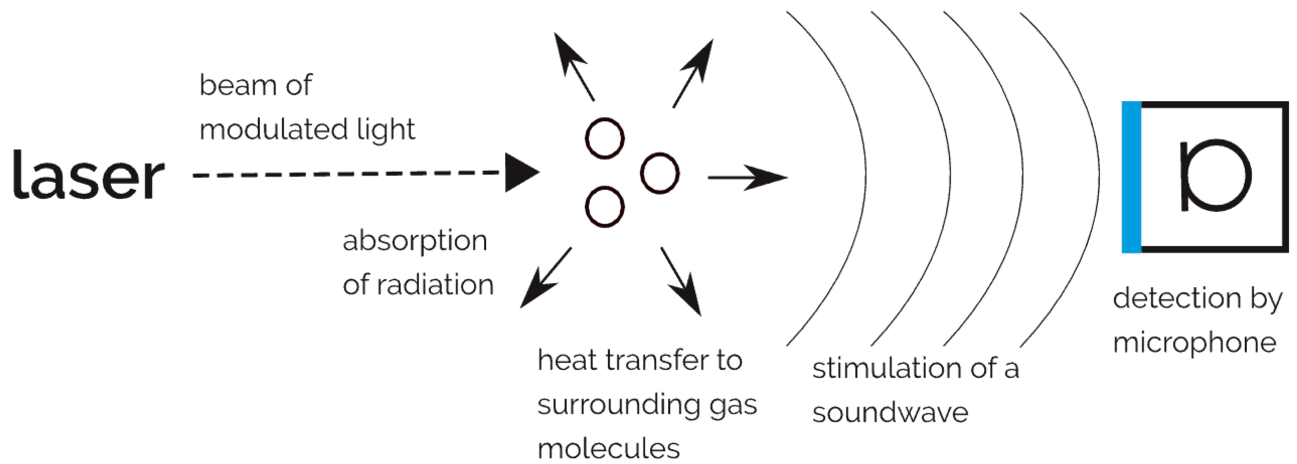




In 1881 A.G. Bell proposed a *spectrophone* "for the purpose of examination of the absorption spectra of bodies in those portio of the spectrum that are invisible".

Photoacoustic effect

- The **photoacoustic effect** is referred to as the occurrence of acoustic effects in the sample under investigation as a result of its localized periodic heating induced by **incident amplitude modulated light radiation**.
- The modulation frequency can take values over a very wide range of 10 to 10^8 Hz, depending on the type of substance to be studied and the type of acoustic detector. Modern microphones in combination with quality electronics can detect acoustic effects corresponding to temperature changes of the order of 10^{-6} to 10^{-7} ° C.
- The phenomenon occurs in **gaseous, liquid and solid** substances and according to the way in which heat is distributed from the source, two functional modes are distinguished - thermoacoustic and thermoelastic.



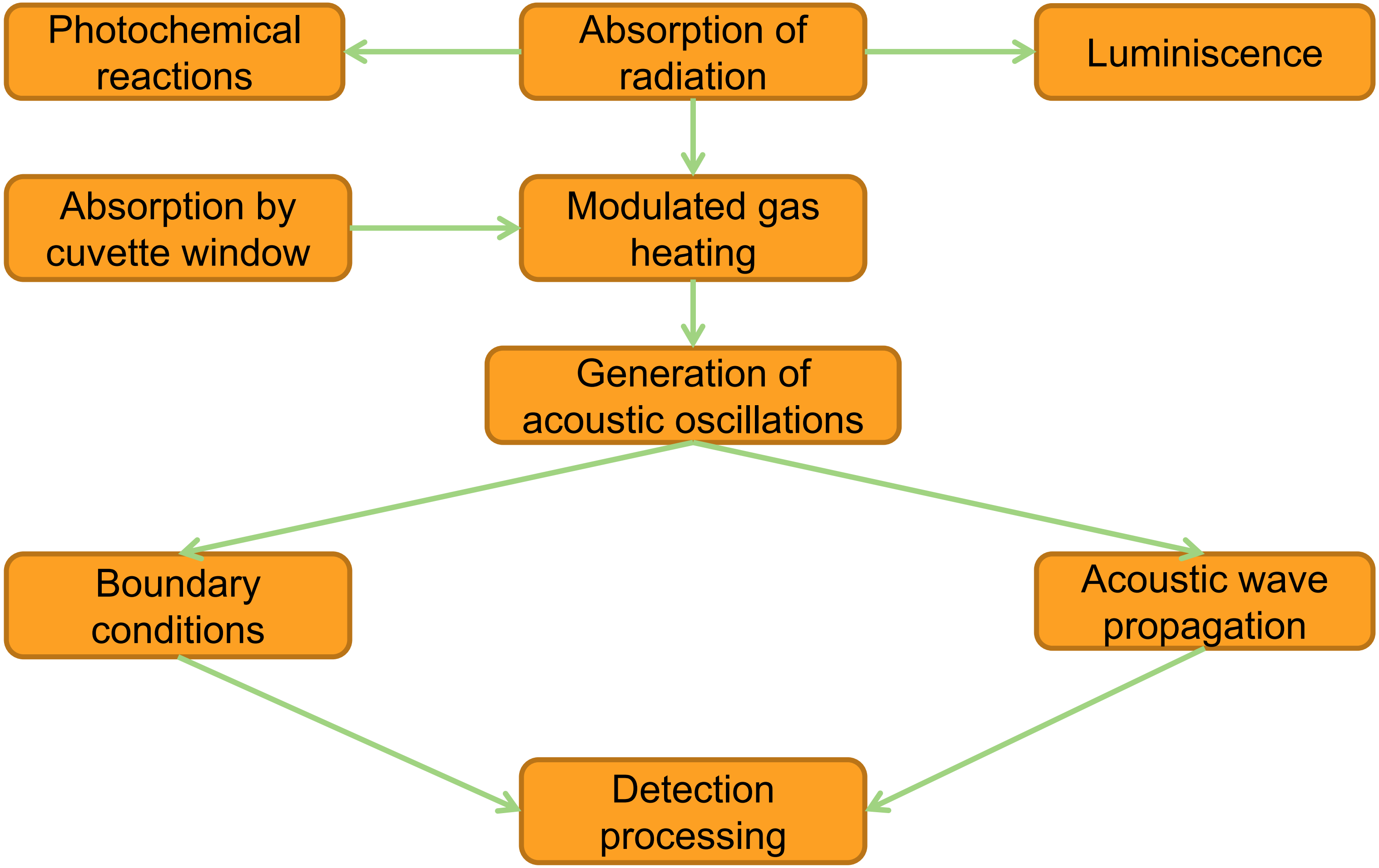
(Photoacoustic Spectroscopy - PAS)

- The level of acoustic effects depends on the amount of radiation absorbed - by measuring the photoacoustic effect at different wavelengths of light to determine the absorption spectrum of the test substance. PAS has some advantages over conventional optical spectroscopy:
- transmitted, reflected or elastically scattered light is not detected and does not interfere with the measurement itself
- allows to measure highly optically permeable materials (gases) containing a small amount of absorbing component (10^{-15} methane in nitrogen)
- Optical absorption can be measured even with high scattering materials (powders, amorphous substances, gels, colloidal suspensions etc.) or even with optically impermeable substances
- analysis of subsurface layers without sample destruction
- offers the possibility of measuring over a wide range of frequencies with the same detector

Instrumentation requirements

- Source of intense radiation
  - Laser is optimal
  - Classic power supplies are also possible (eg. Xe lamp)
- Sensitive detection
  - Microphones
  - Hydrophones
  - Piezo detectors
  - Strain gauges
  - Fiber detectors
    - Strain gauge
    - Piezoelectric
- Analysis of output signal of detectors
  - FT
  - Transition signal analysis
  - Correlation functions

Process flow diagram in OA (gas phase)



Application 1

Measurement of low absorbance

- $A_{min} \approx 10^{-10}\ cm^{-1}$ (pro l = 10 cm), typically cca $10^{-3}\ cm^{-1}$ (pro l = 1 cm)
  - Low concentrations
  - Transitions with low probability
  - Vibration and rotational spectra of high n

Trace content detection

- In gas up to $\approx 10^{-13}$
- Small size with semiconductor lasers
  - Detectors in gas chromatography
  - Field inspection devices
  - Sensors for process control
- Examples:
  - NH_3, $SO_2 \approx 10^{-10}$
  - $NO_2 \approx 10^{-11}$
  - $CH_4 \approx 10^{-12}$
  - $CO \approx 10^{-8}$

Application 2

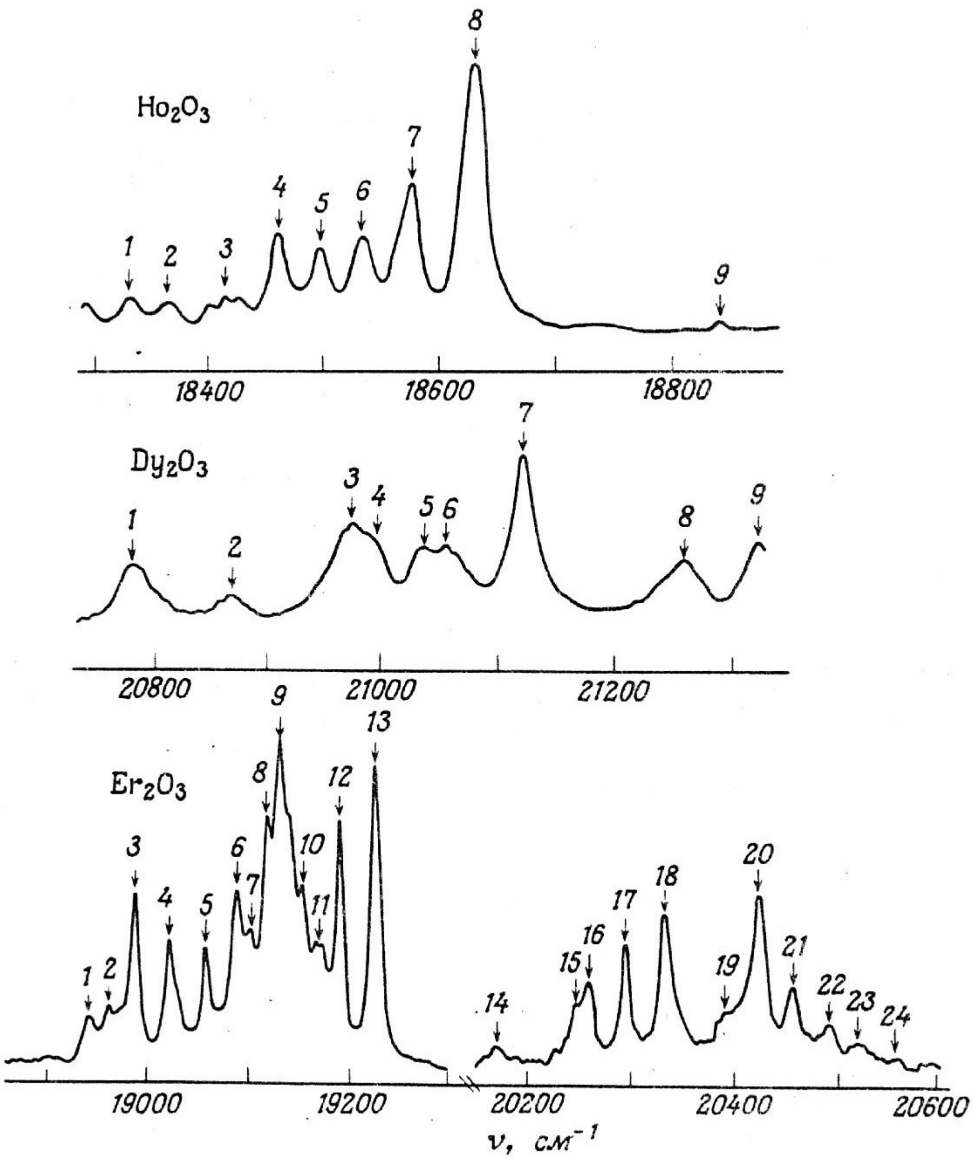
- Absorption from excited states
- Chemical reactions in the gas phase
  - Intermediate concentration measurement
  - Spectra IR, UV, Raman of intermediates
  - Reaction schemes, e.g.:

$$CH_3I \rightarrow CH_3^* + I$$

$$^2P_{1/2} \leftrightarrow {}^2P_{3/2} \ ?$$

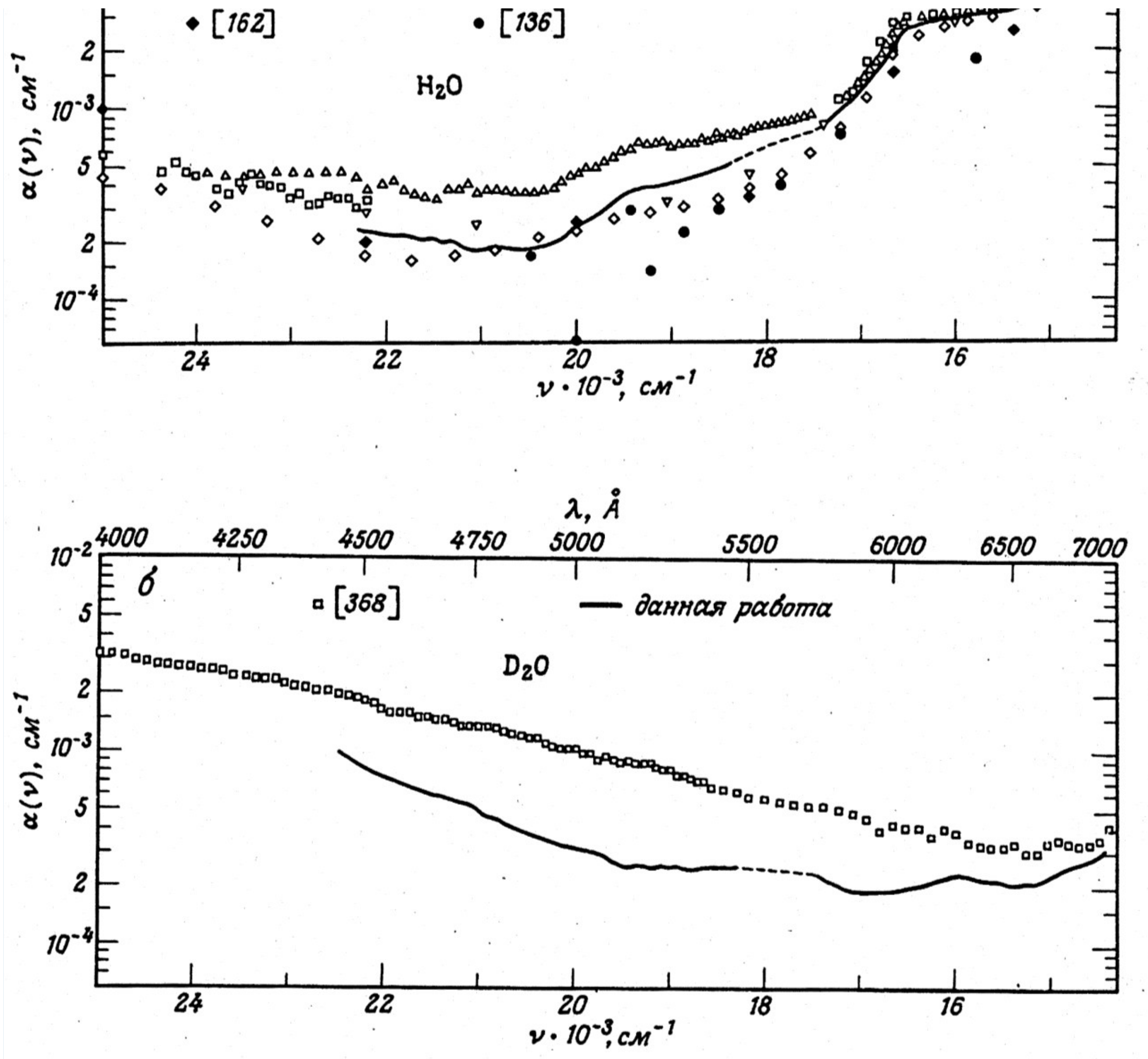
  - Doppler-free spectrometry
  - Spectrometry of condensed phases

Rare Earth Powder Oxide Spectrum

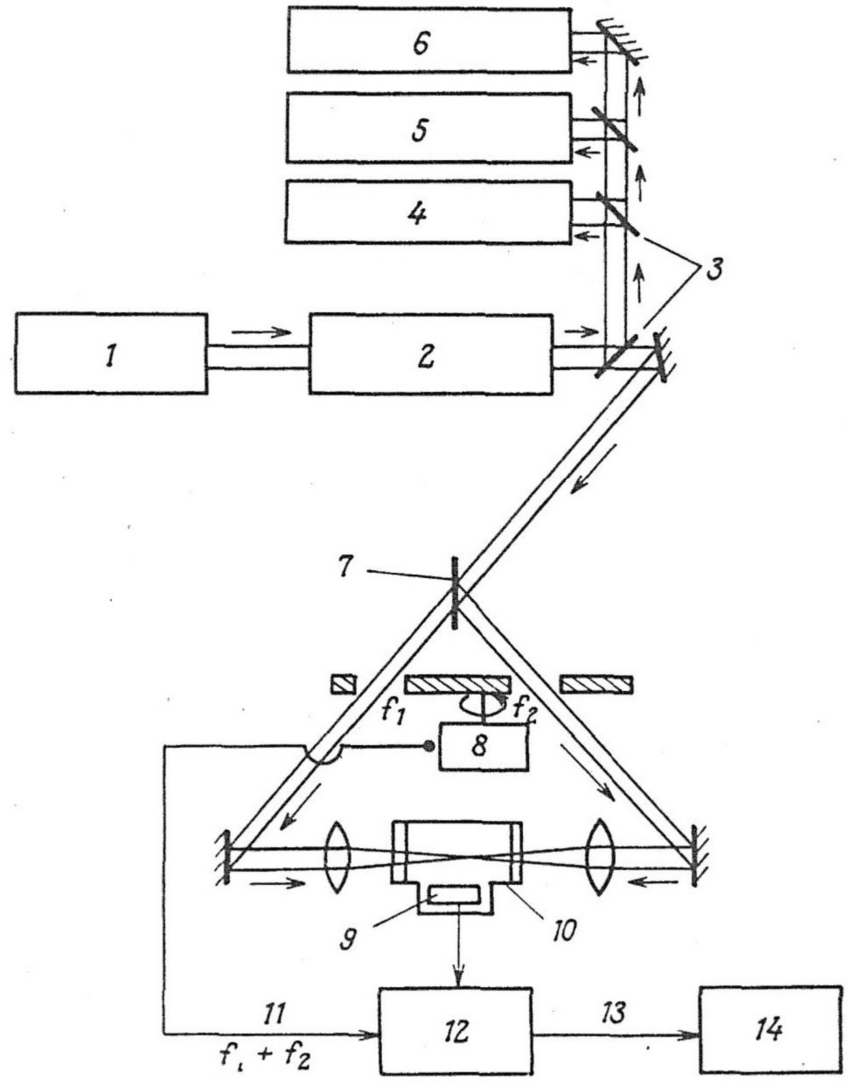


Absorption spectra of water

Absorption optoacoustic spectra of water and heavy water measured by dye lasers (solid line) in comparison with works of other authors.



Doppler-free photoacoustic spectrometry



Description :
1 – Ar^+ laser
2 – single-mode dye laser
3 – beam splitter
4 – spectrum analyzer
5 – reference absorption cell
6 – spectrometer
7 – 50% beam splitter
8 – electric motor
9 – microphone
10 – acoustic cuvette
11 – base frequency f_1 (751 Hz) + f_2 (454 Hz)
12 – lock-in amplifier
13 – output
14 – data evaluation

The frequency equal to the sum f1 + f2 will be generated only if both opposite beams saturate the same particles, ie particles at zero velocity with respect to the beams.

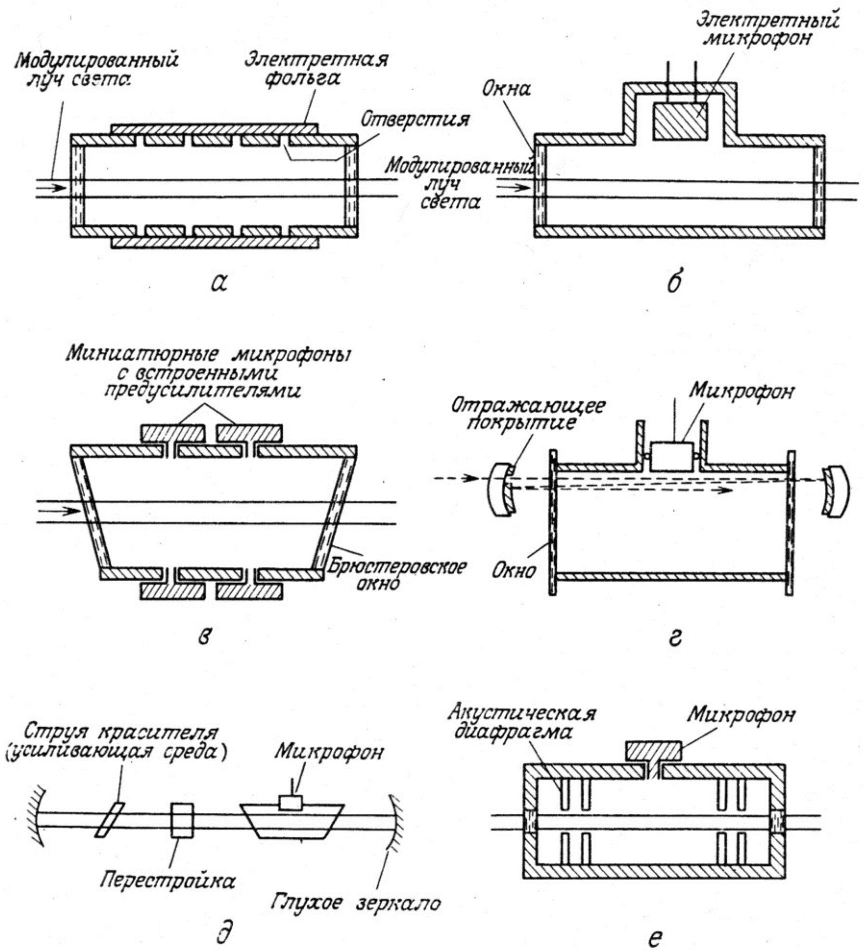


Рис. 1.4. Схематическое изображение нескольких типов описанных в литературе ОА ячеек для измерений ОА сигналов в газовых средах: *а* — простая ячейка с фольгой [192]; *б* — простая ячейка с микрофоном [206]; *в* — усовершенствованная ячейка [283]; *г* — многопроходная резонансная ячейка [186]; *д* — внутрирезонаторная ячейка [27]; *е* — ячейка, в которой минимизировано влияние поглощения окнами [89].

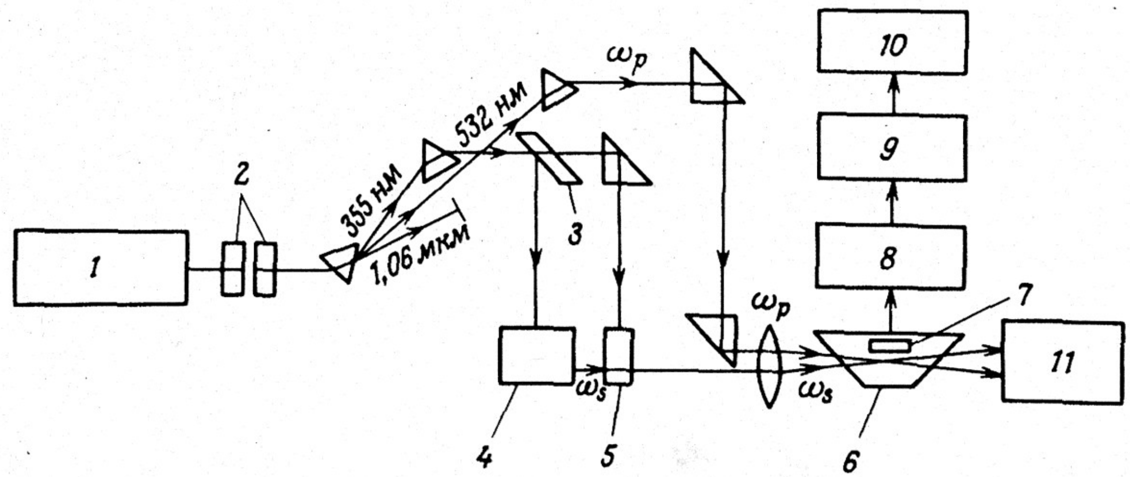


Рис. 1.8. Схема эксперимента по импульсной фотоакустической спектроскопии усиления комбинационного рассеяния (ФАСУКР) [412]: *1* — Nd — YAG-лазер; *2* — нелинейные дейтерированные кристаллы KD*P; *3* — разделитель пучка; *4* — генератор на красителе; *5* — усилитель на красителе; *6* — фотоакустическая ячейка; *7* — микрофон; *8* — усилитель; *9* — строб-интегратор; *10* — самописец; *11* — измеритель мощности.

Resonant optoacoustic cuvettes

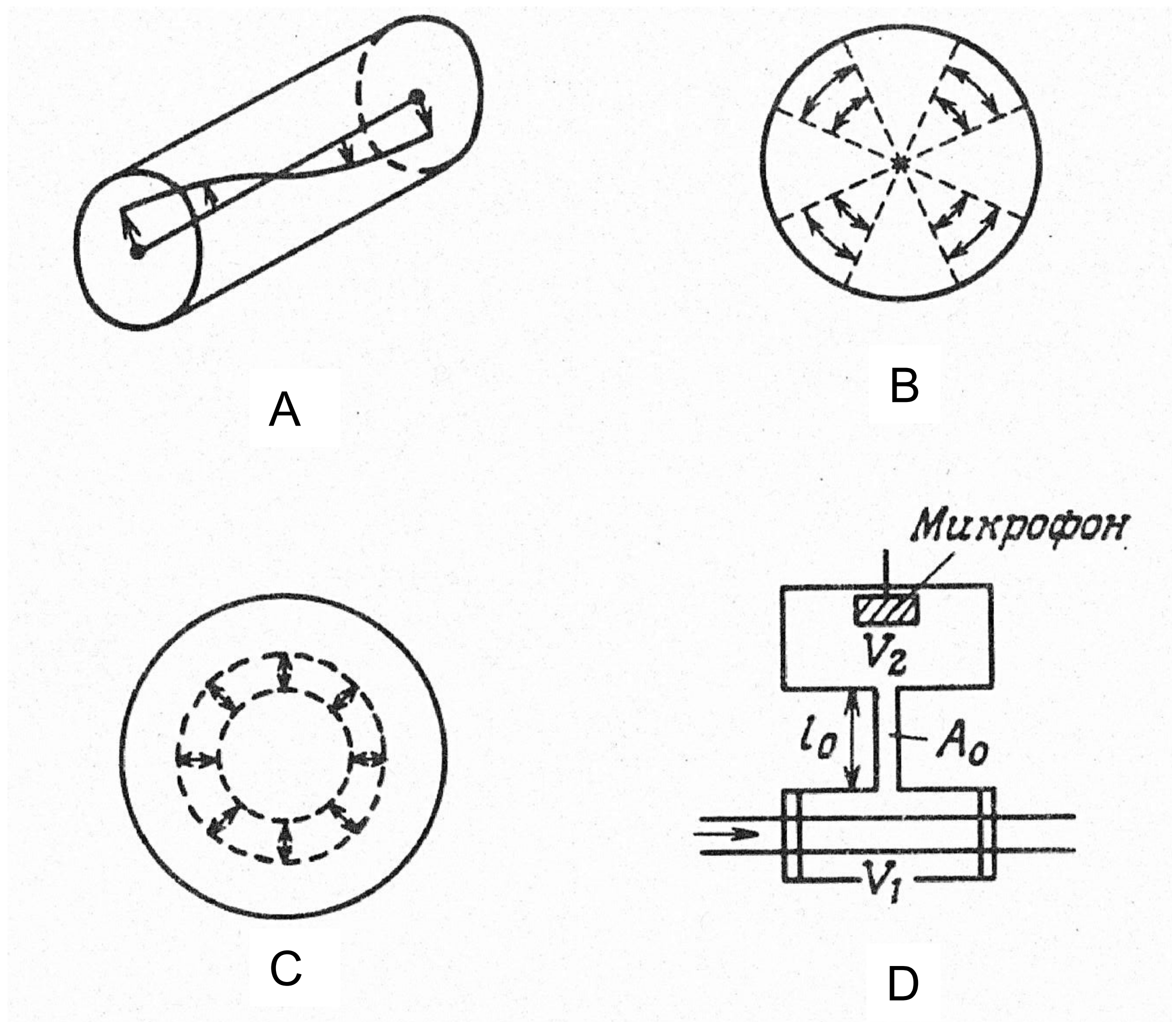
A – longitudinal resonance

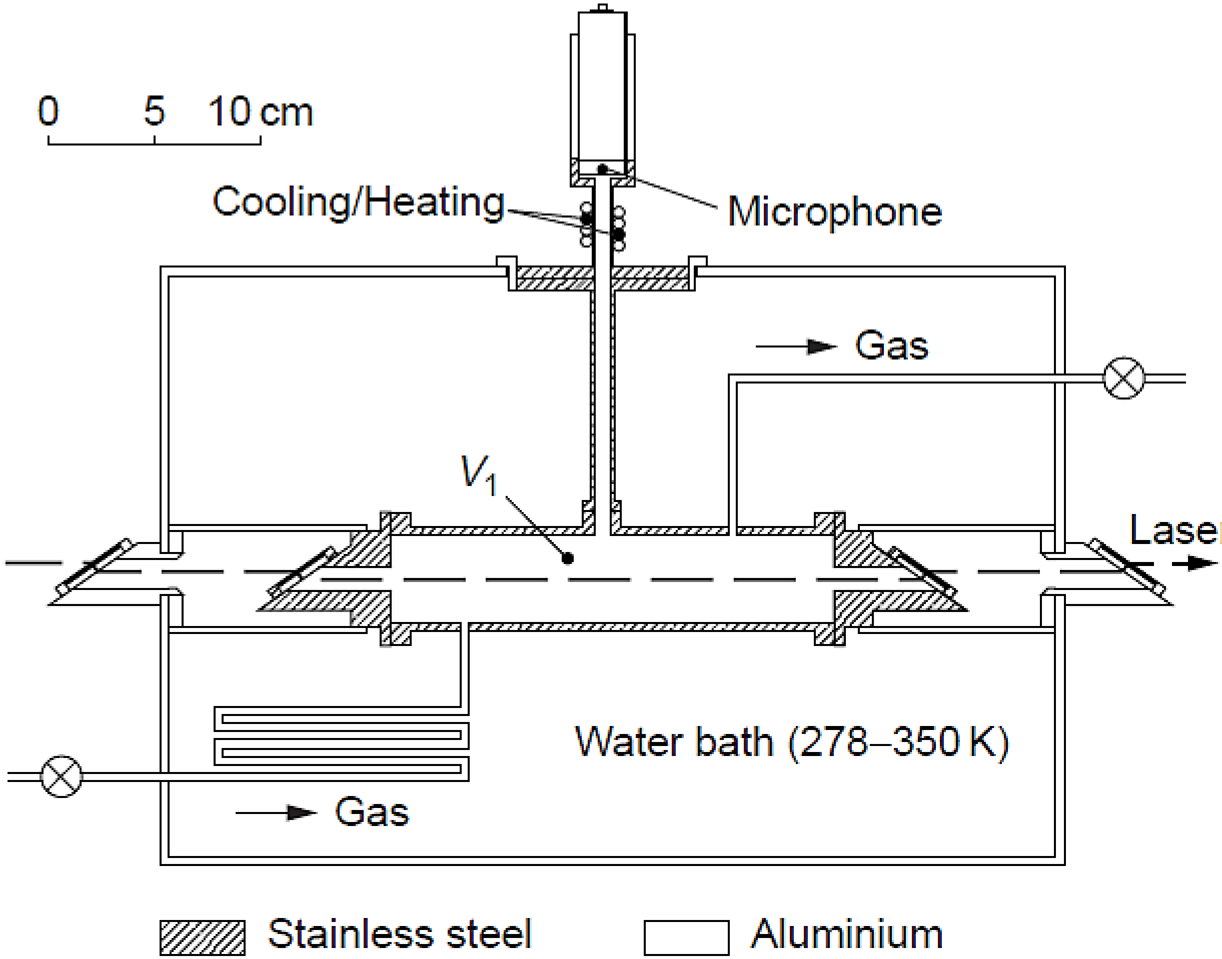
B – azimuthal resonance

C – radial resonance

D – Helmoltz resonator

(A_0 perpendicular cross-sectional area of the tube, l_0 – tube length)





Photoacoustic cell applied for temperature-dependent investigations on fatty acids. The temperature of the water bath was varied between 278 and 350K with a cold finger and two immersion heaters, while the temperature of the microphone was kept constant with a cooling/heating device.

Resonant photoacoustic

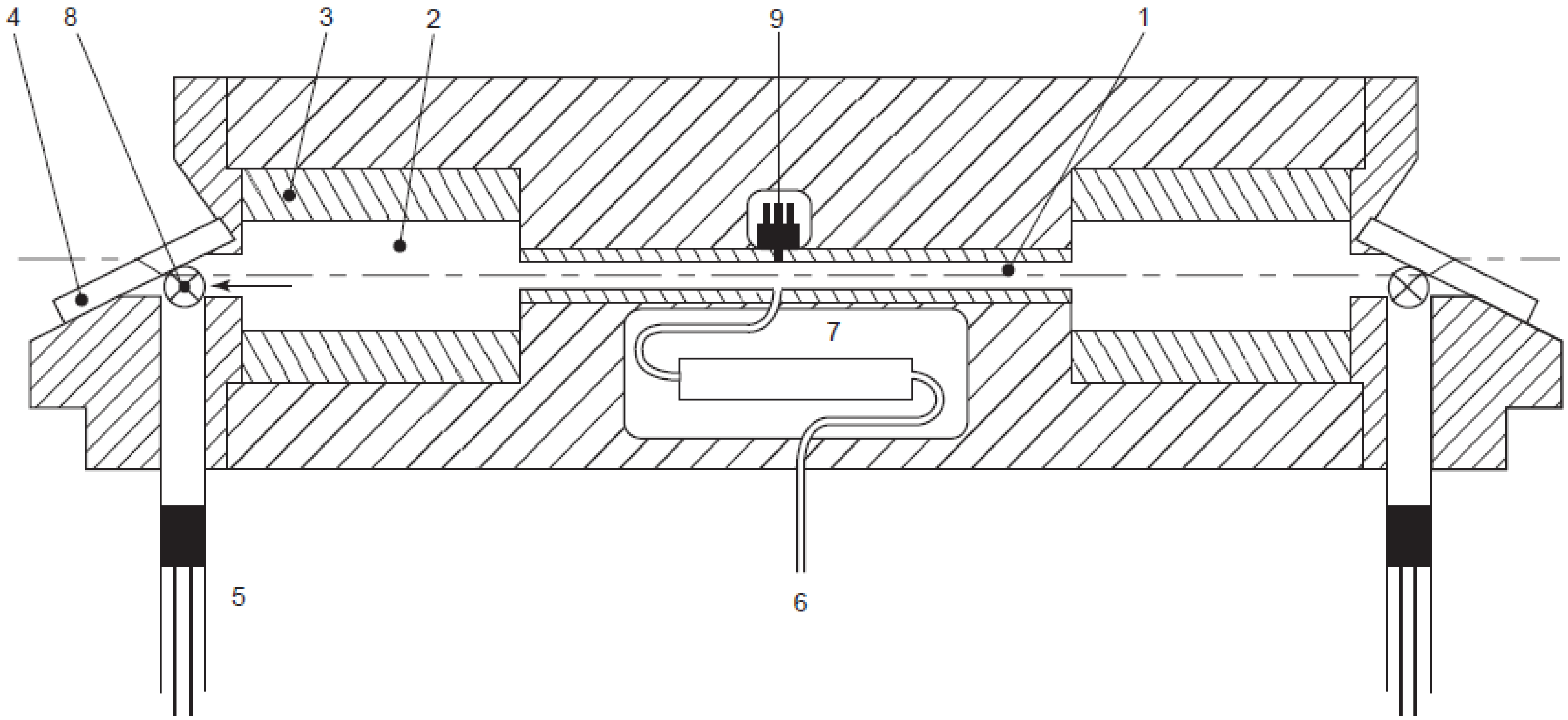
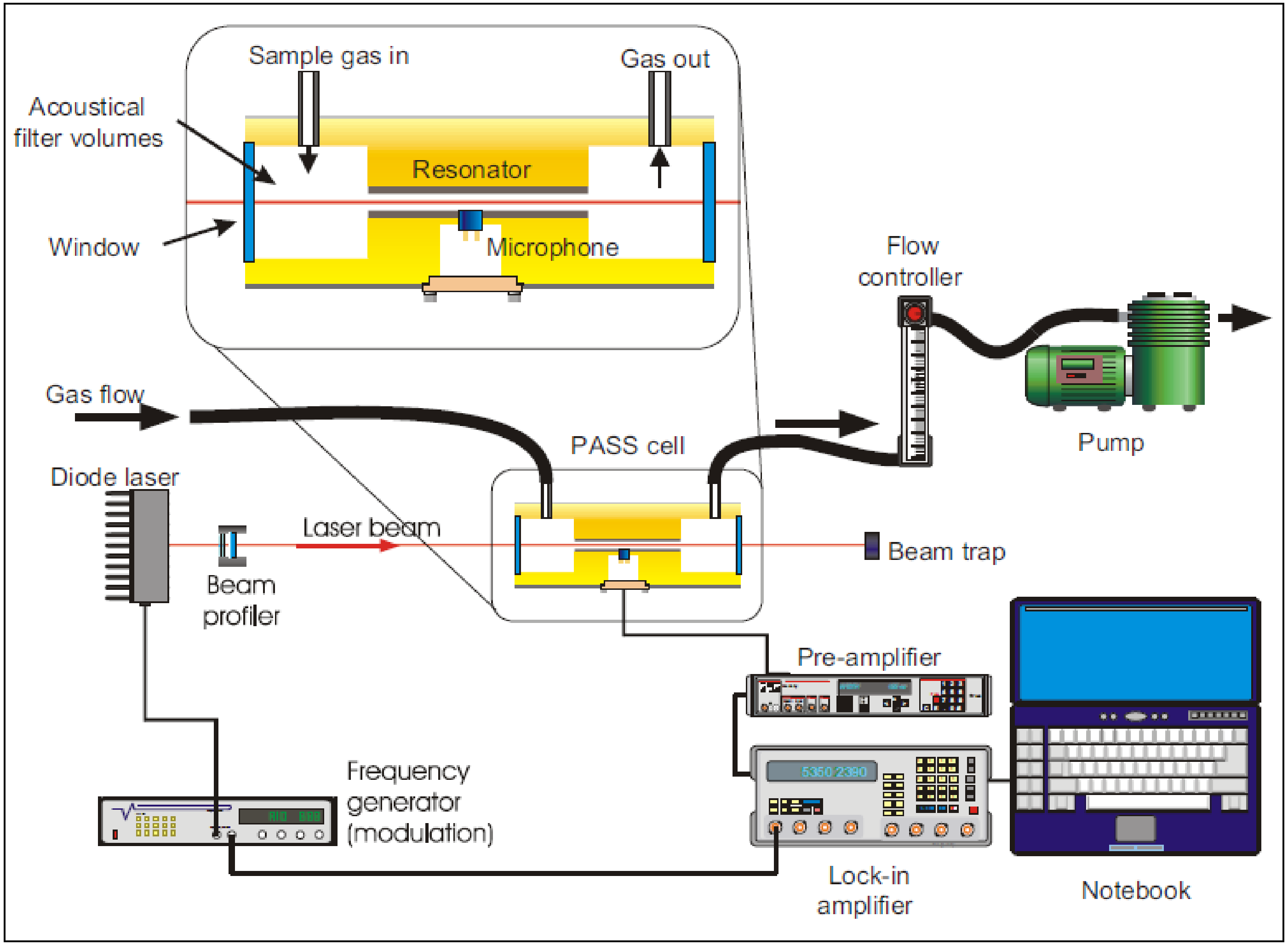


Figure 4 Resonant photoacoustic cell. 1, resonator; 2, buffer volume (maximum diameter 40 mm, length 50 mm); 3, buffer ring to decrease buffer radius; 4, ZnSe Brewster window; 5, adjustable λ/4 notch filter to suppress window signal; 6, inlet gas flow; 7, λ/2 notch filter to suppress flow noise; 8, outlet gas flow; 9, Knowless microphone.

Photoacoustic soot sensor



Spectroscopy Europe 14/5 (2002)

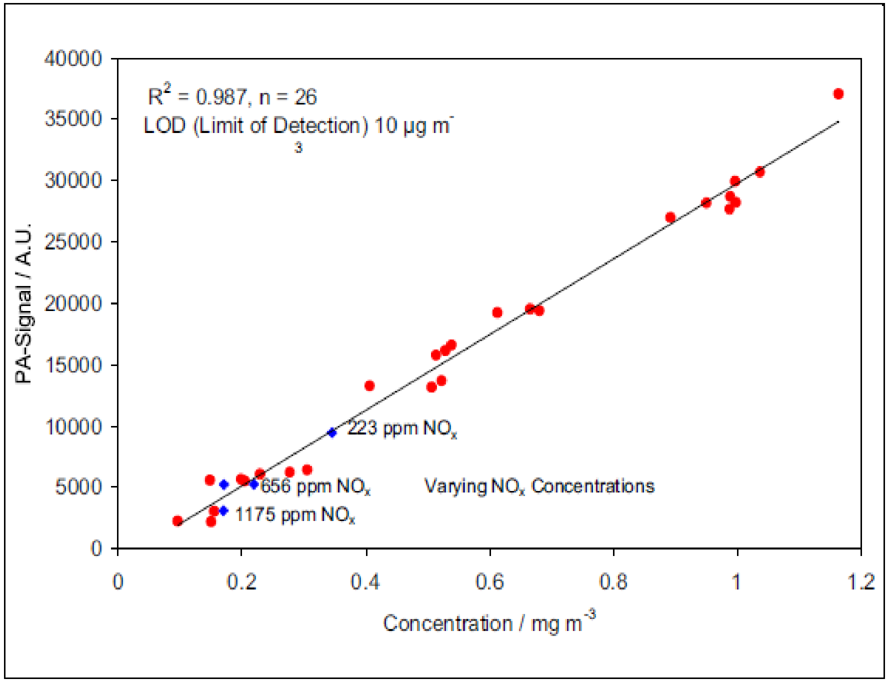


Figure 5. Calibration curve of the PASS system vs thermochemical analysis.

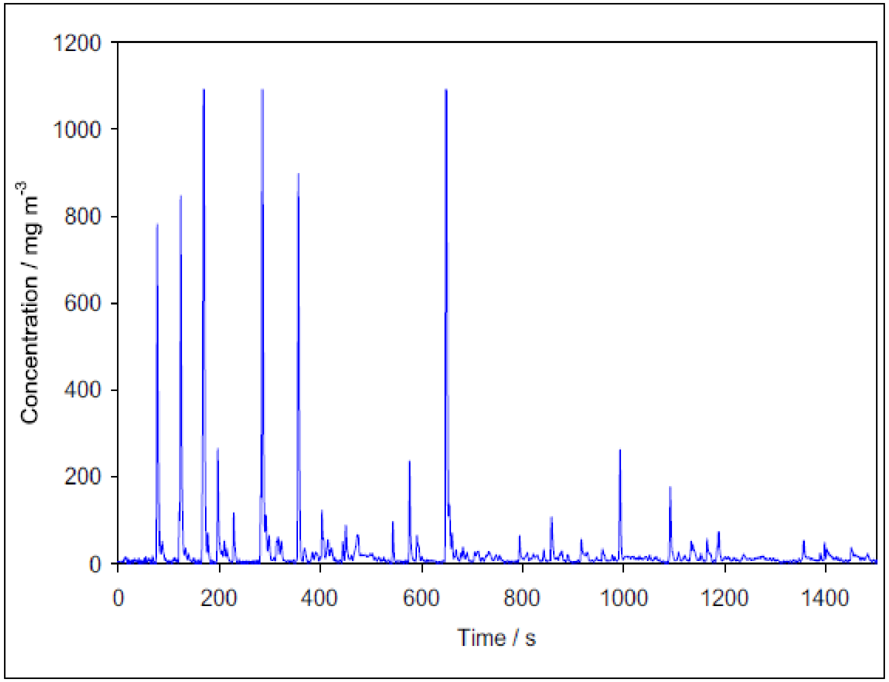


Figure 6. PASS signal of a driving cycle for diesel engine testing.

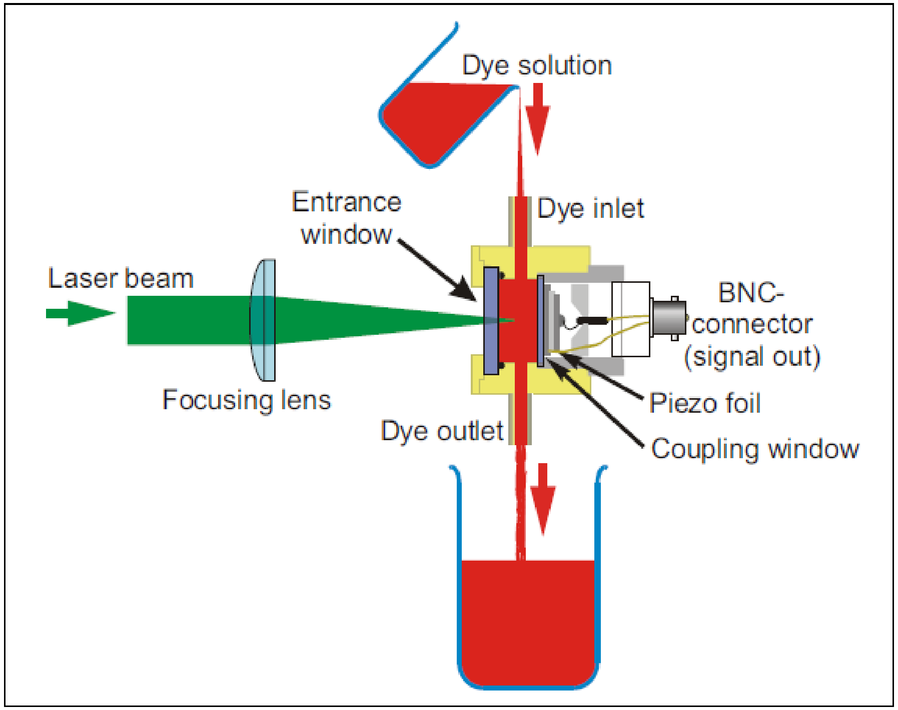


Figure 7. Design of the flow cuvette for the PA analysis of concentrated dyestuff.

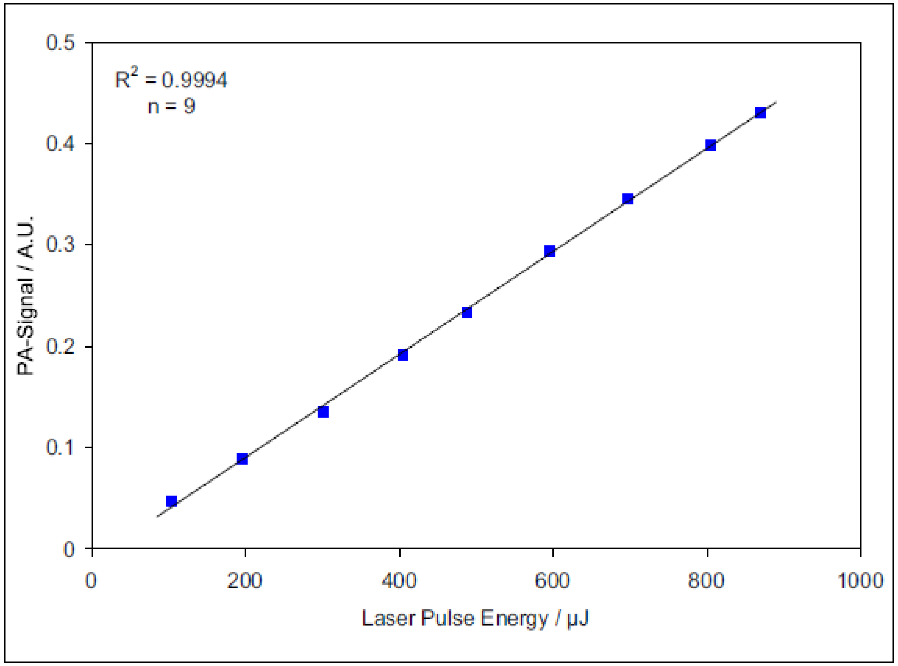


Figure 8. Dependence of the PA signal on the laser pulse energy.

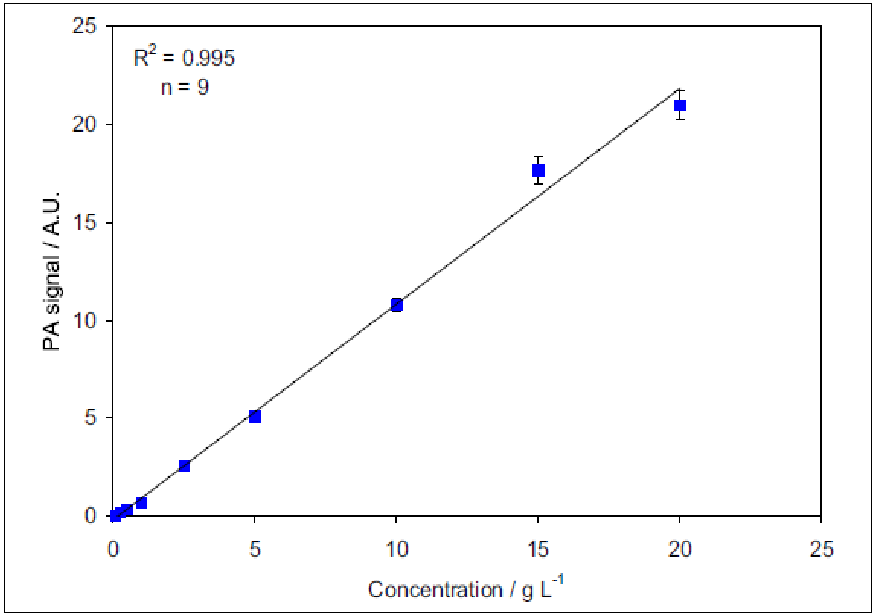


Figure 9. Calibration of the PA sensor system for textile dyestuff.

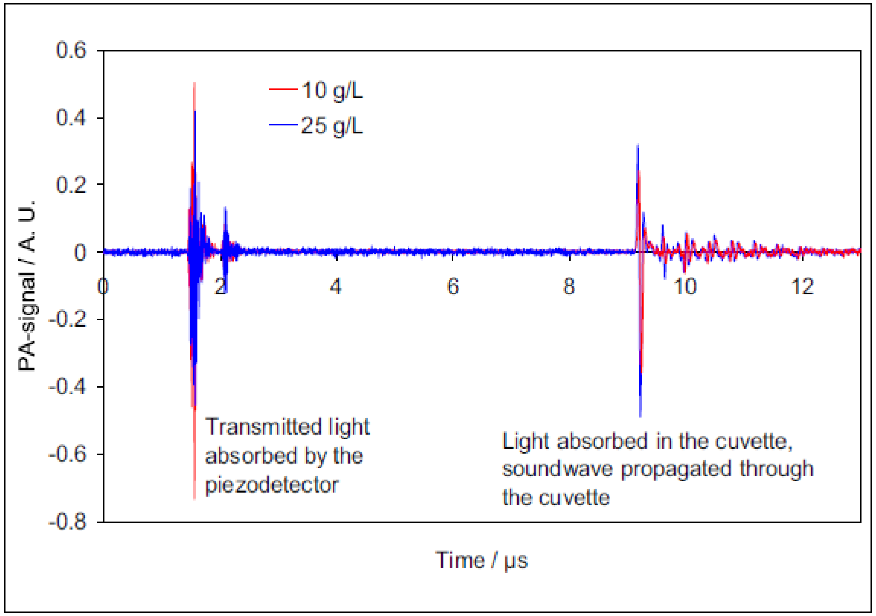


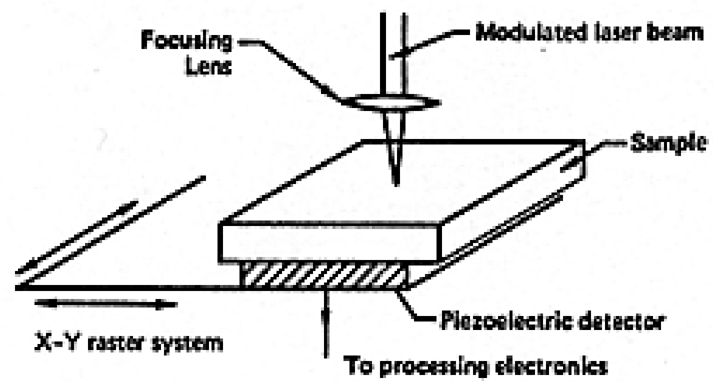
Figure 10. PA signal of two different concentrations of textile dyestuff in water.

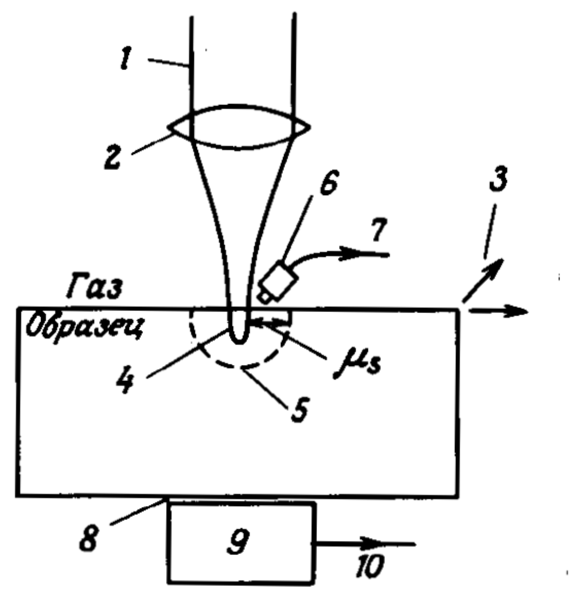
Photoacoustic Microscopy - PAM

- Because light radiation is very easy to focus on an area of the order of 10^{-6} m, it is possible to perform a photoacoustic phenomenon in microscale and to obtain information about the two-dimensional distribution of the photoacoustic signal by sample scanning.
- By computer processing of this information, an image can also be created on the screen where different blackening areas correspond to different intensity of the photoacoustic signal. However, it is a complex function not only of light absorption in the sample but also of its local structure, its elastic and thermal properties, and also the morphology and perfection of the sample surface.
- It always depends on factors influencing not only absorption but also light scattering.

Principles of PAM

- The amplitude-modulated laser light radiation is focused on a spot of about 1μm in diameter on the surface of the sample and the sample is scanned in two dimensions. The resulting photoacoustic signal is detected by a transducer in direct contact with the sample (9) or microphone (6). The electrical signal is further processed and used to create an image on the monitor screen.
- As a transducer, piezoelectric grinding is usually used, which can work with high modulation frequencies, allows faster scanning and has less sensitivity to ambient noise.
- Electret miniature microphones with high sensitivity and frequency range up to MHz are used as microphone.





PAM applications

The method provides visual information in a microscale similar to conventional optical microscopy and further allows e.g.:

- to determine the local optical absorption spectrum or its differences in different places of the surface
- obtain information about local thermal and elastic properties (detection of layered structures on and under the surface)
- detect photovoltaic processes in semiconductor devices (the presence of short circuits or losses can be detected in a timely and non-destructive manner)
- investigate photochemical processes
- measure thin film thickness (by analyzing amplitude and phase of photoacoustic signal)
- determine the depth profile of the examined material (by changing the wavelength of the incident light or by changing the modulation frequency, the depth of the optical penetration and the depth at which the photoacoustic signal is produced can be changed)
- detect the presence of fluorescent dopants (since fluorescence reduces the PAM signal) and possibly their absorption band if it is possible to change the wavelength of the modulated excitation light.