Atomic and Molecular Spectroscopy

Molecular Applied Laser Spectroscopy
GASMAS – LIDAR

Reading instructions:

Section 10.2: Laser Remote Sensing and Applications (page 406 – 425)

Section 10.5.4: Scattering Spectroscopy and Tissue Transillumination (page 454 – 460)

**Individual task:** Imagine you are a developmental engineer in a company specializing in instrumentation for environmental monitoring. The company so far is pursuing development and manufacturing of equipment for chemical analysis of water pollutants, but now would like to extend its activities to measurements of atmospheric gases. You were sent out to visit the Atomic Physics Division at LTH, where you were given a 5 hour demonstration. Now you are expected to write a 3 page report (in Swedish or in English) to your boss Sune Svanberg, the Head of R & D of your company, explaining what you saw, and containing your recommendation for action!
The GASMAS (GAs in Scattering Media Absorption Spectroscopy) method is a new technique to study free gas dispersed in scattering media [1]. Solids and liquids normally have broad absorption features with peaks seldom sharper than 10 nm. Therefore, spectroscopic equipment with modest resolution is normally employed. However, frequently there exist 10,000 times sharper signals due to free gas enclosures. The signature of this gas can be detected and characterized using diode laser spectroscopy. Gas enclosures constitute inhomogeneities, leading to light scattering. This is a complication from the point of view that there exists no well-defined Beer-Lambertian law as when a cuvette of clear solution is studied in analytical chemistry. However, the diffuse light scattering has recently been extensively studied in the field of tissue optics, where it plays a central role in dosimetry for photodynamic therapy and for optical mammography. The GASMAS technique opens up new possibilities for characterization and diagnostics of scattering solids and turbid liquids. The GASMAS project emerged from the interaction of diode-laser gas spectroscopy [2,3] with optical mammography [4,5] and differential absorption lidar [6,7], which all contain elements of the new technique.

Many substances of organic origin, and also many construction materials, are porous and contain free gas distributed throughout the material. For instance, wood, plants, fruits, food, powders, sintered materials, and foams can be considered. A starting point in our studies was to study ordinary molecular oxygen which can be expected to be present in most materials. Oxygen exhibits its characteristic A band around 760 nm, a region which is easily covered by diode lasers. Liquid water does not absorb in this region, which is an important aspect when considering organic materials. Small absorptive features due to oxygen are detected in the diffusely emerging diode laser light using wavelength modulation spectroscopy, as indicated in Figure 1, where two different observation geometries are indicated. In early studies the oxygen content in materials as diverse as polystyrene foam, wood, fruits and flour was readily observed [1].

In order to quantify the gas concentration, the absorption and scattering processes can be disentangled using time-resolved laser spectroscopy, very similar as used in optical mammography [4,6]. A set-up as given in Figure 2 provides a histogram of photon arrival times on the other side of the sample. In this way the relative weight of short and long pathlengths with their corresponding gas absorptive imprints can be elucidated [8]. An experimental time-resolved curve for a 2 cm thick sample of polystyrene foam is shown in Fig. 3.

It can be noted that it is possible to measure the internal gas pressure in the pores by observing the pressure-broadened linewidth [1]. In principle, any gas can be monitored, having a suitable absorption line in a spectral region where the bulk material is not massively absorbing. It can be noted, that by simultaneously monitoring two different gases absorbing at close-lying wavelengths, their concentration ratio can be determined without considering the complication of scattering. This can be an important aspect, e.g. in plant physiology or medicine.

Gas diffusion is of considerable importance, e.g. in plant physiology and when considering construction materials such as wood. We have demonstrated a very simple method using
Fig. 1. Set-up for molecular oxygen gas detection

Fig. 2. Set-up for time-resolved monitoring of light

Fig. 3 Time-resolved curve from a scattering medium

Fig. 4. Oxygen reinvasion in different kinds of woods

GASMAS to study gas diffusion in porous media [1,9]. A piece of the material is exposed to atmospheric pure nitrogen gas during several hours, e.g. by placing it in a plastic bag flushed with nitrogen from a pressurized tank. The piece is then extracted and placed in the spectrometer shown in Figure 1. The rate at which the atmospheric oxygen reinvades the material can then easily be followed logging the GASMAS signal. Examples of diffusion curves taken for different kinds of wood are shown in Fig. 4 [9]. In particular, the influence of a surface layer, such as a paint, can readily be studied. The food sector is also of particular interest, since much of the packaging efforts are aimed at reducing oxygen exposure and avoiding dehydration [9,10]. The greatest challenge to GASMAS is to explore its potential for new medical diagnostics. The similarity between environmental and medical gas monitoring is illustrated in Fig. 5. Diagnosis of human sinusitis by sending laser light through the forehead and observing backscattered light from the brain using a sensitive photomultiplier has just been demonstrated as illustrated in Fig. 6,
where simultaneous monitoring of oxygen gas and water vapour was achieved [11-14]. Gas monitoring in food packages is also feasible [15]. A diversified program of GASMAS application is now being pursued in Lund.

Fig. 5. Similarity between environmental and medical gas monitoring

Maxillary sinus

**Oxygen (760 nm) normalization on Water vapor (935 nm)**

![Diagram of maxillary sinus with oxygen and water vapor measurements](image)

**Density of H\textsubscript{2}O determined by temperature**

**Thermostate at 37°C**

Fig. 6. Monitoring of oxygen gas and water vapour for the cheek sinus cavities allowing the determination of the concentration of oxygen inside the sinus. The concentration of water vapour is determined by the temperature only. Referencing to water vapour allows the unknown pathlength thorough the sinus to be eliminated.
Fig. 7. Illustration of oxygen monitoring in a milk package. The signal does not change when the container is perforated showing that the oxygen concentration in the intact package was ambient (21 percent).

