New innovative methods for non-intrusive optical diagnostics of high-voltage insulator materials

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Abstract

The purpose of this PhD thesis work has been to develop optical techniques that can help utility engineers for assessing the state of insulators in service and in a laboratory. The possibilities to use remote laser-induced fluorescence for detection and imaging of biological growth such as algae and fungi have been investigated. Reflectance spectroscopy has also been investigated as a technique for discrimination between clean and polluted surfaces. Remote laser-induced breakdown spectroscopy has been tested for the detection and removal of salt on metal and insulator surfaces. Optical second harmonic generation has been studied for the purpose of measuring surface charge, and electric field calculations have been performed by using the finite element method.

It has been shown that remote laser-induced fluorescence can be used to detect and measure the distribution of algal contamination on polymeric insulators. Remote fluorescence imaging of fungal growth on polymeric high-voltage insulators has been performed using an Nd:YAG laser equipped mobile Lidar system using a laser wavelength of 355 nm. Insulator areas contaminated by fungal growth could be discriminated from clean surfaces and imaged. It has been shown that the fluorescence from pure fungal growth is shifted to longer wavelengths compared to the fluorescence from clean material. Detailed spectral studies have been performed in the laboratory using a fibre-optic fluorosensor incorporating an optical multi-channel analyser system (OMA) and a nitrogen laser emitting radiation at 337 nm.

The detection of contamination such as salt in outdoor high-voltage insulator systems and its subsequent removal are vital for a reliable transmission of electric power. Remote detection of salt on a copper metal surface was carried out by using a mobile LIBS Lidar system with a laser wavelength of 355 nm. Detection of salt on a polymeric high-voltage insulator was obtained when a lens was inserted into a collimated laser beam and focused the laser light onto the target. The detection sensitivity was estimated from the number of photons that was detected using a calibrated white light source at the target point. Ablative cleaning could readily be carried out with LIBS and was verified by observing the disappearance of the sodium D-line emission.

The second harmonic generation experiments, where the aim was to detect surface charge on metal and polymeric surfaces, did not show any correlation between the signal and the surface charge. Oxide layers and other surface contaminants contributed strongly to the signal, making the technique difficult to implement.
Sammanfattning

Avhandlingsarbetet syftar till att utveckla tekniker för att på avstånd karakterisera ytbeläggningar av biomaterial (alger, svampar) och salt på isolatorer. Möjligheten att rengöra isolatorytor med fokuserade laserstrålar har studerats. Multi-spektrala analyser för att karakterisera ytbeläggningarna har studerats. Möjligheten att mäta ytlattpning på en metalltyta och en isolatoryta med frekvensdubbling har studerats.


För detektion av salt utnyttjas laserinducerad plasmaspektroskopi och experimenten har utförts med det mobila lasersystemet. En laserpuls fokuseras på ytan och salt (natrium och klor) slås loss. Emission vid natriums resonansövergång detekteras och analyseras. För rengöring av ytor ökas lasereffekten och ytbeläggningen avlägsnas genom ablation. Olika beläggningar kan avlägsnas, exempelvis salt, alger, svamp och bakterier.

Möjligheten att mäta ytlattpning på en metalltyta med frekvensdubbling har undersökt under ”naturliga” förhållanden i laboratoriet. Det elektriska fältet har varit under 3 MV/m som är tröskelvärdet för genomslag i luft. Oxidlager och andra föroreningar påverkade signalen för mycket för att det skulle gå att mäta ytlattpningen. En litteraturstudie visar på potentiella framtida experiment där bidraget från ytlattpningen kanske kan isoleras.

Målet har varit att kunskapen genererad i avhandlingsarbetet skall kunna användas till att konstruera ett kompakt, mobilt och driftsäkert instrument för karakterisering av högspänningsisolatorer i drift.
List of papers

This thesis is based on the following papers:


PART I
Chapter 1

Introduction

1.1 Motivation

Within the programme High Performance Outdoor Electrical Insulation (ELIS) supported by the Swedish Foundation for Strategic Research (SSF) a major goal was to develop polymeric insulators with good flashover resistance. Surface discharges constitute one of the most serious problems of outdoor insulators. Surface charging of the insulator and how this affects the flashover resistance capability constitute one of the major issues for insulator performance. It would therefore be highly relevant to monitor the surface charges that are present on the surface prior to the discharges, and to couple the surface charge density of the material to its macroscopic surface discharge/flashover resistance.

When it is raining microbiological growth such as algae, fungi or lichen can cause the formation of a continuous water layer on an otherwise hydrophobic insulator surface. Such water layers can trigger a process leading to a surface flashover, which will lead to disconnection and possibly a power outage. As a part of the development and introduction of new hydrophobic insulator materials, it would be relevant to detect the microbiological growth on insulators installed in high-voltage systems.

The insulator performance is also reduced when a thin layer of salt covers the insulator surface, which is common at the coasts. It would thus be relevant to detect the salt layers that are present on the surfaces, and to clean the insulators.

Today, no fully reliable and truly remote inspection technique for insulators is available. Usually, most utilities inspect their polymeric insulators from the ground, from towers or from helicopters. However, manual inspection is time consuming and it is hence desirable to obtain a remote and non-intrusive inspection technique that can be used to rapidly investigate a larger number of insulators.

1.2 Objective

The objective of this PhD thesis work is to develop laser techniques that can be applied in the high-voltage research, in the development of polymeric insulators and in assessing the state of insulators.
One part of the PhD thesis work is to develop techniques for remote and non-perturbing determination of the charge density on a surface. The amount of surface charge that might be present on a surface should correspond to a weaker electric field than the threshold for electric breakdown in air. At normal temperature and pressure this threshold is approximately 3 MV/m and corresponds to a net surface charge of 27 μC/m². We believe knowing the surface charge density is important for understanding surface discharges which constitute a limiting factor in many electrical insulation systems. Specifically we consider non-linear optical laser measurement techniques, which can be designed such that they are sensitive only to the surface properties. A technique for remote and non-perturbing charge measurements would be a powerful tool for monitoring insulators during operation as well as for the testing and development of new insulators.

The objective of this PhD thesis work is also to develop a remote and non-intrusive technique for imaging of microbiological growth on high-voltage insulators. Specifically we consider mobile Lidar (light detection and ranging) techniques. The imaging of microbiological growth on insulators can be carried out in a way that is similar to previous investigations which have been carried out at the department, such as fluorescence imaging of vegetation status [Svanberg, 1995] and monitoring of facades of historical monuments [Weibring et al., 2001] [Lognoli et al., 2003].

The PhD thesis work also aims at finding a reliable method to detect salt on an insulator surface. We have shown that laser-induced breakdown spectroscopy (LIBS) could be applicable for this purpose.

1.3 Outline

Chapter 1 gives an introduction to the PhD thesis work and describes its objectives. Chapter 2 contains a description of polymeric insulator materials. Chapter 3 contains a description of spectroscopy techniques for remote detection of microbiological growth and surface contamination. In chapter 4 techniques for detection of surface charges and electric field calculations are presented. Chapter 5 provides information about equipment and analysis techniques used in the thesis. Chapter 6 contains a discussion of results and, finally, chapter 7 gives a brief summary of the papers.
Chapter 2

Polymeric insulator materials

Electricity, which is a somewhat colloquial word, can be defined as a physical phenomenon associated with stationary or moving negative or positive charges. The electricity, which came to Sweden about 130 years ago, is something that we take for granted in our daily lives. Our basic needs for power to run our many machines have been dependent largely on electricity and the electric current is one of our most convenient means of transferring energy. Electrical energy can be converted into other usable energy forms, such as light, heat, chemical and mechanical energy and when it is converted to e.g. heat, it can do a lot of work - cook our food, press our clothes, run engines and many other tasks.

Electricity can be obtained, e.g. from nuclear power stations, from oil power stations or from renewable energy sources. Nuclear reactors are releasing the immense power of stored energy in the tiny atomic nuclei. Building the plants for these projects is highly expensive and sometimes politically controversial but a number of countries adopt this technique due to their large need for electrical energy.

Electricity flows through some substances. Any substances that readily allow the flow of electricity are called conductors while substances that do not allow the passage of electricity are called insulators. Most metals are good conductors. Silver is the best solid conductor of electricity at room temperature, and copper, gold and aluminium follow in that order. Examples of good insulators are glass, mica, paraffin, hard rubber and many plastics.

The transfer of electrical energy in high-voltage systems requires insulators that can support the high-voltage parts and insulate them from ground. The mechanical and electrical properties of the insulator are crucial for the performance, and extensive research efforts are aimed at obtaining improved insulator properties, especially under polluted conditions. Insulators, made of porcelain and glass, have been considered to be very reliable but new developments have led to the introduction of the polymeric insulators.

This chapter gives a description of polymeric insulator materials. The advantages and disadvantages of using polymeric insulators, compared with the traditional insulators made of porcelain and glass, are briefly presented. The chapter provides information about some properties, e.g. hydrophobicity, contamination resistance of the insulator material, accumulation of surface charge, and aging of materials, which can affect the insulator performance. The chapter ends with a description of some compounds that are used in the polymeric materials.
2.1 Advantages of using polymeric insulators

Comparing with a traditional insulator made of porcelain or glass, a polymeric insulator offers many advantages [Demfalk, 2004]. For example, lower weight – only 10% of that of a porcelain insulator - gives easier transportation and handling of the insulators. Some polymeric insulator materials are outstanding with regard to high temperature stability, chemical resistance and low temperature flexibility. Other advantages are good thermal and electrical resistance, and resistance to vandalism. One main advantage is that polymeric materials are hydrophobic which makes them more flashover resistant compared to hydrophilic porcelain and glass insulators.

However, one critical question is for how long time the hydrophobicity property will remain. Thus, the aging problems require attention [Demfalk, 2004].

2.2 Important properties for insulator performance

2.2.1 Contamination on porcelain and polymeric insulators

Microbiological growth can be found on porcelain insulators and it is stimulated by high humidity, high temperature, high rainfall and intense sun radiation. Biological growth on porcelain insulators has been observed on many places all over the world [Demfalk, 2004]. Salt deposits on insulators are also common, especially close to the sea. It is generally recognized that the main events leading to flashover of polluted insulators under service voltage are the formation of a conductive layer on the insulator surface. In Sweden, about 1% of the production problems of electricity can be estimated to be due to contamination on insulator surfaces [Arnborg, 2005]. Dirt can also be a problem, and in some countries even desert sand. Ultraviolet light, water, acids, salt and dust - all contribute to insulator failure.

Microbiological growth has also been observed on polymeric insulators; see [Demfalk, 2004]. However, there is a lack of experience and reports, especially of ethylene propylene diene monomer (EPDM) rubber insulators. Insulators made of silicone rubber are known to have a good resistance to biological degradation [Demfalk, 2004].

2.2.1.1 Biological growth

A biofilm is a community of microorganisms, i.e. bacteria, fungi, algae, yeasts, protozoa etc, attached to a solid surface. Damages of a polymeric material can be caused by biofilms by several different processes in the interface of the biofilm-polymer such as fouling, degradation of leaching components (additives and impurities that leak from the rubber to the surroundings), biotic degradation, hydration penetration, colour and odour [Wallström, 2005]. Each process affects the polymer. Fouling changes the surface properties. Degradation of leaching components gives a loss of stability through the interaction of additives and monomers with the polymer. However, the addition of different types of additives in the rubber material can prevent microbiological growth from attacking the insulator surface. In biotic degradation, enzymes and radicals are involved in
the interfacial process and it also gives a loss of stability. The effect of hydration penetration is conductivity and swelling. Discolouration and odour are also unwanted.

2.2.1.1 Algae

Most of the algae have characteristics in common with plants, e.g. cell walls. The pigment in plants including algae is called chlorophyll and is necessary for the photosynthesis. Chlorophyll absorbs light (usually red, violet and blue) necessary for the photosynthesis and reflects green light. The chlorophyll may be masked by other pigments, giving the various types of algae different colours. Six categories can be selected: blue-green (Cyanophyceae), green (Chlorophyceae), yellow-green (Xanthophyceae), brown (Phaeophyceae), red (Rhodophyceae) and diatoms (Bacillariophyceae) [Demfalk, 2004]. Two types of chlorophyll (a and b) differ only slightly in the composition of a side chain. Chlorophyll a has a methyl group and chlorophyll b has an aldehyde group. Chlorophyll a has two main absorption bands, around 430 nm and 660 nm. Chlorophyll b has two main absorption bands, around 480 nm and 630 nm. In the process of photosynthesis, light is absorbed by the pigments of photosystems I and II [Agati, 1998]. As a side product (loss) in photosynthesis some fluorescence light is emitted. Photosystem I yields fluorescence in 730 nm emission band only, while photosystem II contributes to fluorescence both around 685 nm and 730 nm.

2.2.1.2 Fungi

Fungi are eukaryotic, (i.e. have cells containing a nucleus and other membrane-bound organelles) and have rigid cell walls. They may be either unicellular or multi-cellular. Some may be microscopic in size, while others form much larger structures, such as mushrooms and bracket fungi that grow in soil or on damp logs. Unlike algae, fungi do not contain chlorophyll and thus cannot carry out photosynthesis. The composition of the polymeric material is crucial for the extent of biological growth on the insulator surface. Polymeric materials contain both inorganic and organic material. Fungi, which are predominantly mostly found on the insulator surfaces, cannot digest the inorganic material. Nevertheless, it is believed that polymeric insulators are mostly attacked by fungi. Fungi are more difficult to detect than algae by using fluorescence light. Aromatic amino acids, which are found in fungi and human cells, have been shown to absorb light in the wavelength region 200 nm – 400 nm [Coohill and Sutherland, 1989].

2.2.1.3 Lichen

Lichen represent a form of symbiosis, namely, an association of two different organisms. In lichen, a network of fungi thread-like structures contains millions of cells of algae. This is a "symbiotic" relationship, meaning that both the algae and the fungi benefit from it. The fungi give shape, structure, a protective environment, and mineral nutrients to the algae. In return, the algae provide the fungi with the energy-rich nutrients the algae produce via photosynthesis. Fluorescence Lidar spectroscopy of building monuments for remote assessment of algae and lichen growth has been studied by Raimondi et al. [Raimondi, 1998].
2.2.1.4 Bacteria

Algae often live in association with single-cell microorganisms called bacteria. The world of bacteria is extraordinarily varied and plays an immense role in ensuring the existence of other living things on earth. Many bacteria survive in the most primitive conditions, requiring for their multiplication only the simplest molecules containing chemical elements that are part of biological molecules.

2.2.1.2 Salt deposits

Salt on an insulator surface can be a severe problem. For example, a storm can bring a lot of salt-containing sea water into the air (seaspray). A layer of salt can make an insulator surface conductive and there is a risk for an electric power outage. When such salt layers are formed, certain insulators, in particular in switchgear stations, must be cleaned if natural rain is not sufficient.

2.2.2 Aging of insulator materials

Specific research is often performed on insulators used for several years in an outdoor environment. However, it is time consuming and costly to carry out experiments that stretch across several decades. Aging measurements can provide information on insulator long-term performance. There are some different types of methods to accelerate the aging of a material. For example, the polymeric materials can be subjected to ultraviolet light, aged thermally in an oven, immersed in boiling water, immersed in distilled water, or subjected to 90-95% humidity. Measurements on naturally aged insulator materials are reported in [Larsson et al., 2002].

2.2.3 Hydrophobicity

Hydrophilic is a characteristic for materials exhibiting an affinity for water and literally means water-loving while hydrophobic has the opposite meaning, i.e. water repelling. Hydrophobicity status has a large effect on the outdoor insulation performance, e.g. flashover resistance, and is prominently influenced by the aging process of silicone rubber insulators. Optical diagnostics on insulator materials with different degree of hydrophobicity have been carried out by Larsson et al. [Larsson et al., 2002]

When it is raining, the risk to obtain a surface discharge depends on the hydrophobicity. The degree of hydrophobicity, which can be determined by measuring a contact angle [Hillborg, 2001], is important for binding water and attaching biological growth on the insulator surface. On a hydrophobic surface water droplets are formed when it is raining while a water film is formed on a hydrophilic surface. The presence of a water film increases the risk of flashovers. The hydrophobicity effect can be explained by the diffusion of low molecular weight compounds from the bulk to the surface and into the surface pollution layers.
2.2.4 Surface charge

All electrical systems rely on the dielectric strength of their electrical insulation. The electrically weakest point of insulator systems is normally the surface of the insulators. One property of the surface that determines the probability of a surface discharge propagating is the ability of the material to bind electric charge at the surface. The reduction in dielectric field strength depends on surface charge polarity, density and distribution. The initiation and propagation of surface discharges depend on the accumulated surface charge density.

2.3 Polymeric compounds used in high-voltage insulators

A polymer is a molecule made up of long chains of repeating base units called monomers. Each polymer is usually named after the raw material used to make it. For example, the polyethylene \([-\text{CH}_2-\text{CH}_2]-_n\) is made up of many ethylene molecules, \(\text{CH}_2=\text{CH}_2\). The polypropylene is made up of many propylene molecules and is given by \[-\text{CH}_2-\text{C(CH}_3\text{H)}_2]-_n\.

Ethylene and propylene form the simplest chain-growth polymers. A copolymer results from using different monomers. Ethylene-propylene rubber, poly(ethylene-co-propylene), is a random copolymer of ethylene and propylene. The repeating base unit is given by \[-\text{CH}_2-\text{CH}_2]-_n\text{]+[-\text{CH}_2-\text{C(CH}_3\text{H)}_2]-_m\],

where the first part denotes polyethylene and the second part denotes polypropylene. A terpolymer results from using three different monomers.

Dimethyldichloro siloxane and water can form dimethylsilane diol and polydimethyl siloxane (PDMSO) according to

\[
n [\text{Si(CH}_3\text{)Cl}_2] + 2n \text{H}_2\text{O} \rightarrow n [\text{Si(CH}_3\text{)H}_2\text{(OH)}_2] + 2n \text{HCl} \rightarrow [\text{Si(CH}_3\text{)H}_2\text{O}]_n + n \text{H}_2\text{O} + 2n \text{HCl}
\]

Dimethyldichloro siloxane + water \(\rightarrow\) Dimethylsilane diol + salt acid \(\rightarrow\) polydimethyl siloxane + water + salt acid

Blends of PDMSO and EPDM form alloy rubbers.

The polymer’s physical properties are improved when the polymer contains more monomers. Polymers can contain up to about 1 million monomers which is the case for ethylene propylene rubber (EPR). PDMSO materials usually contain 3,000 to 10,000 monomers. A compound of an insulator material can consist of 10 or more ingredients. The ingredients are listed below.

Elastomers
The selection of the elastomer (base polymer) should be based on the properties desired.
Vulcanizing agents
Vulcanizing agents are chemicals which produce a three dimensional structure by formation of crosslinks between the long chain segments of the rubber molecules.

Coagents
Cross-linked bonds between the polymer and vulcanizing agent which are prevented from being torn apart by using coagents.

Antidegradants
Antidegradants are used to slow down the deterioration of a rubber compound which is initiated by oxygen, ozone, heat and light.

Processing aids
Processing aids are added to rubber compound to aid the mixing of the compound.

Fillers
Reinforcing fillers are added to improve the otherwise poor tensile strength of silicones.

Coupling agents
Reactive silane coupling agents can be used to achieve optimal bonding between a silicone rubber material and a substrate.

Plasticizers and softeners
They can be used to aid mixing of the compounds and to modify viscosity. Many ingredients in this group can also be considered as processing aids.

Special purpose materials
Depending on the actuation mechanism, special-purpose materials are used to achieve a given functionality.

Several concepts about polymeric insulators have briefly been described in this chapter. More information about polymeric materials is found in e.g. [Demfalk, 2004] and [Wallström, 2005].
Chapter 3

Spectroscopy techniques for remote detection of microbiological growth and surface contamination

Absorption, reflectance and fluorescence are basic phenomena that could be used for remote detection of microbiological growth. The purpose of this chapter is to give a brief introduction to reflectance, laser-induced fluorescence (LIF) and laser-induced breakdown spectroscopy (LIBS).

3.1 Reflectance experiments

Vegetation can be distinguished from most materials due to its absorption in the red and blue segments of the visible spectrum, its higher green reflectance and its very strong reflectance in the infrared region. Many remote sensing devices (e.g., earth-observing satellites) operate in the green, red, and near infrared regions of the electromagnetic spectrum. Several algorithms exist for detecting vegetation based on spectrally resolved reflection.

Different bands of a reflectance spectrum can be combined to show a vegetated area. For example, the ratio of the near-infrared (NIR) band to the red band is known as the Ratio Vegetation Index (RVI).

\[
RVI = \frac{\text{NIR}}{\text{Red}}
\]

Vegetated areas have higher RVI values compared to non-vegetated areas since vegetation has high NIR reflectance and low red reflectance. Another commonly used vegetation index is the Normalised Difference Vegetation Index (NDVI) given by

\[
\text{NDVI} = \frac{(\text{NIR} - \text{Red})}{(\text{NIR} + \text{Red})}
\]

The NDVI band can also be combined with other bands to yield additional information. Algorithms can also be based on singular value decomposition (SVD) technique (includes factorization of a matrix) or principal component analysis (PCA), e.g., for classification of algal bloom types from reflectance data. PCA is described in chapter 5.6.

In the blue sky radiation experiments several wavelength areas can be of interest. As an example of a substance that can affect the reflectance spectra aromatic amino acids, which are found in cells have shown to absorb light in the wavelength region 300 nm – 400 nm [Coohill and Sutherland, 1989].
From reflectance (absorbance) spectra of the different fungi covered materials and clean substrates one can determine which spectral areas that could lead to differentiation among various types of contamination. Imaging studies can be carried out to map the spatial distribution of the fungi on the insulator surfaces and explore the possibility to discriminate among different types of bio-contaminants on the basis of differences in absorbance and reflectance. The reflectance imaging studies can be compared to LIF studies.

It can be useful to show a quotient between the spectrum of the blue sky radiation and the spectrum of the reflectance from a fungi covered insulator material. Thus a normalised reflectance spectrum is obtained. Vegetation characteristics of reflectance spectra are normally found in the infrared wavelength region and the visible region.

By using a combination of LIF and reflectance the diagnostic performance might be improved. Reflectance experiments using blue sky radiation can also give insight about what excitation wavelength that is useful in LIF experiments.

### 3.2 Laser-induced fluorescence

Energy level diagrams can be useful for visualizing the complex nature of molecules and are a means of analysing the energies molecules can accept (e.g. by absorption of laser light) and release as they undergo a transition from one state to another. The lowest energy level for a molecule, the electronic ground state, is the statistically most occupied energy state for room temperature. An excited state is an energy level which has more energy than the ground state. Actually, a molecular state is comprised of an electronic, vibrational, and rotational component and the character of the light-molecule interaction depends on the wavelength of the laser light. In electronic spectroscopy, dealing with ultraviolet/visible/near-infrared light (200-1000 nm), electrons move from one electronic configuration to another. This spectroscopy gives information about molecular orbitals. Molecular vibrational spectroscopy deals with infrared light in the wavelength region 1-40 μm. When a molecule absorbs light in this region it starts to vibrate and information about the structure of the molecule can be obtained. In molecular rotation spectroscopy radiation in the microwave region (millimetre wavelengths) causes the molecule to change rotation state which can elucidate, e.g., dipole moments, bond lengths and bond angles. Once a molecule has absorbed energy in the form of electromagnetic radiation, there are a number of ways by which it can return to ground state. A Jablonski diagram (Fig. 3.1) can show these processes.

LIF is the emission from molecules (atoms) that have been excited to higher energy levels by absorption of laser radiation. Thus two radiative transitions are involved in the LIF process, the absorption process and the emission process. These processes are shown in a Jablonski diagram.
Figure 3.1 Relaxation mechanisms for excited state molecules can be described with a Jablonski diagram. Besides radiative processes, there are also non-radiative processes such as internal conversion, intersystem crossing and vibrational relaxation.

The absorption process is a quantum mechanical interaction between electromagnetic radiation and the molecule. The absorption process starts at a distinct rotational and vibrational level within the electric ground state. Light is absorbed to a distinct level within an electronically excited state. The energy of the photons must match the excitation energies if the photons should be absorbed by the molecules. From perturbation theory an incident light field can promote molecules from the ground state to an excited state. The rate of absorption can be expressed as $w = B \rho$, where $B$ is the Einstein coefficient of absorption and $\rho$ is the energy density of the radiation at the frequency of the transition. Hence, a stronger electric field of laser light makes the absorption occur faster which leads to a stronger emission.

Excited molecules are unstable and can become de-excited by the emission of photons. This is known as spontaneous emission. The decay probability determines the mean lifetime of the state and the decay usually occurs on a sub microsecond time scale. Fluorescence takes place between states of the same spin whereas phosphorescence is a transition between states of different spin. (Fig. 3.2).
If molecules can get from singlet state to a metastable state, and if the metastable state slowly decays to a singlet state via photon emission, then phosphorescence light is released. Typically, the metastable state is a triplet state, and the ground state is a singlet state.

LIF is a widely used method for optical measurements on gases, liquids and solids, and has a wide range of applications in chemistry, biology, medicine and physics. The technique is a very sensitive, in-situ, non-intrusive spectroscopic method for investigating neutral or charged atomic or molecular species. LIF experiments can be carried out for different excitation wavelengths to assess the usefulness of multi-spectral excitation for characterisation of fluorescent molecules. At the Physics Department of the Lund Institute of Technology the LIF technique has been used for the detection of cancer. This is possible since the fluorescence signal in pre-malignant and malignant tissue deviates from normal tissue [Svanberg, 1992]. The division also has experience from Lidar remote-sensing assessment of the cultural heritage using LIF [Weibring et al., 2001] [Weibring et al., 2003b] [Lognoli et al., 2003]. At the Physics Department of the Lund Institute of Technology, there is also a long tradition of development of the LIF technique for studies of combustion processes.

A typical experimental setup for a LIF experiment contains a laser excitation source, some focusing and collection optics (lenses/fibre optics), a spectrometer and a detection system. The interaction of radiation at a fix wavelength with molecules (many energy levels) gives rise to the emission of a fluorescence continuum with longer wavelengths than the excitation wavelength; see Fig. 3.1. A UV laser is generally used as an excitation source as the short wavelengths are in the energy region of the electronic transitions. A spectrometer and an intensified, gated optical multi-channel analyser (OMA) system can serve for the detection. A multi-channel or array detector system allows a user to simultaneously collect many data points without scanning a monochromator grating, which is the case for a single-channel detector system. The most popular multi-channel detectors are charge-coupled devices (CCDs). CCDs are two-dimensional arrays made of silicon with several hundred elements, or pixels, arranged in a rectangle. For spectroscopy, the longer side of the rectangular array is arranged to coincide with the dispersed spectrum.
3.3 Laser-induced breakdown spectroscopy

LIBS has been used since Theodore H. Maiman constructed the first laser (1960). It is a non-destructive or rather minimally-destructive spectroscopy method for analysing the chemical composition of a solid material, liquid or gas. It seems that new applications of LIBS arise almost every day. These are for example quality assurance in pharmaceutical production, combustion diagnostics, military activities, trace gas detection, environmental monitoring, studies in cultural heritage, research in life sciences, and industrial processing by materials analysis. For the exploration of Mars with the mobile Mars Science Laboratory (MSL) rover, scheduled for 2009, LIBS will ablate surface layers from materials and measure elemental composition of underlying rocks and soils. LIBS is also known as laser-induced plasma spectroscopy (LIPS).

Plasma is a phase of matter distinct from solids, liquids, and normal gases. The plasma state was first discovered by Sir William Crookes in 1879 but it was not called plasma until 1928, when Irving Langmuir coined the term. A plasma is characterized by Debye screening lengths that are short compared to the size of the plasma, that the number of charged particles in a Debye sphere is large compared to unity, and charge quasi-neutrality. A defining characteristic of a plasma is ionization. The degree of ionization is determined by the electron temperature relative to the ionization energy and described by the Saha equation [Foukal, 2004]. As the negative and positive charges are free to move, a plasma is an excellent conductor and is influenced by magnetic and electric fields. The motions of the particles in the plasma also generate fields and electric currents. Plasmas are normally characterized by their electron density, $n_e$, and electron temperature, $T_e$. The solar wind is a natural plasma that has an electron density of $n_e=10^6$ m$^{-3}$ and an electron temperature $T_e=10^5$ K. A fusion core plasma has an electron density of $n_e=10^{20}$ m$^{-3}$ and an electron temperature $T_e=10^8$ K [Radivojevic, 2003]. The plasma temperature in LIBS depends on the pulse energy, the laser pulse duration, the material etc., and is in the range from a few thousand degrees to $2 \cdot 10^7$ K.

Laser-induced breakdown can be defined as the generation of a plasma by a laser pulse [Radziemski et al., 1983]. There are two main mechanisms for the generation of electrons, ionization through a collisional process and multi-photon ionization (MPI). In the first mechanism, laser radiation is absorbed by electrons which collide with neutrals. If the energy of the electrons is large enough the neutrals are ionized through the process

$$e^- + M \rightarrow 2e^- + M^+,$$

The collisional processes cause an exponentially increasing electron concentration, i.e. a cascade breakdown. In the second mechanism, MPI, $m$ photons are simultaneously absorbed by an atom or a molecule. The ionization process is given by

$$M + m\hbar \nu \rightarrow M^+ + e^-,$$

where $m$ is satisfied by

$$m > E_i/\hbar\nu$$

and $E_i$ is the ionization potential. MPI is only likely to occur for shorter wavelengths ($<1 \mu$m) [Radivojevic, 2003].
In a LIBS process several phenomena take place and some of them at the same time. Among the most important phenomena, described in [Radivojevic, 2003], are

1. Heating of the material
2. Evaporation of the material
3. Dissociation of molecules
4. Absorption of the laser radiation by evaporated material
5. Plasma ignition
6. Heating of the plasma via inverse bremsstrahlung and photoionization
7. Plasma shielding occurs at the surface of the plasma
8. Expansion of the plasma
9. Plasma cooling
10. Formation of clusters

When a laser pulse is focused onto a non-transparent sample, the material will be heated by absorption of energy. A transparent material needs higher irradiances to become heated. If the absorbed energy is sufficiently high, evaporation of material will occur and molecules will be dissociated. The evaporated material continues to absorb laser radiation and the time required for vapour breakdown depends on many factors such as concentrations of electrons and atoms, intensity of the laser light, reflectivity of the sample, temperature of vaporization, initial temperature of the material, density, specific heat, and thermal conductivity [Radivojevic, 2003]. A mechanism for the plasma ignition is described in [Weyl, 1981]. The plasma is then heated via inverse bremsstrahlung (bremsstrahlung is produced when charges are accelerated) and photoionization. A very high electron density can be generated at the surface which can change the reflecting properties of the surface and lead to full reflection of the laser beam by the plasma - a phenomenon that is called plasma shielding. Laser light that is incident to a plasma will be reflected if the angular frequency is less than the plasma frequency; see Eq. (4.49) in the following chapter. The atmosphere around the vapour plasma is heated and gases which were initially cold start to absorb laser radiation. When a critical number of electrons are generated in the heated gas it will absorb strongly and lead to an expansion of the plasma. The plasma expands adiabatically towards the laser beam until the irradiation is stopped or decreased. As the plasma cools, excited electrons and ions relax back into their ground states, emitting light at characteristic atomic wavelengths. In the LIBS process material clusters can be produced by laser vaporization of solids. Clusters, generated at the early stage of laser ablation, can absorb laser radiation, thus reducing the ablation efficiency.

In LIBS spectra the emission lines are superimposed on a continuum background (bremsstrahlung) which is produced by the electron-ion recombination in the plasma. The continuum background dominates the spectra the first 1 μs to 3 μs after the plasma ignition (generation of an electron density \( n_e \sim 10^{22} \, \text{m}^{-3} \) [Radivojevic, 2003]). When the plasma temperature falls, the continuum background decreases, and the emission from the atoms and ions dominate the spectra between about 1 μs and 20 μs after the plasma ignition. As the plasma cools further, the atoms inside the plasma start to recombine to create molecules and molecular emissions are intense, typically from 5 μs to 50 μs after the plasma ignition. The exact timing varies with the type of sample.

A typical LIBS system consists of an Nd:YAG laser or an excimer (excited dimer) laser, some focusing and collection optics, a spectrometer, a delay generator and a time gated detector. The detector response is typically between 1100 nm (near infrared) and 170 nm
(deep ultraviolet), where all elements have emission lines. Since the atomic emission lines are very narrow, a spectrometer with a high resolution system is needed. In combination with the spectrometer and detector there is a delay generator which makes it possible to temporally resolve the LIBS spectrum. A gated OMA system can serve for the detection.

Remote LIBS in the long range operation regime, using a container-integrated mobile femtosecond terawatt laser system with integrated detection unit (Teramobile), has been demonstrated [Rohwetter et al., 2005] [Bogue, 2005]. The Teramobile project is a French-German research project and a cooperation between institutes in Berlin, Jena, Lyon and Palaiseau. The Teramobile was constructed for Lidar applications. The main goal of the Teramobile project is to study nonlinear propagation of femtosecond-terawatt laser pulses over long distances in the atmosphere, and their applications to atmospheric research. Lidar remote sensing of atmospheric pollutants and lightning protection and triggering are included in this project.

The Teramobile system is based on a fs-TW Ti:Sapphire laser system which contains a commercial chirped-pulse-amplification (CPA) chain. The laser chain consists of an oscillator, a stretcher, a regenerative amplifier, a preamplifier, a main amplifier and a compressor. The system is operating at a wavelength of 795 nm and a repetition rate of 10 Hz, the chain can deliver pulses of up to 350 mJ in energy and compressed to 70 fs pulse duration.

By using femtosecond laser pulses the laser-induced ablation from metallic targets has been performed at a distance of 180 m [Rohwetter et al., 2005]. This can be compared to remote LIBS measurements performed at distances of 45 m and 120 m by using nanosecond pulses [Palanco et al., 2002] [Rohwetter et al., 2005]. The minimum diameter of a focused laser beam of given diameter increases linearly with focusing distance as a consequence of diffraction. To increase the focusing distance using nanosecond pulses would require larger laser energy and larger diameter focusing optics which is difficult in practice. Therefore, the peak power can instead be increased by decreasing the pulse length.
Chapter 4

Techniques for measuring of surface charge density and electric fields

During the initial period of my thesis work considerable time was spent on trying to develop a technique for surface charge determination based on second harmonic generation. In this chapter some techniques for measurements of surface charge density and electric fields are presented. The chapter contains some existing methods of measuring surface charge, an introduction to second harmonic generation, and a suggestion for measurements of electric fields within a bulk volume using Stark effect in combination with gas in scattering media absorption spectroscopy (GASMAS).

4.1 Some existing methods of measuring surface charge

In this section three techniques for measuring surface charge are explained. A “two-photon photoelectric emission” method is described since it is more sensitive to surface charge than second harmonic generation [Tomas et al., 1999]. Two other methods are also described; one which is based on the Pockels effect and one based on an electrostatic field probe where the surface charge is detected electrostatically. I have chosen to describe the method based on the Pockels effect since it is a laser method and the field probe method due to its simplicity. Several other techniques exist to measure surface charge, e.g. atomic force microscopy [Raiteri et al., 1996], Kelvin probe [Nalbach and Kliem, 2000], and surface enhanced Raman scattering (SERS) [Weiss and Haran, 2001].

4.1.1 The Pockels effect

Nowadays, experimental devices for optical measurement of surface charge have become less expensive than before. Highly sensitive electro-optical crystals, powerful and highly stable single wavelength laser sources, high-quality optical elements, high-speed highly sensitive charge-coupled device (CCD) cameras, high-capacity frame memories and computers have all become available at lower prices.

Information about the surface charge distribution can be obtained by studying the polarisation of light transmitted through a crystal, that exhibits the Pockels effect. This effect is a dielectric anisotropy caused by an electric field, which in this case is due to the surface charge.
One example of utilising the Pockels effect as a means for measurement of surface charge is presented in Fig. 4.1 [Zhu et al., 1995].

**Figure 4.1** *Measurement system which makes it possible to observe the surface charge distribution using the Pockels effect and an optical phase modulation technique.*

Surface charge is deposited on the insulating film by the application of a high-voltage impulse to a needle electrode. The charge is attached to one side of a Bi$_{12}$SiO$_{20}$ (BSO) single crystal plate that has an earthed transparent indium tin oxide (ITO) electrode on the opposite surface.

A light beam from a He-Ne laser is expanded in diameter from 1 mm to 50 mm by a beam expander. A polarised beam splitter (PBS) polarises the light beam linearly. The optical phase modulation is described later. The light beam is then transmitted into the BSO crystal and reflected from the interface between the insulating film and the BSO crystal. The reflected light beam has a retardation (delay) between the two polarisation components (ordinary ray and extraordinary ray) of the electro-magnetic field and this retardation is proportional to the electric field due to the Pockels effect. The surface charge causes the electric field. The Pockels effect is an electro-optical effect in which the application of an electric field produces a birefringence (also known as double refraction) which is proportional to the field. The reflected light intensity is recorded by a high-speed CCD camera connected to an image lock-in amplifier computer system for image processing to get the surface charge distribution. The light intensity is recorded and by using two images it is possible to derive the retardation distribution $\theta(x,y)$, i.e. the delay between the two polarisation components as a function of $x$ and $y$.

The light intensity is detected as images. The light intensity distribution is expressed as

$$I(x, y) = \gamma(x, y)I_0(x, y)\sin^2 \vartheta(x, y) + I_{off-set}(x, y),$$

(4.1)
where $\theta(x,y)$ is the total retardation distribution, $I_0(x,y)$ is the maximum light intensity distribution of the incident light and $I_{\text{off-set}}(x,y)$ is the DC off-set component due to the dark current in the camera and the leakage light intensity of the PBS. Transmission and reflection ratio distributions of the optical devices and the sensitivity of the CCD camera’s imaging sensor matrix are incorporated by $\gamma(x,y)$.

All optical devices have a certain amount of natural birefringence caused by the residual mechanical stress. The total retardation $\theta(x,y)$ is expressed as a sum between the natural retardation distribution and the retardation distribution due to the surface charge distribution $\sigma(x,y)$ and the Pockels effect:

$$\theta(x,y) = \theta_{\text{nat}}(x,y) + \theta_{\sigma}(x,y) \quad (4.2)$$

The DC off-set term $I_{\text{off-set}}$ is eliminated in the following way: Between the PBS and the test cell there is a spatial optical phase modulator (OPM). It modulates in pulsed mode the optical phase difference between the two components of light parallel and perpendicular to the fast axis of the optical phase modulator. A square wave drives the OPM with an amplitude of $V_m$ and two light intensity images are recorded during the positive and negative amplitude of the pulse. The recorded images, $I_{s+}(x,y)$ and $I_{s-}(x,y)$, may be written as

$$I_{s+}(x,y) = \gamma(x,y)I_0(x,y)\sin^2[\theta(x,y) + \theta_m] + I_{\text{off-set}}(x,y) \quad (4.3)$$

$$I_{s-}(x,y) = \gamma(x,y)I_0(x,y)\sin^2[\theta(x,y) - \theta_m] + I_{\text{off-set}}(x,y), \quad (4.4)$$

where $\theta_m$ describes to what extent the optical phase is modulated during the positive and negative amplitude of the modulating pulse voltage. The light intensity difference between the two images is

$$\Delta I_s(x,y) = I_{s+}(x,y) - I_{s-}(x,y) = I_M(x,y)\sin[2\theta(x,y)] \quad (4.5)$$

$$I_M(x,y) = \gamma(x,y)I_0(x,y)\sin(2\theta_m), \quad (4.6)$$

where $I_M(x,y)$ is called the equivalent maximum light intensity distribution. Now the total retardation distribution can be calculated as

$$\theta(x,y) = \frac{1}{2}\arcsin[\Delta I_s(x,y)/I_M(x,y)] \quad (4.7)$$

In this way the DC off-set term $I_{\text{off-set}}(x,y)$ due to the dark current of the CCD camera is removed. The natural retardation distribution is affecting the total retardation distribution as

$$\theta_{\sigma}(x,y) = \theta(x,y) - \theta_{\text{nat}}(x,y) \quad (4.8)$$

and it is also possible to derive $\theta_{\text{nat}}$ and
\[ \theta_{\text{nat}}(x, y) = \frac{1}{2} \arcsin[\Delta I(x, y) / I_M(x, y)], \]  

(4.9)

where \( \Delta I(x, y) \) is the light intensity distribution of the difference image between two images but when there does not exist any surface charge on the film. The surface charge \( \sigma(x, y) \) is proportional to the retardation distribution \( \theta_{\text{nat}}(x, y) \) and hence

\[ \theta_{\text{nat}}(x, y) = K \cdot \sigma(x, y), \]  

(4.10)

where \( K \) is the optical constant of the BSO crystal. The equations (4.8), (4.9), and (4.10) determine the surface charge \( \sigma(x, y) \).

The lower limit of the sensitivity of the surface charge density is 10 \( \mu \text{C/m}^2 \) [Zhu et al., 1995]. This electro-optical method has the advantage of simultaneous visualization of electric charge and it is feasible to quantify the surface charge density. It is also possible to study the temporal development of the surface charge. Since the charge image data are stored in a computer, the spatial noise can be reduced to achieve adequate information. A minor disadvantage with this technique is the necessity of the lock-in amplifier to observe the dynamic of the surface charge. It is also difficult to apply this method to outdoor field experiments.

The technique is further discussed in [Zhu et al., 1996].

4.1.2 The electrostatic field probe

Interpretation of potential probe measurements has been discussed extensively since the early 80’s. The electrostatic field probe makes it possible to obtain the charge distribution on a solid insulator. Charges are electrostatically induced on the sensor plate of the probe by the surface charge on the insulator. A low-loss capacitor is connected to the probe and the charge induced on the probe can yield the potential across the capacitor. To be more specific, as the probe is moved parallel to the surface it is the variation in probe potential which is the measured parameter.

A long cylindrical shaft at earth potential with a circular conducting disc constitute the field probe; see Fig. 4.2. The disc is insulated from the shaft and coaxially mounted.

\[ \theta_{\text{nat}}(x, y) = \frac{1}{2} \arcsin[\Delta I(x, y) / I_M(x, y)], \]  

(4.9)
Three methods have emerged to evaluate probe measurements: the direct method, the capacitive approximation and the indirect method.

4.1.2.1 The direct method

Basically, this method is utilising the solution of Poisson’s equation where interface surface charge and all other charges in the space between the electrodes and on the electrodes represent unknown sources. Known parameters are the probe potential and its location. This approach demands a lot of numerical analysis and therefore very few studies have adopted this method.

4.1.2.2 The capacitive approximation

This method assumes that the probe response can be related to an equivalent capacitive circuit. Due to the simplicity of the method it has been used in the majority of the probe investigations. For further information see, e.g., reference 9-19 of [Crichton and McAllister, 1992].
4.1.2.3 The indirect method

A probe function named the $\lambda$-function connects the charge induced on the probe to the surface charge density at the dielectric interface [Rerup et al., 1996]. If the volume charge density inside the solid dielectric is assumed to be zero, the relationship can be expressed as

$$q_i = -\int_{A_0} \lambda \sigma dA$$  \hspace{1cm} (4.11)

where $q_i$ is the Poissonian induced charge on the sensor plate [Pedersen et al., 1993], and $\sigma$ is the surface charge density on the surface element $dA$ of the solid dielectric surface $A_0$. The dimensionless parameter $\lambda$ is shown to be a solution of the general Laplacian equation for the complete measuring-system geometry:

$$\nabla \cdot (\varepsilon \nabla \lambda) = 0$$  \hspace{1cm} (4.12)

At the probe sensor plate the boundary condition is $\lambda = 1$, and at all other electrodes $\lambda = 0$. Further, at the dielectric interface the normal component of the derivatives of $\lambda$ must satisfy the condition

$$\varepsilon_+ \left( \frac{\partial \lambda}{\partial n} \right)_+ = \varepsilon_- \left( \frac{\partial \lambda}{\partial n} \right)_-,$$  \hspace{1cm} (4.13)

where the positive and negative signs are the opposite sides of the interface. Eq. (4.12) can be solved numerically to evaluate the variation of $\lambda$ across the surface.

Practically, a scanning probe technique is employed to monitor the variation in $\sigma$ across the dielectric surface. Since $\lambda$ is geometry dependent it is necessary to find $\lambda$ as a function of probe location. Due to the variation of probe location a system of integral equations similar to Eq. (4.11) have to be solved. The solution determines the interface charge distribution.

The lower limit of the sensitivity of the surface charge density for the field probe is 0.1 nC/m$^2$ or less for an electric field at 50 Hz [Rerup et al., 1996]. However, the probe technique is only effective in limited situations. There are measurement errors due to the following factors: thickness of the insulator affects $\lambda$, area of surface charging, distance between probe and solid insulator, coexistence of positive and negative charges, and bulk charging. Hence, the analysis of the probe potential outputs is the crucial problem that has to be solved to obtain a method to measure surface charge more accurately. On the other hand, it is experimentally fairly uncomplicated.

4.1.3 Two-photon photoelectric emission

Photoemission spectroscopy is a powerful and an accurate tool for investigating the electronic structure of metals. Photoemission spectroscopy techniques can be used to study adsorbates, oxide formation, surface roughness, and laser cleaning.
By applying an external electric field to a surface, surface charge can be accumulated. In the two-photon photoelectric emission technique the basic idea is that a laser beam impinging the surface will generate photoelectrons. By collecting the photoelectrons it is possible to determine the net amount of surface charge that is accumulated on the surface.

A picosecond Nd:YAG laser system is used; see Fig. 4.3, delivering pulses at the wavelength of 1064 nm with a repetition rate of 10 Hz [Tomas et al., 1999]. This fundamental wavelength is frequency-doubled to 532 nm (green light) by a potassium dihydrogen phosphate (KDP) crystal. The laser beam enters an ultrahigh vacuum chamber with a pressure of the order of $10^{-7}$ Pa, and hits a sample made of gold, which constitutes the photocathode. The anode is placed 5 mm above the photocathode and the electron attracting electric field is delivered by a high-voltage system (0 to 30 kV). A digital multimeter (used as a coulombmeter) measures the emitted photoelectrons.

![Diagram of experimental arrangement](image)

**Figure 4.3** A part of the experimental arrangement for two-photon photoelectric emission from Au.

The photoemitted charge increases with the voltage and seems to limit as a plateau-like saturation. Photoelectrons are generated as a thin disk due to the incoming light and with a diameter that depends on the laser spot size on the target. Image charge and space charge must be considered. Due to Coulomb forces, the electrons are attracted by the image charge that is created in the cathode but repulsive space charge forces also exist between the electrons. Thus the electric field must be stronger than these forces that pull back the electrons to the material. Hence the collected charge increases with voltage and reaches the plateau when the voltage is large enough.

High-energy X-rays could be a problem and one could argue that a high voltage together with electrons might generate high-energy X-rays, which would hit the cathode and induce photoemission of high-energy electrons. If the high voltage increases both intensity and maximum energy of these X-rays might increase and thus the photoemitted charge too from the cathode. It is possible that such phenomena take place but the photoelectric signal is not enhanced once saturation is reached. Therefore these effects seem to be very small.

A lower limit of the sensitivity of the surface charge density is about $5 \mu \text{C/m}^2$ [Tomas et al., 1999]. In the first approximation the photoelectric signals show quadratic law
dependence with the incident laser intensity (two-photon thermally assisted process) in accordance to a two-photon process. Unfortunately, the experimental set-up is complicated and intrusive. Further, the technique is only useful in the laboratory and not outdoors. It cannot be ascertained that the contribution to the photoemission is only a surface effect; the bulk may contribute [Tomas et al., 1999].

4.2 Introducing second harmonic generation

Second harmonic generation (SHG) is a well-known and widely used process in nonlinear optics and was demonstrated on surfaces by Bloembergen et al. [Bloembergen et al., 1968] in the end of the sixties. A comprehensive theoretical description of the various contributions to SHG is for example given by Guyot-Sionnest et al. [Guyot-Sionnest and Shen, 1987] [Guyot-Sionnest et al., 1986]. Some basic principles introduce this section, which is then devoted to the SHG theory on surfaces. The basic principles of second harmonic generation are described in section 4.2.1. Sections 4.2.2-4.2.5 describe SHG on surfaces, quadrupolar contribution from localized orbitals, contribution from free electrons and the intensity relationship between surface charge induced SHG and the fundamental wave. For a perfect conductor, the SHG signal is proportional to the square of net amount of surface charge. As discussed in chapter 6, although a strong SHG signal was detected, no surface charge induced SHG was found. The derivation of the mathematical expressions in this section is completely based on the material in [Bloembergen et al., 1968].

4.2.1 Basic principles of second harmonic generation

Second harmonic generation or frequency doubling is present at scattering or reflection at surfaces and in bulks that do not display inversion symmetry. If a spatial asymmetry is present, a second harmonic (SH) wave can be generated. Reflection at a surface and surface charge fulfil this spatial asymmetry. The polarisation, P, is in classical linear optics expressed by the linear relationship

\[ P = \varepsilon_0 \chi^{(1)} \cdot E, \]  \hspace{1cm} (4.14)

where \( \chi^{(1)} \) is the linear susceptibility, \( \varepsilon_0 \) the electric permittivity of free space and \( E \) the electric field strength of the applied optical field. However, a more general description of the polarisation of a medium can be obtained by expressing it as a power series in the electric field strength.

\[ P = \varepsilon_0 (\chi^{(1)} E^1 + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots ) \]  \hspace{1cm} (4.15)

where \( \chi^{(2)} \) and \( \chi^{(3)} \) are the second and the third-order nonlinear optical susceptibilities [Boyd, 1992]. In classical linear optics only the first term is considered such that Eq. (4.15) simplifies to Eq. (4.14) but nonlinear effects commonly have to be incorporated into the theory when dealing with laser beams of high power. If a laser beam with the electric field \( E = E_0 \cdot \cos \omega t \) is reflected at a surface and if the intensity of the beam is high enough it is possible to observe the SH wave at \( 2\omega \). This is illustrated in Fig. 4.4. The incident
wave at the fundamental angular frequency \( \omega \) creates a polarisation including a component at \( 2\omega \) at the surface as can be understood from the second term in Eq. (4.15) since
\[
E^2 = (E_0 \cos \omega t)^2 = E_0^2 \cos^2 \omega t = E_0^2 \left( \frac{1}{2} + \frac{\cos 2\omega t}{2} \right). \tag{4.16}
\]
The polarisation is a driving term in the general wave equation (for wave propagation) that is given by
\[
\nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = -\mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2}, \tag{4.17}
\]
where \( \mu_0 \) is the magnetic permeability of free space.

The solution to the general wave equation renders the electric field vector at the harmonic angular frequency \( 2\omega \).

For example, if a laser beam with infrared light of 800 nm is frequency-doubled a small fraction of this light is converted into blue light of 400 nm.

![Figure 4.4](image)

**Figure 4.4** Second harmonic generation from a surface. Incoming infrared light of 800 nm is marked by the gray beam. After the reflection in the surface two beams with the same reflection angle emerge, the infrared and the SH wave of 400 nm (beam marked in black).

An alternative description of SH generation can be seen in Fig. 4.5. This can be viewed in terms of converting two photons of 800 nm to one photon of 400 nm. This takes place in a single quantum mechanical process.

Second harmonic generation depends on the medium; in a noncentrosymmetric medium the contribution from the bulk is non-vanishing. For example a ruby laser beam can be converted in a quartz crystal to a blue second harmonic wave [Maker et al., 1962]. Phasematching has also to be considered and the rotation angle of the crystal, i.e. the angle between the optic axis and the propagation vector, is of utmost importance [Boyd, 1992]. Second-order processes are forbidden in centrosymmetric media due to symmetry considerations, but they are never forbidden at the surface layers as the centrosymmetric symmetry is broken at the surface. However, liquids, gases, amorphous solids (such as glass), and many crystals with inversion symmetry have vanishing bulk susceptibilities.
Since the SHG is a two-photon process it displays a quadratic-law dependence between the fundamental wave intensity at $\omega$ and SH wave intensity at $2\omega$. This can be expressed as

$$I_{2\omega} = \text{const} \cdot I_{\omega}^2,$$

where the constant is specific for the material. The constant depends on many parameters, e.g. the surface charge. Eq. (4.18) can be deduced from the solution to the general form of the wave equation (4.17) and substituting the polarisation with Eq. (4.15) [Boyd, 1992]. $I_{2\omega}$ depends also on the surface roughness, the pressure, and if the sample is a thin film or a solid material.

### 4.2.2 Second harmonic generation on surfaces

Bloembergen et al. studied the optical second-harmonic generation in reflection from media with inversion symmetry [Bloembergen et al., 1968]. A brief introduction to the theory of the second harmonic generation at surfaces is presented in this section. A more in depth presentation can be obtained from different books and articles in nonlinear optics, [Shen, 1984], [Bennemann, 1998], and [Liebsch, 1997].
Fig. 4.6 shows a sketch of a centrosymmetric medium where the inversion symmetry is broken at the surface.

$$\chi^{(2)}_{\text{surface}} \neq 0$$

$$\chi^{(2)}_{\text{bulk}} = 0$$

Figure 4.6 A schematic view of second harmonic generation at a surface.

The various terms of the nonlinear polarisation can be derived as follows. The interaction Hamiltonian is given by

$$H_I = -\bar{P} \cdot \vec{E}(\bar{R},t) - \bar{M} \cdot \vec{B}(\bar{R},t) - \bar{Q} : \nabla_x \vec{E}(\bar{R},t)$$

(4.19)

with

$$\bar{P} = -e \bar{x}$$

(4.20)

$$\bar{M} = -\frac{e}{2m} (\bar{x} \times \bar{p}) = -\frac{e}{2m} \bar{L}$$

(4.21)

$$\bar{Q} = -\frac{1}{2} e \bar{x} \bar{x},$$

(4.22)

where \(\bar{p}\) is the momentum, \(\bar{P}\) is a dipole operator, \(\bar{Q}\) is a quadrupole operator, \(\bar{M}\) is a magnetic dipole operator, \(\bar{R}\) is the origin of the unit cell of the crystal and \(\bar{x}\) is the relative displacement operator. The double dot notation denotes a tensorial contraction. The total current density, \(\vec{J}\), due to all electrons is given by

$$\vec{J} = N \left[ \frac{\partial}{\partial t} \langle \bar{P} \rangle_{\text{cell}} + \nabla_x \times \langle \bar{M} \rangle_{\text{cell}} - \frac{\partial}{\partial t} \nabla_x \langle \bar{Q} \rangle_{\text{cell}} \right],$$

(4.23)

where \(N\) is the number of unit cells per unit volume and \(\langle \rangle_{\text{cell}}\) is the expectation value for all the electrons in the cell. The first term in Eq. (4.23) can be understood from

$$-Ne \frac{\partial \bar{x}}{\partial t} = -Ne \bar{v}$$

(4.24)
and thus is a current. The second term is also a current and appears in the classical electrodynamics. The third term is a quadrupolar term that exists if the electric quadrupole moment depends on time and is similar to the first term which is non-zero if the dipole moment depends on time.

By expanding $E$ and $B$ as

\begin{align}
E(R,t) &= \sum_\omega E(R,\omega)e^{-i\omega t} \\
B(R,t) &= \sum_\omega B(R,\omega)e^{-i\omega t}
\end{align}

and using time-dependent perturbation theory, the mathematical expressions in section 4.2.3 can be derived.

### 4.2.3 Quadrupolar contribution from localized orbitals

The lowest-order nonlinear contribution from bound electrons in non-magnetic crystals with inversion symmetry can be estimated following the procedure in [Bloembergen et al., 1968]. From bound electrons for a cubic or isotropic material in the low-frequency approximation the nonlinear source term is

\begin{equation}
P_{\text{NL},0}(2\omega,\omega \to 0) \approx \frac{3}{4\Pi \hbar}\chi^L_0(E_j \nabla_j E_j - E_j \nabla_j E_j),
\end{equation}

$I_0$ is the density of valence electrons and Einstein summation is used to sum over $j=x,y,$ and $z$. The linear susceptibility is given by

\begin{equation}
\chi^L_\omega (\omega) = \frac{2 I_0}{\hbar \omega_0} \langle 0 | x^2 | 0 \rangle,
\end{equation}

where $|0\rangle$ denotes the ground state in the unperturbed system and $x^2$ comes from the quadrupolar operator. The factor $\hbar \omega_0$ is an average energy (closure approximation) [Bloembergen et al., 1968]. The SHG of light in a medium with inversion symmetry was first detected in calcite by Terhune and co-workers [Terhune et al., 1962]. The contribution to the SHG signal came from a quadrupolar type of interaction. In section 4.2.4, Eq. (4.27) will be included in a general form of the nonlinear polarisation. The contribution to the nonlinear polarisation from the free electrons is derived in section 4.2.4.

### 4.2.4 Contribution from the free electrons

Interband transitions, e.g. in KBr where the 3d and 4s bands overlap with the 3p band, influence the agreement between theory and experiments. This is because the effective density of electrons in valence bands is higher. Thus, if $\omega$ or $2\omega$ are close to an interband transition, a correction term has to be added to the polarisation. If there are no interband transitions,
transitions of the valence electrons then it is possible to have a classical approach. The low-frequency approximation above is not applicable here [Bloembergen et al., 1968]. In addition the magnetic-dipole contribution (from the motion of the electrons) cannot be neglected [Bloembergen et al., 1968] The nonlinear source terms of the polarisation that will be derived are in a form appropriate for comparison with the bound-electron contribution. The symmetry properties of the core electrons are the same as for the conduction electrons.

The free electrons in the conduction band are treated as an electron gas where the individual electrons have an average effective mass $m^*$. The hydrodynamic equation of motion for the average velocity $\bar{v}$ can be written as

$$\frac{\partial \bar{v}}{\partial t} + \bar{v} \cdot \nabla \bar{v} = -\left(\frac{e}{m^*}\right)(\bar{E} + \bar{v} \times \bar{B}).$$

(4.29)

There is further the Maxwell equation

$$\nabla \cdot \bar{E} = \frac{-e(n - n_0)}{\varepsilon_0}$$

(4.30)

and the continuity equation

$$\frac{\partial n}{\partial t} = -\nabla \cdot (n \bar{v}),$$

(4.31)

where $n$ is the number density of electrons and $n_0$ is related to $n$ by the expansion

$$n = \sum_{k=0}^{\infty} n_k e^{-ik\omega t}.$$  

(4.32)

The electric current density is given by

$$\bar{J} = -ne\bar{v}.$$  

(4.33)

By expanding the average velocity $\bar{v}$ (and $\bar{E}$ and $\bar{B}$ in the same way) as

$$\bar{v} = \sum_{k=1}^{\infty} \bar{v}_k e^{-ik\omega t} + \text{complex conjugate terms}$$  

(4.34)

and solving Eqs (4.29), (4.30) (together with Eq. (4.23), Eqs (4.25-4.26) and (4.31-4.34)) by successive approximations the nonlinear part of the second order polarisation created in the electron gas is formed as

$$\bar{P}_{\text{conductor, media}}^{\text{NL}}(2\omega) = \frac{\bar{P}_{\text{conductor}}^{\text{NL}}(2\omega)}{2i\omega} = -\frac{\epsilon}{2i\omega} (n_0 \bar{v}_2 + n_i \bar{v}_1) =$$

$$\left(\delta - \beta\right)(\bar{E}(\omega) \cdot \nabla)\bar{E}(\omega) + \beta \bar{E}(\omega)(\nabla \cdot \bar{E}(\omega)) + a\bar{E}(\omega) \times \bar{B}(\omega)$$

(4.35)
according to [Bloembergen et al., 1968]. The relations between the coefficients are given below. The second term in Eq. (4.35) stems from both electric and magnetic contributions from the bulk (see Eq. (4.38)). Normally, the electric polarisation $\overline{P}$ is defined as

$$\overline{P} \rightarrow \sum_{\text{surf}} \frac{e \overline{F}}{\Delta V} \quad \text{as} \quad \Delta V \rightarrow 0 ,$$

and includes the volume of consideration and $\overline{J}$ is given by

$$\overline{J} = -ne \overline{v} = - \frac{\partial (ne \overline{F})}{\partial t} = - \frac{\partial \overline{P}}{\partial t}$$

where $n$ is the number density. Eq. (4.37) together with Eq. (4.36) are similar to the first term in Eq. (4.23). The denominator, $2i\omega$, in Eq. (4.35), originates from the time derivative of the polarisation in Eq. (4.37). To obtain the third expression in Eq. (4.35) $\overline{J}$ is expanded in $\overline{v}$ and the second order terms are collected.

Four different source terms contribute to SHG according to Eq. (4.35) together with the non-centrosymmetric contribution from the surface (adsorbates can also be included into the surface term). The nonlinear polarisation can be expressed as

$$\overline{P}_{\text{NL}}(2\omega) = (\delta - \beta - 2\gamma)(\overline{E}(\omega) \cdot \nabla)\overline{E}(\omega) + \beta \overline{E}(\omega)(\nabla \cdot \overline{E}(\omega)) + \overline{\gamma}(\overline{E}(\omega) \cdot \overline{E}(\omega))$$

or equivalently

$$\overline{P}_{\text{NL}}(2\omega) = (\delta - \beta)(\nabla \times \overline{E}(\omega) \cdot \nabla)\overline{E}(\omega) + \beta \overline{E}(\omega)(\nabla \cdot \overline{E}(\omega))$$

$$+ a \overline{E}(\omega) \times \overline{B}(\omega) + \chi^{(2)}_{\text{surface}} : \overline{E}(\omega) \cdot \overline{E}(\omega) \quad \text{.}$$

The transformation from Eq. (4.38) to Eq. (4.39) is seen from the identity

$$\overline{E} \times (\nabla \times \overline{E}) = \frac{1}{2} \overline{\nabla}(\overline{E} \cdot \overline{E}) - (\overline{E} \cdot \overline{\nabla})\overline{E}$$

and the Maxwell equation

$$(\nabla \times \overline{E}) = i \omega \overline{B} .$$

The coefficients $\alpha, \beta, \gamma$ and $\delta$ are called nonlinearities and $\alpha$ is given by

$$\alpha = (2i\omega)\gamma .$$

For an isotropic (or cubic) insulating (valence electrons) medium, in the low-frequency limit [Bloembergen et al., 1968] (see Eq. (4.27) and Eq.(4.38)),
For free electrons (plasma abbreviated ‘pl’) the nonlinear plasma contribution must be added. The nonlinearities are [Bloembergen et al., 1968]

\[ \beta_{pl} = \frac{e}{2m\epsilon_0 \omega} \]  
\[ \gamma_{pl} = \frac{1}{2i\omega} \alpha_{pl} = -\frac{n_0 e^3}{8\epsilon_0 m \epsilon_0 \omega^3} = \beta_{pl} \left( \frac{\omega_{pl}^2}{4\omega^2} \right) \]

The nonlinearities are additive for free electrons and bound electrons [Bloembergen et al., 1966]:

\[ \alpha = \alpha_{pl} + \alpha_b \]  
\[ \beta = \beta_{pl} + \beta_b \]  
\[ \delta_{pl} = \beta_{pl} + 2\gamma_{pl} \]

where ‘b’ stands for bound electrons, and

\[ \omega_{pl}^3 = \frac{n_0 e^2}{\epsilon_0 m} \]

is the angular plasma frequency.

The first two terms in Eq. (4.39) are of electric quadrupole character and the contribution is determined by \( \delta \) and \( \beta \). The third term corresponds to the magnetic dipole contribution and determined by \( \alpha \). The fourth term describes the electric dipole source from the broken symmetry at the surface. The terms in Eq. (4.39) depend on the polarisation direction of the second harmonic output and sometimes a term exists in the surface but not in the bulk. This is one good reason for separating the bulk from the surface as depicted in Fig. 4.6.

The nonlinear polarisation can always be expressed as Eq. (4.39) regardless of the mechanism and model for the nonlinearity. These phenomenological relationships are valid irrespective of whether the electrons are free or bound.

For metals usually only the first atomic layers contribute to SHG [Weber and Liebsch, 1987]. Bloembergen et al. [Bloembergen et al., 1966] showed that the electrons of the 4d-valence band make a comparable contribution to that of the conduction electrons to SHG in silver and gold. For insulating materials and semiconductors (using below-bandgap excitation) the bulk contribution can be sizeable and may even dominate the contribution to SHG.

For metal surfaces the plasma contribution to the nonlinearity is usually larger than the nonlinear contribution arising from interband transitions of the valence electrons. The only
way of finding the correct $\delta$ and $\beta$ is to calculate the actual potential at the boundary. This should be done for appropriate wave functions for the surface state rather than the bulk and then determine $J_N^d$ for these states.

### 4.2.5 Intensity relationship between surface charge induced second harmonic generation and the fundamental wave

The SHG signal due to surface charge can be obtained from the nonlinear polarisation [Corn et al., 1984]. Electric field induced SHG is deduced from a dc field independent nonlinear polarisation $P_0$ and a dc field dependent nonlinear polarisation $P_1$:

$$P_0(2\omega) = (\delta - \beta)(E(\omega) \cdot \bar{\nabla})E(\omega) + \beta E(\omega) (\bar{\nabla} \cdot \bar{E}(\omega))$$

$$+ a\bar{E}(\omega) \times \bar{H}(\omega) + \chi^{(3)}_{\text{surface}} : \bar{H}(\omega) \cdot \bar{E}(\omega) \tag{4.50}$$

$$P_1(2\omega) = \chi^{(3)}_a \bar{E}_d \left| E(\omega) \right|^2 + \chi^{(3)}_b \bar{E}(\omega) \left[ \bar{E}_d \cdot \bar{E}(\omega) \right], \tag{4.51}$$

The total polarisation is the sum of $P_0$ and $P_1$ [Corn et al., 1984] where the latter polarisation is a third order nonlinear optical effect. The polarisation at $2\omega$ is the result of the second order interaction of an optical field at $\omega$ and a static field. This effect is for example used in electric field induced second harmonic in the field of nonlinear optics and in nonlinear electroreflectance measurements.

The signal is proportional to the square of the total nonlinear polarisation and given by

$$I_{2\omega}(E_\omega) \propto a + b^2 \cdot (E_d - c)^2 \tag{4.52}$$

where $a,b,$ and $c$ are given by $\left| \text{Im} P_0 \right|^2$, $(\chi^{(3)}_a + \chi^{(3)}_b) \left| E(\omega) \right|^2$ and $\text{Re} P_0 / b$, respectively.

For a perfect conductor Eq. (4.52) can be written as

$$I_{2\omega}(\sigma) = a + b^2 \cdot \frac{(\sigma - c)^2}{\varepsilon_0} \tag{4.53}$$

Thus recording the second harmonic intensity vs electric field could provide information about surface charges.

### 4.2.6 Polarisation ($\phi$) and incident angular ($\theta$) dependence

Imagine the surface and the incident plane in Fig. 4.4. We define $\phi$ as the angle between the light polarisation direction and the plane of incidence. When $\phi$ equals $\pi/2$ the light is perpendicular to the incident plane (s-polarised) and when $\phi$ is zero the laser light is parallel to the incident plane (p-polarised). P-polarised light is sensitive to the breaking of the centrosymmetry at the surface. The frequency-doubled light generated by s-polarised
laser light arises only from higher order effects and surface roughness [Tomas et al., 1999].

Nonlinear dominant surface terms are responsible for a $\cos^4 \phi$ dependence of the SH intensity. We define the incidence angle, $\theta$, as the angle between the surface and the incident laser light direction. The $\theta$ dependence is roughly determined by $\sin^2(\theta)\cos^4(\theta)$ [Bloembergen et al., 1968].

4.3 Measurements of electric fields within a bulk volume using Stark effect in combination with the GASMAS technique

This section discusses the possibility to measure electric fields within polymeric materials using the Stark effect in combination with so called gas in scattering media absorption spectroscopy (GASMAS). Knowledge about the internal state of an insulator can reveal defects that manufacturers may oversee. Insulators with defects may fail immediately when energized. Below the principle for a potential GASMAS experiment is described.

4.3.1 Gas in scattering media absorption spectroscopy

GASMAS (gas in scattering media absorption spectroscopy) is a new method to investigate free gas in scattering media [Sjöholm et al., 2001] [Somesfalean et al., 2002] [Alnis et al., 2003]. It seems to be possible to use this technique to monitor an electric field within a bulk volume.

In the experiments (referred to above) the radiation from a diode laser, with a wavelength tuned to an absorption line for the gas investigated, is focused into an optical fibre, which brings the laser light to the sample. The laser injection current is swept at a low (few Hz) repetition frequency allowing a linear scan over the absorption line. The sample is placed on a long-pass coloured-glass filter, which is attached directly to the cathode surface of a photomultiplier. The lower and upper boundaries of wavelength sensitivity of the experimental set-up are constituted by the filter and the detector, respectively. The PMT gain is adjusted by changing the negative supply voltage to achieve high amplification and linearity in the detected signal. A sine wave modulation in the 50 kHz range is superimposed on the current ramp and the absorption signal is detected at the second harmonic of the modulation frequency using a lock-in amplifier. The absorption and the light intensity reaching the detector is proportional to the peak-to-peak value of the wavelength modulation spectroscopy (WMS) signal. The GASMAS signal, which is related to the gas concentration, is calculated by dividing the peak-to-peak value from the WMS signal with the interpolated intensity of the direct signal at the line centre [Sjöholm, 2001].

In Fig. 4.7, an example of an experimental set-up is shown. The diode laser light is focused into the optical fibre. The laser frequency is tuned by using a diode laser driver that regulates the current to the diode laser. By changing the current to diode laser driver, the diode laser power is also changed. The time axis on the oscilloscope can also be considered as a frequency or wavelength axis. The absorption dip cannot be seen because it is too small. The frequency generator sets the frequency of the current ramp. Another
frequency generator superimposes a 55 kHz sine wave on the current. Channel 1 on the oscilloscope measures the direct signal and channel 2 the frequency modulated WMS signal. Channel 2 is shown in the lower picture of Fig. 4.8 which shows data from a 20 mm thick slab of apple. The second harmonic signal resembles the second derivative of the direct signal and contains no offset. The first derivative, which could also have been chosen on the lock-in amplifier, contains an offset, and could be more difficult to handle in the presence of fluctuations.

![Diagram of experimental set-up](image)

**Figure 4.7** The experimental set-up.
4.3.2 Phase sensitive detection

Phase sensitive detection and narrow-band amplification is achieved in a lock-in amplifier which receives a reference and a weakly modulated signal at the reference frequency. The signals are mixed in a multiplier. The result is sum and difference frequencies. By using a low-pass filter the difference of the frequencies is obtained. By adjusting the phase difference to zero and choosing the same frequency of the reference- and the input signals, we achieve a DC output proportional to the amplitude of the absorption signal. Fourier analysis of the power of the transmitted light shows signal components at \( f \) (modulation frequency of 55 kHz), \( 2f \), \( 3f \), etc. The WMS signal is taken at \( 2f \), which is selected on the lock-in amplifier.

4.3.3 Detection of Stark shifts using the GASMAS approach

Certain molecular species, such as nitric acid and ammonia, exhibit strong Stark shifts in an external electric field [Höjer, 1990]. Oxygen, which has been studied much with GASMAS, can be investigated at 760 nm. Ammonia absorbs at 1.23 μm.

The electric dipole moment of ammonia is \( 4.9 \times 10^{-30} \text{ Cm} \) with an estimated accuracy of 1 % [Höjer, 1990]. The Stark effect in the absorption can be observed when the probe molecule...
has fundamental bands with appreciable oscillator strength and a sufficiently large electric dipole moment, as for ammonia. The calculated Stark shift according to Sasada [Sasada, 1984] is of the order of few GHz when using an external field of 2.5 MV/m.

Two electrodes, i.e. two thin plates, made of aluminium, together with a high-voltage system generate an external electric field. The plates surround the sample. The gas and a part of the system are contained in an earthed cell (cathode), and the laser-detector direction is parallel to the plates. The cathode and the optical bench are earthed as well as everything else except the anode. A rod of Delrin plastic isolates the anode from the ground. Electric fields can be applied up to approximately 3 MV/m without causing an electrical breakdown in air at ambient pressure. This means that a 4 cm thick sample needs 120 kV to reach this threshold. Sasada [Sasada, 1984] used a dc Stark field of 2.5 MV/m and with a modulation amplitude of 0.5 MV/m. The desirable effect of applying an alternating external electric field in the GASMAS experiment is a change of the WMS signal.

In Fig. 4.9 a schematic absorption profile is shown and the laser frequency is tuned to position of the vertical arrow. Perturbation of the absorption is achieved through the Stark effect, which shifts molecular transitions into or away from the fixed-probe laser frequency. The change in absorption due to the applied electric field should be quantified.

![Figure 4.9](image-url)  
*Figure 4.9* The absorption and a sensitive electric field probing point are indicated.
Chapter 5

Equipment and analysis techniques used for the experiments

Equipment and analysis techniques used during the experimental work performed in this PhD thesis work are presented in this chapter. A Lidar system was used for remote fluorescence and LIBS measurements, and a fluorosensor served as a detection system. Laboratory experiments (fluorescence) have been carried out by using the fluorosensor only. An optical parametric oscillator (OPO) has been used in the multi-wavelength excitation experiments. The terawatt laser system was used in the second harmonic generation experiments. Imaging of fungal growth has been based on principal component analysis (PCA) technique.

5.1 Lidar system

A mobile Lidar system [Weibring et al., 2003a], based on all solid-state laser technology and housed in Volvo F610 truck was used in several of the LIF and LIBS experiments; see Fig. 5.1 and Fig. 5.2. Normally, the light source used was a frequency-tripled Nd:YAG laser operating at 355 nm. The laser light pulses had a duration of about 4-5 ns and were delivered at a 20 Hz repetition rate.

The light was sent out from the Lidar truck, by a roof-top transmission and receiving optical dome that could be horizontally rotated 360 degrees using a computer controlled stepper motor with a resolution of 0.0035 degrees. Similarly, a folding mirror could handle the vertical directionality of the light in the range of −10 to +55 degrees with a resolution of 0.011 degrees. That corresponds to a resolution of 3.7 mm and 12 mm, respectively, at the target insulators which were mounted at a 60 m distance from the Lidar system. The beam diameter at the target was 3 cm as adjusted with a Galilean transmitting telescope, and the separation between adjacent measurements points was 3 cm. The change in position of the laser beam at the target due to mechanical instability of the whole truck was estimated to about 1 cm. The laser transmitter system is fully computer controlled and located in over-pressured housings to protect the optics from moisture and dust. The transmitter, dome and light receiving unit are illustrated in Fig. 5.1.

Part of the laser-induced fluorescence light was captured by a 40-cm-diameter Newtonian telescope via the roof-top transmission and receiving optical dome, and focused into an optical fibre. A GG 385 coloured-glass cut-off filter was inserted in the optical path to block the elastically scattered laser light while passing most of the fluorescence light for wavelengths longer than 385 nm. An optical fibre with a 600 μm core diameter and a
numerical aperture of 0.22 guided the fluorescence light to an optical multi-channel analyser (OMA) system, consisting of

![Diagram of optical system](image)

**Figure 5.1** Dome and light receiving unit of the Lidar system.

![Schematic overview of part of the Lidar system](image)

**Figure 5.2** Schematic overview of part of the Lidar system.

a crossed Czerny-Turner spectrometer, a time-gated image intensifier, and a CCD camera; see Fig. 5.3. An image intensified CCD camera from Andor (DH50125U-01) was used for this purpose. The Peltier cooled detector had a CCD array of 1024x128 pixels where the
128 vertical pixels were binned. The resolution of the OMA system, set by the 100 \( \mu \text{m} \) slit width, was 2.2 nm, and the spectrum could be recorded up to 805 nm. A time gate of 40-50 ns was used during the experiments to suppress ambient light. The time gate was delayed with respect to the transmission of the laser pulse, to match the arrival of the fluorescence burst, some 400 ns later. Spectra from the OMA system were gathered by a data collection computer that stored the spectrum together with information about the measurement coordinates.

### 5.2 Lidar system for laser-induced breakdown spectroscopy

When the Lidar system was used for LIBS experiments, the laser beam was expanded and transmitted through a low- aberration telescope which was designed with the aid of a raytracing program (Linos Photonics, WinLens 4.3). One planoconcave and two planoconvex lenses with focal lengths of -25, 300 and 1000 mm and spaced by ~20 and ~25 cm were employed. In order to avoid optical damage of the aluminized folding mirror the laser pulse energy in the 4-5 ns long pulses at 355 nm, generated by the Nd:YAG laser, was normally limited to 180 mJ,. The measured focal spot diameter at the target was about 5 mm (as compared to the theoretical value calculated one at 0.7 mm based on a TEM\(_00\) laser profile). The intensified CCD detector was activated with a temporal window of typically 150 ns to observe the emission lines from the plasma [Grönlund et al., 2005].

![Fluoresensor diagram](image)

**Figure 5.3** The fluoresensor consists of a nitrogen laser, a dye laser, some optical components and an optical multi-channel analyser system. (From [Klinteberg et al., 2005])
5.3 Fluorosensor

A compact point-measuring fluorosensor was used for the detection of fluorescence [Klinteberg et al., 2005]. The fluorosensor contains two lasers, a nitrogen laser (wavelength 337 nm) and a dye laser (in this case 4,4'-diphenyl-stilbene DPS, operating at a wavelength of 405 nm) which is pumped by the nitrogen laser. A motorized flip-in mirror makes it possible to switch between the two lasers. The pulsed (3 ns, 15 Hz, ~1 μJ) nitrogen laser produced excitation light that was expanded in a telescope (two lenses) and guided through a single 600 μm diameter fused silica optical fibre to the sample under investigation. The end of the fibre was located near the sample. A small volume of the sample close to the tip of the fibre absorbed the laser light. The fluorescence light, induced typically on a nanosecond time scale, was spatially emitted in all directions. A fraction of it was collected by the same fibre and directed to the OMA system described above. Time-integrated accumulation of fluorescence emission was obtained by using a time gate of 100 ns. The time gate makes it possible to integrate fluorescence light only, and the gate is synchronized relative to the laser. The gating procedure enables ambient light to be suppressed by approximately a factor of 10^6. Each spectrum was stored by a PC, which was used to control the acquisition.

5.4 Optical parametric oscillator system

The Lidar system also has multi-wavelength excitation capabilities. The light source is a rapidly tuneable Nd:YAG pumped optical parametric oscillator (OPO) combined with a doubling- and difference frequency generating system that makes it possible to produce narrow band light in the wide range from UV to mid IR, i.e., 220-1800 nm and 2600-4300 nm with maximal pulse energies of 100 mJ and 20 mJ, respectively [Weibring et al., 2004]. Wavelength, line width and power stability are monitored in real time by a surveillance system that is based on a Fabry-Perot interferometer. The average linewidth is better than 0.2 cm⁻¹ at a pulse length of 3-4 ns.

5.5 Terawatt laser system

A brief description of the terawatt laser system, which has been used in parts of the experiments on SHG, is presented here. The terawatt system was here not used because of its high peak power but just because it was the most conveniently operated sub nano-second source at the department at the time of the SHG measurements. A good description of the terawatt laser which is the main system of the Lund high-power laser facility is given in [Svanberg et al., 1994]. Although much has been changed since the paper was published the principle is still the same.

The research carried out using the terawatt laser generally requires high optical field strengths, for example generation of X-rays from a laser produced plasma and white-light generation with applications in medicine, biology and chemistry.

The terawatt laser relies on chirped pulse amplification (CPA), see Fig. 5.4, to achieve high optical intensities from a system that fits on top of a few optical tables. The fundamental idea is to stretch a short pulse in time before amplification. This decreases the
peak intensity in the amplifier stage and does not to avoid damage of the optical components. In this way large beam diameters and consequently large and expensive laser systems are avoided.

A diagram of the laser system is shown in Fig. 5.5 and the components are explained below. The gain medium used in the terawatt laser system is titanium doped sapphire (Ti:S) crystals. Ti:S can easily be pumped by green light at 532 nm from a frequency-doubled Nd:YAG laser. Due to the short lifetime of Ti:S in its excited state (3 μs), flashlamp pumping is unsuitable. The gain profile of Ti:S is spectrally broad and enables amplification of very short laser pulses (50 fs); the minimum duration of a laser pulse is inversely proportional to the spectral bandwidth.

**Figure 5.4** Chirped pulse amplification. The oscillator delivers a short pulse, A, that is stretched in time by the stretcher. The stretcher decreases the pulse peak intensity through temporal stretching, B. The pulse is then amplified, C, and finally compressed into a pulse with a shorter time duration and a higher peak power, D. [Svanberg et al., 1994].
The terawatt laser system uses an Ar\textsuperscript{+}-laser pumped Kerr-lens mode locked Ti:S oscillator that produces pulses with a time duration of about 100 fs. The repetition rate of the oscillator is 80 MHz and the average power approximately 350 mW (4 nJ/pulse). The group velocity dispersion in the oscillator limits the pulsewidth, but the spectral bandwidth allows for much shorter pulses. The mode-locking is obtained by exploiting the Kerr-effect. The change in the refractive index is proportional to the square of the electric field (the Kerr effect). Due to the self-focusing that follows from this effect the Ti:S crystal can act as a lens. Three adjacent longitudinal laser modes with different frequencies.
Figure 5.6  Mode-locking can be described by superposition of waves, in this case three modes are superposed and within a specific time interval constructive interference takes place and yields a short pulse [Roos, 2001].

and the sum of these is shown in Fig. 5.6. [Roos, 2001]. Fig. 5.7 illustrates Kerr-lens mode locking. Constructive interference occurs at one time and the high-intensity light is focused due to the Kerr effect. Unfocused continuous light from modes with random phases can be blocked.

Figure 5.7  Kerr-lens mode locking [Roos, 2001].
The 100 fs pulses from the oscillator are stretched approximately 2500 times. This is done in a grating and lens arrangement shown in Fig. 5.8a. It is a double-pass arrangement which means that the light is going through the system and is then being reflected and passes the optical components a second time on its way back. The low-frequency components emerge first after the reflection back through the system due to a shorter optical path.

In the compressor, see Fig. 5.8b, the opposite happens. The stretched pulse is converted to an ultra-short pulse. It is important that all frequency components experience the same amount of amplification to obtain a short pulse duration.

![Figure 5.8](image.png)

**Figure 5.8** *The principle for the grating stretcher (a) and the compressor (b) [Svanberg et al., 1994]*.

The stretched, horizontally polarised oscillator pulse is injected into a regenerative Ti:S amplifier, see Fig. 5.5. By switching the transmitted polarisation, using Pockels cells, only ten pulses per second are allowed to be amplified. This effectively lowers the repetition rate from 80 MHz to 10 Hz.

The final power enhancement is performed in a four-pass Ti:S amplifier crystal to attain 450 mJ. Two high-energy Nd:YAG lasers with frequency-doubled green light pump this amplifier.
At this stage a part of the pulse is sent to a second multi-pass amplifier and a vacuum compressor to obtain pulses of 35 fs and 1.2 J. This part is not shown in Fig. 5.5 because it was not used in the experiment presented herein.

Finally, the pulse is compressed. After the compressor the high frequency part of the pulse has caught up with the low frequency part, and the pulses are short (~50 fs). The pulse energy is usually not allowed to exceed 100 mJ (2 TW) in order to keep the effects of the non-linear interaction with air small.

Presently, the system has been upgraded so it is possible to use the system for experiments, which demand more than 30 TW. The new system consists of two beams; one of the beams has a maximum energy per pulse of 250 mJ (standard level is 100 mJ) and the other beam has a maximum energy per pulse of 1.2 J. Both beams produce pulses with a duration less than 50 fs. The SHG experiments have been performed in the so-called application lab at the Lund High Power Laser Facility. A reflection from a mirror in the terawatt laser was sent to the application lab, while the main output of the system could be used for other experiments.

5.6 Principal component analysis

Principal component analysis (PCA), also known as the Hotelling transform or the Karhunen-Loève transform, is a classical statistical method and has proven to be extremely useful in the study of physical and biological systems and phenomena. The objective of a PCA is to reduce the dimension of data to representative principal components (PCs) without losing much information and to simplify the representation. The PCA is an efficient data compression technique if the variables are correlated.

The first step in analysing multivariate data using PCA is computing the mean vector and the covariance matrix. A PCA can be an eigenanalysis of the covariance matrix (without dividing by the standard deviation). The principal components (PCs) are found by calculating the eigenvectors of the covariance matrix of the data. By ordering the eigenvectors of the order of descending eigenvalues, one can create an orthogonal basis with the first eigenvector (PC) having the direction of largest variance (=eigenvalue) for the data. This gives the PCs of the order of significance. One can now decide to ignore the PCs of lesser significance. Some information is lost when the data is compressed but if the variances are small, one does not lose much.

PCA is a powerful visualization technique. Use of the top several components may lead to more efficient data analysis and suppression of the effects of noise. Direct uses of PCA are identification of groups of inter-related variables and highlighting the variables which contain similar or completely independent information [Esbensen, 2002].

The difference between each spectrum and the mean spectrum can be expressed as a sum of the PCs. Thus a PCA shows the differences between analysed spectra. If no intensity normalisation of the spectra is performed PC 1 will normally contain the intensity variations. During the analyses intensity normalisations have been carried out and spectral differences are captured with PC 1 as well as with PC 2. If an insulator surface is scanned with laser light, a PCA technique can be used to obtain information about what parts of the surface that is more fungi covered than others.

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In this study most experiments have compared two parameters only. By applying a PCA for imaging it is assumed that the most interesting information is related to PC 1 and PC 2. Weak correlations almost buried in noise can be difficult to capture with a PCA since only the first PCs are considered.

Assume that we have a number of spectra that should be analysed with a PCA. Sometimes the spectra look very similar and are not so easy to distinguish by a direct look. Fig 5.9 shows a spectrum expressed as a linear combination of mean spectrum, PC 1 and PC 2. Since the spectra only have minor differences in the shape but contain intensity variations, the mean spectrum and PC 1 look similar. The PCA also renders a score plot (i.e. showing all spectra projected to a pair of PCs); see Fig. 5.10. Fluorescence images can be based on identified groups of spectra in a score plot.
Figure 5.9  A spectrum can be expressed as one times the mean spectrum and a linear combination of the PCs. In this case -443 of PC 1 and 44 of PC 2 are added to the mean spectrum. $(PC_1, PC_2) = (-443, 44)$ is the point within the circle in Fig. 5.10.
Figure 5.10 A score plot shows spectra projected to a pair of PCs. Artificial spectra have been created and analysed. \((PC_1, PC_2) = (-443, 44)\) is the point within the circle, see Fig. 5.9.
Chapter 6

Discussion of results

6.1 Reflectance measurements

Ozone in the stratosphere absorbs all of the incoming ultraviolet light for shorter wavelengths than about 300 nm. Only the principle for blue sky radiation experiments is shown here. Fig. 6.1 shows a spectrum, captured with a fluorosensor [Gustafsson et al., 2000], of blue sky radiation within the spectral region 333 - 1013 nm.

![Figure 6.1 Spectrum of blue sky radiation detected during 10 s.](image)

Fig. 6.2 shows the reflectance of blue sky radiation from algae on agar-agar.
Figure 6.2 Blue sky radiation reflected from algae on agar-agar detected during 10 s.

A normalised spectrum can be obtained by dividing the curve of Fig. 6.2 with the curve of Fig. 6.1. The quotient is shown in Fig. 6.3. It can be seen that green light is reflected more than blue light, and wavelengths longer than approximately 670 nm have a higher reflectance.

Figure 6.3 Quotient between the curve of Fig. 6.2 and the curve of Fig. 6.1.

Blue sky radiation reflectance from algae on agar-agar, fungal growth (Cladosporium cladosporioides) and clean silicone rubber material have been compared, see Fig. 6.4.
It is possible to use reflectance spectra to discriminate between fungal growth (*Cladosporium cladosporioides*), algal growth and clean material. The reflectance of blue sky radiation from fungal growth is lower than the reflectance from clean material consistent with the observation that the fungal spots are dark. Spectral differences between fungal growth and clean material are shown in Fig. 6.5.

Fungal growth (*Cladosporium cladosporioides*) could readily be discriminated from a clean material by judging the spectral information. Discrimination between fungal growth, algal growth, clean material and other pollutants can be studied with this type of normalised reflectance spectra.
6.2 Laser-induced fluorescence experiments

6.2.1 Laser-induced fluorescence for the detection of algal growth

The experiments are aimed to perform remote imaging of biological growth on insulators. Imaging of algae has been performed on insulators of line suspension type, and on insulators of apparatus type that had a hollow core. All insulators had sheds and sheath of silicone rubber. The fluorescence Lidar system was used and the spectral data were analysed by taking the average intensity for different wavelength bands. A typical fluorescence spectrum showing the signature from algae is shown in Fig. 6.6. Mean intensity in the 670-690 nm band could for example be used with good result for the discrimination between algal contaminated surfaces and non-algal-contaminated ones.

![Figure 6.6](image)

**Figure 6.6** Typical remote spectra obtained from a region with algal growth and a region without algal growth. The 410-500 nm band and 670-690 nm band are shown.

In Fig. 6.7 algal growth on an insulator of apparatus type is imaged. A tripled Nd:YAG laser, emitting radiation of 355 nm, has been used and the recorded fluorescence spectrum from algae constitutes of the two characteristic emission bands, at 685 nm and 730 nm.
Image a) shows a photograph of an insulator covered with algal growth, b) shows the average fluorescence intensity in the 410-500 nm band, while c) shows the average intensity in 670-690 nm band. The ratio of the light fluoresced in the two bands is shown in d), where the dark areas are well corresponding to the regions covered with algal growth. The influence of geometrical artefacts is also eliminated in d).

6.2.2 Laser-induced fluorescence for the detection of fungal growth

The measurements of fungi covered insulators have shown that the fluorescence spectrum from a fungi covered insulator material normally is wider than the spectrum from a clean material. It is explained by the fluorescence from pure fungi, which was shown to start for longer wavelengths; see Fig. 6.8.
The spectrum, with maximum at about 500 nm, shows the fluorescence from Cladosporium cladosporioides only and was accumulated from 150 laser pulses. The spectrum, with maximum at about 430 nm, shows the fluorescence from a clean material. The fluorescence from the fungi is shifted to longer wavelengths.

It is thus possible to understand that increased fungi coverage makes the fluorescence spectrum wider; see Fig. 6.9.
Figure 6.9 a)-e) compare theoretically fluorescence spectra from fungi covered areas with spectra from a clean region. In each plot the same fluorescence spectrum from a clean region is shown. The wider spectra are calculated as a sum of two spectra, a part from the fungi signature and a part from the spectrum of the clean region. a) 50% clean and 50% fungi, b) 40% clean and 60% fungi, c) 30% clean and 70% fungi, d) 20% clean and 80% fungi, and e) 10% clean and 90% fungi. Consequently the fungi coverage can be estimated from the fluorescence signal.

However, if both the fungi species and the amount of growth are changing at the same time (or the material is changed by the infection of fungal growth) a careful study has to be carried out.
Usually the intensity of the fluorescence light depends on many factors such as angle of incidence of the laser light, pulse energy, surface roughness, pulse duration, beam profile and so on. To be able to compare fluorescence spectra, all spectra can be normalised to have the same area. As discussed in section 5.6, if no normalisation of spectra is performed a PCA usually defines PC 1 as the description of intensity and PC 2 as the description of the change of the spectra from the average spectrum. By normalising the spectra to have the same area, PC 1 will instead describe the change of the spectra. A typical spectrum for PC 1 when intensity normalisation has been used is shown in Fig. 6.10. Data are often pre-processed by normalisation and centering to improve analysis performance [Esbensen, 2002].

![Graph showing fluorescence spectra](image)

**Figure 6.10** The difference between fluorescence spectra can be explained by this type of PC. By adding a negative contribution of the PC to the average spectrum, wider fluorescence spectra are obtained, and vice versa.

Fig. 6.11 shows quasi-imaging of fungal growth. Spectra were collected using the Lidar system remotely and compared to spectra collected from clean surfaces in the laboratory using the same excitation wavelength (355 nm).
Figure 6.11 Two insulators were partly covered with fungal growth, the third (PDMSO) and the fourth (EPDM) from the top-left insulator. Spectra were recorded remotely using the Lidar system, and the white pixels show where the insulators were hit by the laser beam. The total image size is about 0.8 m x 1.1 m. For each image point, data from 50 laser pulses were averaged. The total recording time for the image was about 50 minutes. Imaging of fungi covered insulators requires reference spectra (or spectra from clean areas). Fluorescence spectra are shown for the fungi covered PDMSO and EPDM insulators in the upper row and a PDMSO insulator that has been exposed to weather and wind in the lower row. In each diagram the spectra have been normalised to have the same area. Spectra were collected using the Lidar system remotely (wider spectrum) and compared to spectra collected from clean surfaces in the laboratory using the same excitation wavelength (355 nm).
By analysing differences between spectra from adjacent pixels it is possible to obtain information about which regions of the insulator that are more fungi covered. When analysing the spectra of some fungi covered insulators, see Fig. 6.12, the spectra from dark spots were wider, noisier and had a significant lower intensity (un-normalised spectra) than the areas that were less infected.

LIF, as seen above, has proven to be useful in the high-voltage research. To summarize the LIF measurements it has been shown that chlorophyll on a silicone rubber insulator surface can readily be detected, using the fluorescence signature with two characteristic emission bands (at 685 nm and 730 nm), at a distance of 60 m using a Lidar system. The fluorescence from eight fungal species gives wider spectra than the fluorescence from the clean material. The measurements also show that detection of fungi demands better signal-to-noise ratio than the detection of algae. The discrimination between fungal growth and other bio-contaminants can be improved by performing more laboratory experiments. The fluorescence signature of fungal growth has to be compared to that of other pollutants such as dust, bacteria, dirt etc. However, it seems promising to use a combination of the LIF technique and PCA to image fungal growth. It would be interesting to apply the LIF technique to accelerated aged polymeric materials, materials with different hydrophobicities, insulators that have been exposed to different weather conditions and insulators that have been installed in high-voltage systems (AC or DC).

Figure 6.12  Dark spots of fungal growth gave wider fluorescence spectra than those from less infected areas.
6.2.3 Multi-wavelength excitation experiments

To improve the discrimination between fluorescence spectra from fungi and clean insulator materials an optical parametric oscillator system in the Lidar system was used to investigate laser-induced fluorescence for different excitation wavelengths. The choice of excitation wavelengths was based on the information in [Coohill and Sutherland, 1989]. Excitation wavelengths of 250 nm, 290 nm, 337 nm, 355 nm, 375 nm were chosen. The wavelength of 355 nm could be generated by the frequency tripled Nd:YAG laser. The reason for including the wavelength 337 nm was that this is also the emission wavelength of the nitrogen laser which has been used in the laboratory spectroscopy studies of the bio-contaminants. It was found that 355 nm and 375 nm gave the best discrimination. In Fig. 6.13 the excitation wavelengths are compared.
Figure 6.13 a)-e) compare fluorescence spectra (different excitation wavelengths) from fungi covered areas with spectra from a clean region, and the wider spectra are due to fungal growth. The excitation wavelengths: a) 250 nm b) 290 nm c) 337 nm d) 355 nm and e) 375 nm. The best discrimination between fungal growth and clean area was obtained with 355 nm and 375 nm.
6.3 Laser-induced breakdown spectroscopy experiments

The laser-induced breakdown experiments have been carried out for the purpose of evaluating the possibility of detection and removal of salt on metal and high-voltage insulator surfaces. The lower limit for LIBS breakdown at a metal target was about $1.5 \times 10^{12}$ W/m$^2$. A LIBS spectrum from a copper metal target is shown in Fig. 6.14, and the vertical lines correspond to tabular values of prominent emission lines [Lide, 1993] [Fu et al., 1995] [Grönlund et al., 2005].

![Figure 6.14](image)

**Figure 6.14** Remote LIBS spectrum from a copper target. The spectrum was obtained by averaging over 500 laser pulses. The spectral lines (solid lines) are presented in the table.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>427.511</td>
<td>$3d^14s(^3D)5s-3d^14s(^1D)4p$</td>
</tr>
<tr>
<td>465.112</td>
<td>$3d^14s(^1D_2)5s-3d^14s(^1D)4p$</td>
</tr>
<tr>
<td>510.554</td>
<td>$3d^{10}(1S)4p-3d^44s^2$</td>
</tr>
<tr>
<td>515.324</td>
<td>$3d^{10}(1S)4d-3d^{10}(1S)4p$</td>
</tr>
<tr>
<td>521.820</td>
<td>$3d^{10}(1S)4d-3d^{10}(1S)4p$</td>
</tr>
<tr>
<td>578.213</td>
<td>$3d^{10}(1S)4p-3d^44s^2$</td>
</tr>
</tbody>
</table>

Salt was applied to the copper surface and could be detected in the LIBS experiment by observing the sodium D-line at about 589 nm, see Fig. 6.15.

![Figure 6.15](image)

**Figure 6.15** Remote LIBS spectrum from a salt covered copper target in motion. The spectrum was obtained by averaging over 200 laser pulses. The sodium D-line is visible at about 589 nm.
Remote LIBS measurements were tried on a salt covered polymeric insulator surface, but the intensity was too low to create a breakdown spark. To obtain breakdown in salt on a silicone rubber surface a collimated laser beam (LIF Lidar system) was utilized instead and an extra lens (focal length ~ 50 cm, diameter 10 cm) was inserted into the beam path to focus the laser light onto the salt covered insulator target (spot diameter 0.7 mm). An energy of 15 mJ/pulse was sufficient to create breakdown in salt on a silicone rubber insulator surface and to detect the sodium D-line. Fig. 6.16 shows emission lines from a saturated saline solution (~22% salt) on a silicone rubber surface where the sodium D-line clearly can be seen. A pulse energy of 25 mJ was used for this recording. When using the LIBS Lidar system a spot diameter of 0.7 mm was calculated (5 mm in practice). If the laser beam profile and the low aberration telescope had been diffraction limited, there would have been no need for an additional lens and the performance of the optical system would be sufficient for the detection and removal of salt on a silicone rubber insulator.

The number of photons that contributed to the sodium D-line in Fig. 6.16 was determined using a calibrated white light source (200 W calibrated quartz tungsten/halogen lamp, Oriel 63355) with known photon flux. According to the calibration results of the white light source, the spectral irradiance at the position of the lens at 589 nm is 8.3·10^{-6} J/(s·cm^{2}·nm), i.e. 2.5·10^{13} photons/(s·cm^{2}·nm) where the energy of each photon is $hc/\lambda$. The diameter of the lens was 2 inches and the lens was hit by

$$2.5·10^{13}·\pi·(2.54)^{2} \text{photons/(s·nm)} = 5.0·10^{14} \text{photons/(s·nm)}.$$  

One pixel sees 0.5 nm which means that 2.5·10^{14} photons/s was directed towards one pixel. During a detection time of 40 s there are 1.0·10^{16} photons which gave 1.55·10^{6} counts (at 589 nm), with the calibrated white light source at the target point, i.e. 1 count equals 6.4·10^{9} photons. Thus about 6.1·10^{13} photons in the plasma contributed to the sodium D-line (9416 counts) in Fig. 6.16.

![Figure 6.16 LIBS spectrum (LIF Lidar system with an extra lens) from a saturated saline solution on a silicone rubber target. The spectrum was obtained by averaging over 200 laser pulses. The sodium D-line at about 589 nm can clearly be seen.](image-url)
Fig. 6.17 shows a LIBS spectrum, captured by a single laser pulse, that contain the sodium D-line.

![LIBS spectrum](image)

**Figure 6.17. LIBS spectrum from a salt covered silicone rubber target. The spectrum was obtained from a single laser pulse.**

Ablative cleaning could readily be performed and was verified by the disappearance of the sodium D-line, see Fig. 6.18. Parallel investigations of ablative cleaning of cultural heritage have been performed in the Physics Department of the Lund Institute of Technology [Grönlund et al., 2005].

![LIBS spectrum](image)

**Figure 6.18**  LIBS spectrum (solid line) (LIF Lidar system with an extra lens) from a saturated saline solution on a silicone rubber target. The spectrum was obtained by averaging over 200 laser pulses. The removal of salt is verified by the disappearance of the sodium D-line emission (dashed line).

LIBS has successfully been applied for remote detection of salt on metal surfaces. By using a quasi-remote LIBS system salt has also been detectable on a silicone rubber insulator surface.
6.4 Electric field simulations

In the second-harmonic generation experiment, the amount of surface charge was calculated using the finite element method. Section 6.4.1 contains some calculations which were performed during the training period of the numerical analysis, and relate to the work described in Paper 1.

6.4.1 Cavities in dielectric liquids

The finite element method (FEM) has been applied to electrostatic problems, containing no sources and with specified boundary conditions, solved by using the Laplace equation which is given by

\[ \nabla \cdot (\varepsilon \nabla V) = 0, \]  
(6.1)

where \( \varepsilon \) is the permittivity and \( V \) the electric potential. FEM uses the minimum principle meaning that the solution to the Laplace equation is equivalent to minimising the electrostatic energy, \( W(V) \). The mathematical expression for this is expressed as

\[ W(V) = \frac{1}{2} \int_\Omega |\nabla V|^2 \, d\Omega. \]  
(6.2)

FEM has been used on a two-dimensional problem concerning Mid-Gap Laser-Triggered Electrical Breakdown in Liquid Dielectrics, [Larsson et al., 2001]. Larsson et al. had earlier studied pre-breakdown and breakdown phenomena in oil and combined laser-triggering and the laser shadow method together with pre-breakdown current measurements [Larsson et al., 2001]. By doing this, the physical mechanisms and the timing sequence of the dielectric breakdown were revealed.

The electrode gap consisted of two hemispherically-tipped brass electrodes placed in oil. The electric field strength in oil was 12 MV/m which was achieved by using either 50 or 55 kV depending on the adjustable electrode distance that ranged between 4 and 5 mm. Ace [Ace version 3.0], a user friendly FEM software package, rendered the electric field calculations. The boundary conditions were 50 kV or 55 kV applied on the anode and an earthed cathode.

A laser pulse was focused in the middle of the electrode gap, and a pulse energy of 30 mJ was required for plasma formation (‘breakdown threshold’). A gas-filled cavity was formed by the laser-initiated plasma, and the relationship between the expansion time \( t \) of the cavity and the cavity radius \( R \) is

\[ t = R_{\text{max}} \sqrt{\frac{3\rho}{2p_0}} \int_0^{R_{\text{max}}} \left( \frac{1}{1 - \beta} \right)^{3/2} \beta^{1/2} \, d\beta, \]
where \( R_{\text{max}} \) is the maximum radius of the cavity, \( \rho \) is the mass density of the liquid and \( P_a \) is the ambient pressure [Lord Rayleigh, 1917].

Calculations of the development of the electric field distribution in the gap with an expanding and perfectly dielectric cavity are shown in Fig. 6.19 and Fig. 6.20. The relative permittivity of the gas \((\varepsilon_{\text{rel,air}} = 1)\) is less than the one for the oil \((\varepsilon_{\text{rel,oil}} = 2.2)\) which leads to a field enhancement in the cavity, as shown in Fig. 6.19 and Fig. 6.20. In the figures, the electric field strength is represented by the field enhancement factor, which is defined as the quotient between the field strength and the applied voltage.

![Expanding dielectric cavity](image1)

**Figure 6.19** The development of the electric field strength along the central axis of the electrode gap. The cavity expands with a constant step in radius.

![Expanding dielectric cavity](image2)

**Figure 6.20** The development of the electric field strength along the central axis of the electrode gap. The cavity expands with a constant step in time.
The development of the maximum electric field strength in the electrode gap for a perfectly conducting cavity is shown in Fig. 6.21 and Fig. 6.22.

**Figure 6.21** The development of the maximum electric field strength in the electrode gap for a perfectly conducting cavity. The applied voltage was 50 kV.

**Figure 6.22** The development of the maximum electric field strength in the electrode gap for a perfectly conducting cavity. The applied voltage was 50 kV.

From the experimental studies a typical example of breakdown conditions would be an applied voltage of 50 kV with a cavity radius of 1 mm for a 4 mm gap. Fig. 6.23 shows that the calculated breakdown voltage for a perfect conducting cavity is approximately 30 kV which is too low compared to the results of the experiments. This information
reveals that the cavity has not been a perfect conductor. By calculating the electric field strength along the central axis for a cavity radius of 1 mm the critical field for breakdown (22.5 MV/m) was exceeded in the whole oil gap. When the cavity was assumed to be a perfect dielectric (non-conducting) the electric field strength too low to trigger a discharge in the oil between the cavity and the electrodes. The conclusion is that some charge redistribution must occur within the cavity to render the required field enhancement. Still the electric field calculations led to insight in the physical mechanisms and the timing sequence of the dielectric breakdown, as described in Paper 1.

![Figure 6.23](image)

*Figure 6.23* For a given applied voltage, the radius of the cavity is shown that gives rise to breakdown in oil. A perfect conducting cavity is assumed.

### 6.4.2 Second harmonic generation experiments

In the second harmonic generation experiments the FEM software package ANSYS [ANSYS release 5.7] was applied to find the electric field strength (and thus the surface charge) at the gold mirror target and specifically across the whole area where the laser light hit the mirror. A description of the surface charge detection using second harmonic generation is given in section 6.5.1. These calculations were performed in collaboration with Mose Akyuz at the Division for Electricity and Lightning Research at Uppsala University.

The electrode gap consisted of an anode (rod and sphere) and the cathode (circular mirror) and was placed in air. The distance between the anode and the cathode (earthed gold/silver
mirror) was approximately 3 cm and the applied potential was 4 kV on the anode. The geometry is shown in Fig. 6.24.

![High-voltage geometry diagram](image)

**Figure 6.24** The high-voltage geometry. Anode to the left and cathode to the right. The white spot indicates where the laser hit the mirror. The diameter of the spot was 0.5 cm.

It can be seen in Fig. 6.25 that the surface charge was approximately 1.1 μC/m² where the laser light interacted with the mirror. A more detailed study is shown in Fig. 6.26.
Figure 6.25 Surface charge along a diameter on the mirror (see the line in Fig. 6.24) and parallel to the rod of the anode. The x-axis is defined as negative along the line under the rod of the anode.

Figure 6.26 The surface charge varied across the laser beam when it hit the mirror. The radius of the laser beam was 2.5 mm. The laser spot went from -2.5 mm to +2.5 mm in this graph. The arrows in the picture indicate the end points of the laser light on the mirror.
Fig. 6.25 shows that the surface charge along the line in Fig. 6.24 is quite large below the rod of the anode and decreases as the distance between the mirror and anode increases. Fig. 6.26 shows that the surface charge did not vary very much where the laser hit the mirror. The excess surface charge on the mirror varied ±2%.

Fig. 6.27 shows the equipotential surfaces. The blue colour denotes a potential interval close to zero and the red colour close to 4 kV. The large circle defines the design space that encapsulates the region in space where the high-voltage system experiments were performed.
Figure 6.27 The equipotential surfaces.
6.5 Surface charge detection using second harmonic generation

6.5.1 Experimental arrangements

The experimental set-up (Fig. 6.28) has been optimised during the PhD thesis work and the final set-up is described here. To avoid laser irradiation damage of the plate (the measurement object) a collimated laser beam was used and the energy density was kept at 20 J/m². However, in the beginning of the work some experiments were performed with an additional lens (not shown in the figure) to focus the laser light into the plate. The time duration of the pulses was approximately 100 fs and the wavelength approximately 800 nm, i.e. infrared light.

Pulses (10 Hz, 1 mJ, 100 fs) were delivered from the terawatt laser system as described in section 5.5. The beam size was determined with a circular aperture. The terawatt laser radiation was horizontally polarised. P-polarised (parallel to the incident plane) infrared light (800 nm) was reflected e.g. on a polished gold mirror. Due to nonlinear interaction between the light and the mirror, light that has a frequency equal to twice the input frequency was created. Two photons of the infrared light at 800 nm were converted into one photon with the wavelength 400 nm, blue light. A Pellin-Broca prism separated the two wavelengths almost completely. A mirror (both silver and gold have been used) reflected the blue light (400 nm) and a bandpass filter (Schott BG 38, i.e. a blue green optical glass-filter) transmitted this wavelength while attenuating the 800 nm light. A monochromator (Bausch & Lomb) was used to remove remaining infrared light. The blue light was detected by a photomultiplier (type 9558, cathode material S20, i.e. Na-K-Sb-Cs) connected to an oscilloscope (Tektronix TDS 540). The beam path for the blue light was aligned using a frequency-doubling crystal. To ascertain that no blue light came from the other optical components the filter, that removed the blue light from the laser system, was placed after the target mirror. In that case there was not any SH signal detected on the oscilloscope.

Figure 6.28 Experimental set-up.
A photodiode was inserted into the experimental arrangement to measure the laser intensity fluctuations. The photodiode and the photomultiplier were connected to the oscilloscope with shielded coaxial cables. The oscilloscope was connected to a computer with a GPIB cable, i.e. a general purpose interface bus (GPIB). LabView, a data measurement system installed on the computer, was used for processing the signals from the oscilloscope.

A high-voltage electrode was placed close to the plate (earthed) and a net surface charge was induced on the plate due to an applied high-voltage on the anode. One of Maxwell’s postulates gives the surface charge as the divergence of the net electric field. If the electric field lines are parallel then the surface charge, \( \sigma \), is given by

\[
e_{0}E = \sigma.
\]  

(6.3)

In the experiment which was illustrated in Fig. 6.28 the electric field lines were not entirely parallel, and hence one has to apply a numerical method to calculate the surface charge more accurately (see section 6.4.2). The goal has been to detect a change in the blue light when the surface charge was varied. The corresponding applied electric field must not exceed the breakdown voltage in air, \( \sim 3 \) MV/m.

### 6.5.2 Results and discussion

The typical signal measured by the photodiode from an incident laser pulse to a gold mirror is shown in Fig. 6.29(a). The generated SHG signal captured by a photo multiplier tube is seen in Fig. 6.29(b). For the SHG signal the area of the graph in (b) was taken as a measure for \( I_{2\omega} \) and the height of the graph in (a) as a measure of \( I_{\omega} \). The oscilloscope used a sample rate of 250 MS/s per channel.
In Fig. 6.29a the height of the graph corresponding to \( I_\text{ss} \) has been taken as the difference between point A and the background level established for long delays. It has been checked with some optical density filters that the height of the graph indeed is proportional to \( I_\text{ss} \). Since focused laser light deteriorated the mirror a collimated unfocused laser beam was used. The quotient between the standard deviation and the mean value is a useful measure for signal fluctuations. The fundamental wave intensity \( I_\text{ss} \) showed small fluctuations. The fluctuations \( F \), defined as two times the standard deviation divided by the mean, for \( I_\text{ss} \) and \( I_\text{SHG} \) were typically 7.6 \% and 15.4 \%, respectively, for a gold mirror with a \( \lambda/10 \) surface.
roughness. An aluminium plate that was only polished down to a surface roughness of some micrometer showed 1_2ω fluctuations of 50.8%.

Fig. 6.30 shows a plot (log-log scale) of the SHG signal, I_2ω, from a gold mirror as a function of the fundamental field intensity, I_ω. By attenuating the laser power with attenuation filters three different input intensities were investigated. The correlation coefficient C is defined as

\[ C = \frac{\langle I_\omega I_{2\omega} \rangle - \langle I_\omega \rangle \langle I_{2\omega} \rangle}{\sigma(I_\omega) \cdot \sigma(I_{2\omega})} \]  

(6.4)

where σ is the standard deviation and \( < > \) is taken as the expectation value. The correlation coefficient of shot-to-shot fluctuations between I_2ω and I_ω using the data for just one of optical density filters was calculated to 0.06. The slope for the mean values I_ω was calculated for each of the three filters to 1.7, i.e. approximately 2. The presence of shot-to-shot fluctuations could be easily inferred from the figure and this determined the experimental accuracy.

![Figure 6.30](image)

Figure 6.30 Correlation between SHG signal and incident laser beam.

In Fig. 6.31 SHG experiments on a silver mirror have been carried out by alternating a zero electric field and a field of 0.12 MV/m (corresponds to a net surface charge density, σ, of 1.1 µC/m²). The time elapsed between the experiments was less than a minute.
Figure 6.31 SHG experiments on silver mirror. Stars and plus signs denote the mean value of ratio $I_{2\omega}/I_\omega^2$ at zero field and 0.12 MV/m (corresponds to a net surface charge density, $\sigma$, of 1.1 $\mu$C/m$^2$) respectively. Each point in the diagram is calculated by averaging data from roughly 1000 laser pulses. Error bars denote the standard deviation.

Several experiments have been carried out to establish how the relationship between $I_\omega$ and $I_{2\omega}$ might change due to increased surface charge at the mirror. The conclusion of the SHG experiments was that the increased surface charge did not give any reproducible change in $I_{2\omega}$. From these experiments, it has also been verified that the surface roughness of the mirror strongly affected the fluctuations of $I_{2\omega}$. For small changes in $I_\omega$ random shot-to-shot fluctuations leads to a weak correlation between $I_\omega$ and $I_{2\omega}$ and this was the major difficulty. However, for larger changes the relationship between $I_{2\omega}$ and $I_\omega$ approximately fulfilled a square dependence, see Eq. (4.18).

During the PhD thesis work we have improved the experimental set-up and the set-up used in the last experiments is the one presented here in chapter 6.5. In the beginning we focused the laser light by a lens and the beam waist reached a minimum at the aluminium plate. Several gold mirrors were also used to direct the laser light to the plate. Two dichroic mirrors were placed after the Pellin-Broca prism, see Fig. 6.28 in chapter 6.5.1, to completely remove scattered infrared light in the direction of the frequency doubled beam. The second harmonic light was rather weak and both blue and infrared light were detected by the photomultiplier. The laser light intensity was initially too large and deteriorated the aluminium plate.
The focusing lens was removed and collimated laser light was used. This enhanced significantly the detected blue light. The metal plate was not deteriorated any longer.

Every gold mirror created SH light and we had to remove the gold mirrors in the set-up. The dichroic mirrors were also removed. A gold mirror replaced the aluminium plate. We found that the laser contained quite a lot of blue light. It was comparable to the SH light that was created from one gold mirror. By using the experimental set-up in Fig. 6.28, we detected only blue SH light that was created at the gold mirror target. Second harmonic light was easily detectable and all infrared light had been removed.

The conclusion of this experiment was that the detection sensitivity was limited by the laser intensity fluctuations. There were fluctuations both in the fundamental and the SH signal. The fluctuations made it impossible to get any valuable information and a much better correlation from shot-to-shot between the fundamental and SH pulses would have been desirable. In SHG experiments there will often be at least 1-3 % fluctuations that cannot be easily removed, e.g. if the time duration of the pulse is changed from 50 fs to 52 fs. The choice of sample material is crucial for the outcome of the experiment. The sample was changed during the experiments from a solid aluminium plate to a thin film (gold mirror) since it reduced the fluctuations. However, the goal of the PhD thesis work aimed to study a solid metal by applying an external electric field strength less than 3 MV/m. The constants a, b and c are unknown in Eq. (4.52). The relative change, $\Delta I/I$, depends on these constants. Thus it has been difficult to predict the outcome of the experiment.

In [Corn et al., 1984] the SH signal on a silver-mica capacitor was studied as a function of applied electric field (range 0-100 MV/m). They showed the SH signal varied significantly as the electric field strength was changed. Looking at the data in this paper it might be possible to detect a change in the SHG (the signal in [Corn et al., 1984] was created from plasmon surface polaritons (PSPs) and thus was not a pure surface charge effect) by studying a silver-mica interface if the electric field is less and changed less than 3 MV/m. The SH fluctuations of 15 % should be compared to the expected $\sim11\%$ (maximum) change of the signal.
Chapter 7

Summary of papers

Paper 1

Experiments on mid-gap laser-triggered electrical breakdown in liquid dielectrics have been performed. The sequence of events that leads to the disruptive discharge is described and accompanied by electric field calculations. It is believed that the described process is valid for mid-gap laser-triggered electrical breakdown in general where an expanding cavity has a lower dielectric strength than the surrounding medium. The author’s contribution to the paper was mainly the electric field calculations in ACE (FEM software package).

Paper 2

It has been shown that remote LIF measurements can be used to detect and measure distribution of biological contamination on polymeric insulators. The experiments were carried out by using the fluorescence Lidar system. Processed images of the algal covered insulator were produced. By selecting some wavelength bands (\(\Delta \lambda\)) and choosing a proper function of the intensity in these intervals (contrast function), each spectrum could be reduced to a single value. These values were converted to a specified scale of colour in the processed image and information about the insulator surface could be displayed in an easily interpreted format. In comparison with conventional photography it was shown that the LIF laser technique was more sensitive. The author took part in the planning of the experiment and prepared the communication between the fluorosensor and the Lidar system. The author carried out the experiments together with Rasmus Grönlund and Andreas Dernfalk and took part in the analysis of the spectra.

Paper 3

Fluorescence Lidar imaging of fungi covered insulators has been performed by analysing the spectral shape of the fluorescence signal. It was concluded that an obtained fluorescence spectrum had to be compared to reference spectra from a clean surface in order to be able to discriminate between clean and fungi infected surfaces. The imaging process was simplified by using PCA where one PC could discriminate between fungal growth and clean surface. It was revealed that a sample that looked clean by the naked eye could contain fungi, which was verified by using a scanning electron microscope and LIF measurements. The author was responsible for and carried out major part of the work.
Paper 4

Mixed biofilms were grown on silicone rubber substrates in the laboratory, using specially designed microenvironment chambers. Areas covered by biological growth could be estimated by using photography and digital image analysis. LIF spectroscopy showed that UV-light exposure and zinc borate (added as flame retardant) hindered the growth of the biofilms, but the addition of aluminium trihydrate (ATH) did not have any effect. LIF spectroscopy was explored as a tool for detection of biofilms on silicon rubber samples. The results of the experiment indicate that LIF spectroscopy in combination with image analysis can be used for field diagnostics of biological growth on insulators in service. The author carried out the LIF experiments and analysis together with Stina Wallström. The author wrote the text about the laser system.

Paper 5

PCA was used in combination with LIF to explore the possibility to simplify the imaging process of fungal growth in field experiments. Eight fungal cultures and four insulator materials have been analysed. Fluorescence from pure fungal growth showed to be wavelength shifted compared to the fluorescence from clean silicone rubber. This can explain the wider fluorescence spectrum of a fungi covered sample and render new possibilities for making more accurate remote measurements of fungal growth on insulator surfaces. If for any reason the insulator material is not known, laboratory experiments showed that a PCA can be useful to determine it. The author was responsible for and carried out major part of the work.

Paper 6

The detection of contamination such as salt in outdoor high-voltage insulator systems and its subsequent removal can be vital for a reliable transmission of electric power. Remote detection of salt on a copper metal surface was carried out by using a mobile LIBS Lidar system with a laser wavelength of 355 nm. Detection of salt on a polymeric high-voltage insulator was obtained when an additional lens was inserted into the beam path, and the number of photons that was detected could be calculated by using a calibrated white light source. Ablative cleaning could readily be carried out with LIBS and was verified by observing the disappearance of the sodium D-line emission. The author was responsible for and carried out major part of the work. The experiments were carried out together with Rasmus Grönlund.
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The Sequence of Events in Mid-Gap Laser-Triggered Electrical Breakdown in Liquid Dielectrics

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ABSTRACT
Recent experiments on mid-gap laser-triggered electrical breakdown in liquid dielectrics have been scrutinized. The sequence of events that leads to the disruptive discharge is described and accompanied by electric field calculations.

1· INTRODUCTION
Pre-breakdown and breakdown phenomena in liquid dielectrics have been studied extensively during the last decades. New diagnostic tools and techniques have rendered deeper understanding of these phenomena [1]. Recently, an elaborate technique presented by Larsson et al [2] combines laser-triggering and the laser shadow method. This technique, integrated with pre-breakdown current measurements, was used in experimental research on mid-gap laser-triggered dielectric breakdown in transformer oil, where the physical mechanisms and the timing sequence of this dielectric breakdown were revealed [2, 3]. The elicited information gives, as presented in this paper, the sequence of events in the breakdown process together with electric field calculations [4, 5].

Typical experimental conditions were as follows: The electrode gap, was placed in a cell filled with Nytro lOx transformer oil, consisted of two hemispherically-tipped brass electrodes with a tip radius of 10 mm. The adjustable electrode distance ranged between 4 and 5 mm. The oil was stressed with an electric field strength of 12 MV/m which was achieved by applying either 50 or 55 kV depending on the electrode distance. The self-breakdown electric field strength of the oil was 22.5 MV/m. A laser pulse (wavelength, 1064 nm; pulse duration, 8 ns) was focused in the middle of the electrode gap, and a pulse energy of 30 mJ was required for plasma formation ('breakdown threshold'). In our experiments, we varied the pulse energy between the breakdown threshold and 100 mJ. The experiments were performed at room temperature and at ambient pressure. The expansion of the gas-filled cavity formed by the laser-initiated plasma was monitored by the shadowing technique and the pre-breakdown current was measured simultaneously.

The filamentary structures observed in electrical discharges in liquid dielectrics are traditionally called 'streamers'. This is also the case in this paper. However, this term may give confusing association when compared to its namesake in gas discharges. Recent research points out numerous similarities between the discharge channel propagation in liquids and leader propagation in gases [6].

2· SEQUENCE OF EVENTS IN MID-GAP LASER-TRIGGERED DIELECTRIC BREAKDOWN
The sequence of events in mid-gap laser-triggered electrical breakdown in liquid dielectrics is depicted in Figure 1. The focused laser pulse creates a plasma in the electrode gap (step 1 in Figure 1). If the laser pulse energy is close to the breakdown threshold, the initial plasma appears as a spot. If the energy is increased, the plasma will be larger and will assume a cigar-like shape. The lifetime of the plasma is less than 100 ns, and it causes a high-pressure gas-filled cavity to form (step 2). The high pressure expands the cavity. The dynamics of an expanding cavity in a liquid can be expressed by a simple equation assuming that the liquid consists of an infinite mass of homogenous and incompressible fluid acted upon by no forces. With these assumptions, the relationship between the expansion time t of the cavity and the cavity radius R is [7]

\[ t = R_{\text{max}} \sqrt{\frac{3\rho}{2p_0 R_{\text{max}}^2}} \frac{R_{\text{max}}^2 \beta^3}{(1 - \mu^2)} \]

where \( R_{\text{max}} \) is the maximum radius of the cavity, \( \rho \) is the mass density of the liquid and \( p_0 \) the ambient pressure. The integral of (1) lacks a simple analytical solution, but can easily be calculated numerically. Figure 2 shows a calculation of the expansion and collapse of a cavity with \( R_{\text{max}} = 1.4 \text{ mm} \) at an ambient pressure of \( p_0 = 1013 \text{ kPa} \) and a liquid density of \( \rho = 876 \text{ kg/m}^3 \). Strictly speaking, (1) is only valid for the expansion phase. However, it can easily be shown that the expansion and collapse are sym-
metrical in time around the instant of maximum size of the cavity. In the figure, measured data of expansion and collapse of a cavity are also included, for the case without applied electric field. The agreement is satisfying.

Several $\mu$s after the plasma initiation, partial discharges (PD) are observed to occur within the cavity, and these occur before the liquid starts to break down dielectrically (step 3). These PD can be explained by the following analysis. Calculations of the development of the electric field distribution in the gap with an expanding and perfectly dielectric cavity are shown in Figure 3. In the figure, the electric field strength is represented by the dimensionless field enhancement factor, which is defined as the quotient between the local field strength and the average field strength, that is, $E(x)/U_{av}$. The relative permittivity of the gas ($\varepsilon_{\text{gas}} = 1$) is less than the one for oil ($\varepsilon_{\text{oil}} = 2.2$) which leads to a field enhancement in the cavity, as shown in the figure. The dielectric strength of the oil is significantly greater than the dielectric strength of the gas in the cavity, which is a gas mixture of various hydrocarbons. Hence, the field inside the cavity as shown in Figure 3 will cause PD within the cavity, and these PD will deposit charge on the cavity walls facing the electrodes and thus limit the field strength within the cavity. Effectively, the charge redistribution within the cavity will limit the cavity electric field strength to be less than the breakdown field strength of the gas in the cavity. Figure 4 shows calculations of the development of the electric field distribution for a cavity where the cavity is assumed to be a perfect conductor (zero electric field within the cavity).

About 70 $\mu$s after the plasma initiation, positive streamers are observed to launch from the cavity towards the
Figure 4. Development of electric field distribution along central axis for an expanding perfectly conducting cavity. Conditions as in Figure 3.

(cathode (step 4 in Figure 1). Since the voltage is constant across the electrode gap, the limitation of the field strength in the cavity will give rise to increased field strength in the liquid, as evident from the calculations presented in Figure 4. This field enhancement will eventually trigger positive streamers that are launched from the cavity towards the cathode, since positive streamers have lower inception field strength than negative ones [1, 6]. The development of the field enhancement factor in the gap for a perfectly conducting cavity is shown in Figure 5. Note that the maximum field strength is at the cavity as evident from Figure 4, but that the maximum field strength is located at the electrodes for the case without any cavity.

When the positive streamers have bridged the gap between the cavity and the cathode, a charge transfer occurs between them. Consequently, the field strength in the gap between the cavity and the anode is further enhanced, resulting in negative streamers to be launched towards the anode (step 5). When a negative streamer has bridged the gap between the cavity and the anode, the disruptive discharge is imminent (step 6). The propagation of the positive streamers and the spark formation (step 4 and step 6) were not time-resolved (sub-microsecond processes), but the propagation of the negative streamers took a few microseconds (propagation speed ~ 250 m/s).

Figure 5. Development of maximum electric field strength in the electrode gap for a perfectly conducting cavity. Dots at $R = 0$ and $t = 0$ represent maximum field enhancement in a gap without a cavity. Conditions as in Figure 3.
A certain combination of cavity radius and applied voltage will give rise to the breakdown field strength of the oil in the gap (22.5 MV/m), for a certain condition for the electrical properties of the cavity. Figure 6 shows this combination for a perfectly conducting cavity, that is, for a given applied voltage, what is the radius of the cavity that give rise to a maximum field strength in the gap that is equal to the breakdown field strength of the oil? The breakdown voltage according to Figure 6 is too low since a typical example of breakdown conditions from the experimental studies is an applied voltage of 50 kV with a cavity radius of 1 mm for a 4 mm gap. Thus, the assumption of a perfectly conducting cavity is not appropriate. Figure 7 gives the calculated breakdown voltage for a 1 mm cavity in a 4 mm gap as a function of the voltage gradient inside the cavity. From this figure, it is suggested that this voltage gradient is about 7 MV/m.

3 CONCLUSION

We believe that the process, as illustrated in Figure 1, is qualitatively valid for mid-gap laser-triggered electrical breakdown in general where the expanding cavity has a lower dielectric strength than the surrounding medium. A gas-filled high-pressure cavity is formed from the laser-induced plasma in the focal region of the laser radiation. This cavity expands and distorts the electric field distribution in the electrode gap. Since the gas in the cavity has a lower dielectric strength compared to the surrounding liquid, PD will occur in the cavity before the liquid starts to break down dielectrically. These PD create charge redistribution within the cavity and, in effect, limit the within-cavity electric field strength to be less than the breakdown field strength of the gas in the cavity. The field limitation in the cavity gives a field enhancement in the liquid. When the field enhancement is sufficient, dielectric breakdown of the liquid is induced.

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REFERENCES

Abstract: A new technique for remote detection of biological contamination on high-voltage outdoor insulators has been investigated. The technique, which is based on laser-induced fluorescence (LIF) spectroscopy, has been applied to study surfaces of real silicon rubber insulators from a distance of approximately 60 m. Measurements were performed outdoors on a number of clean, as well as, biologically contaminated insulators. Several types of biological contamination were included, as five of the studied insulators had become covered when installed in Sweden, and another three had been contaminated by fungal growth in laboratory. Fluorescence spectra obtained from the surfaces of the described insulators is based on laser-induced fluorescence (LIF) spectroscopy, has been applied to study surfaces of insulators had become covered when installed in Sweden, and another three had been contaminated by fungal growth in laboratory. Fluorescence spectra obtained from the surfaces of the described insulators is based on laser-induced fluorescence (LIF) spectroscopy, has been applied to study surfaces of real silicon rubber insulators from a distance of approximately 60 m. Measurements were performed outdoors on a number of clean, as well as, biologically contaminated insulators. Several types of biological contamination were included, as five of the studied insulators had become covered when installed in Sweden, and another three had been contaminated by fungal growth in laboratory. Fluorescence spectra obtained from the surfaces of the described insulators are presented and the applicability of the technique is discussed and compared with photographic methods.

1. Introduction

Reports on biological growth on outdoor insulators reveal that microbiological colonization of ceramic as well as composite insulators can take place in all parts of the world [1-14]. Since the impact of biological growth on insulator performance is not fully understood, it makes utility engineers concerned [14, 15]. The fact that microorganisms grow on composite insulators is of special concern. Silicone rubbers are known to exhibit high resistance to biological degradation. One of the reasons is that the material consists of both organic as well as inorganic components, and that microorganisms like fungi cannot digest the inorganic parts [16]. However, it is believed that in service, composite insulators are mostly attacked by fungi [8, 17].

There is a number of reports on biological contamination of composite insulators [1, 2, 4-13, 15, 18], about half of them from tropical climate [2, 6-8, 11, 15, 18]. Different types of silicon rubber (SIR) insulators, epoxies and blends of silicone and ethylene-propylene-diene monomer rubber (EPDM) have been found to support growth of bacteria, algae, fungi and lichen. However, so far there is not much information published on the growth on EPDM insulators.

This study is a step in a process of investigating the influence of biological growth on insulator performance. More specifically, the aim is to develop a method that can be used to remotely detect and measure/characterize growth and growth distributions.

At close distance, presence of for instance algae on an insulator surface can be detected through visual inspection. However, in order to get a measure of its “severity”, more refined techniques have to be used. An example of such a diagnostic technique is photography followed by digital image analysis, which has been proposed by one of the authors [19, 20]. Using this technique, it is possible to get measures of area covered by the growth and its distribution. However, it is difficult to differentiate between regions covered by microorganisms and regions covered by other contamination.

The technique investigated in this study, laser-induced fluorescence (LIF) spectroscopy, has e.g. been utilized for imaging of historical monuments [21] and previously been suggested for insulator diagnostics [22]. In the latter report, the authors presented fluorescence spectra obtained in laboratory from different SIR and EPDM materials and from SIR surfaces where its hydrophobic properties had been reduced through water immersion. In the present study, LIF spectra have been obtained from real insulators partly covered by biological growth using a mobile measuring system. To simulate a real situation, i.e. studying insulators installed in a HV-system, measurements were performed outdoors at a distance of about 60 m.

2. Experimental set-up

The used mobile Light Detection And Ranging (LIDAR) system, housed in a Volvo F610 truck, is based on all solid-state laser technology, and can be used for multi-wavelength excitation and detection in fluorescence imaging, gas concentration- and flux measurements [23]. The system is self-contained, with a diesel powered electrical generator, making it well-suited for field measurements.

In the present experiment, only a part of the laser system, a frequency tripled Nd:YAG laser (Quanta-Ray) was used. This laser delivers pulses with a duration of 4-5 ns at a repetition rate of 20 Hz and a wavelength of 355 nm. The laser beam is passed through an aperture to produce a better mode, rendering a beam diameter of 5 mm and a pulse energy of around 25 mJ. After a totally reflecting 90 degree prism, the laser beam is expanded in a vertically mounted Galilean quartz telescope to 3 cm in diameter. This gives sufficiently low laser intensity...
on the computer controlled output folding mirror mounted in a dome, Figure 1, not to damage the mirror. The transmitted excitation light is directed towards a remote target, which in the present work was a number of insulators.

From a control computer, the dome can be rotated 360 degrees (resolution of 0.0035 degrees) with a stepper motor in the azimuthal angle and the folding mirror can be tilted from −10 to +55 degrees (resolution of 0.011 degrees) in the polar angle. At the target located 60 m from the laser source, this corresponds to a resolution of 3.7 mm and 12 mm respectively. However, if using this resolution the time for acquiring spectra from the complete insulator surface would be very long. Therefore, a beam diameter of ∼20 mm and a separation between adjacent measurement points of ∼20 mm at the insulator were used. The change of position of the laser beam at the target due to mechanical instability of the whole truck was estimated to 5 mm.

![Figure 1. Dome and light receiving unit.](image)

The remotely emitted fluorescence light is received by a 40 cm diameter Newtonian telescope (f=1 m), coaxially mounted with the Galilean telescope. By using a cut-off filter in front of the focus of the telescope, the excitation light is discriminated. An optical fibre, 600 μm core diameter and numerical aperture 0.22, guides the fluorescence light to a compact time-gated Optical Multi-channel Analyser system (OMA) designed for medical use. It consists of a spectrometer and a charge coupled device (CCD) camera. In the OMA system a beamsplitter and a cut-off filter selects only wavelengths longer than approximately 385 nm, effectively suppressing the dominating excitation light which is still of appreciable intensity.

A crossed Czerny-Turner spectrograph diffracts the fluorescence light to the image intensified CCD. The thermo-electrically cooled detector has a CCD array with 1024x128 pixels where the 128 pixels are binned. The resulting resolution for the OMA system, set by the slit width (100 μm), is 2.2 nm up to 805 nm. Ambient daylight is suppressed by using a time-gate of 100 ns, positioned in time by a properly delayed trigger signal from the laser. Spectra from the OMA system are acquired by a data collection computer that stores the spectrum together with information about the measurement coordinates.

### Studied insulators

The present study included eight insulators partly covered by biological contamination and one clean reference insulator. The insulators have been divided into three categories, A-C, according to their design. Type A and B are of line suspension type, while insulators of type C are of apparatus type and have a hollow core. All insulators have sheds and sheath of SIR. However, the formulation differs between the three categories.

The three insulators A have been installed in a 10 kV distribution system in Sweden for approximately 12 years, where they have become covered by a rather thick green growth. However, at the time of the measurement, the growth had turned brown/grey, as the insulators had been kept in laboratory for 6 months. Three of the four insulators B had been exposed to fungal spores and kept in a climate chamber for approximately two years [19]. This treatment lead to colonisation of the insulator surfaces by fungi in spot-like manner. The insulators of the third type, C, have been installed in a test station 30 km south of Gothenburg, Sweden, since 1995. They had become covered by a greenish growth on the surfaces shaded from direct sunlight.

During the measurements, the insulators were placed about 60 m away from the truck. To get a better view of the growth, which mainly was located on the upper side of the sheds, the insulators had to be turned up-side-down, tilting away from the point of observation. The insulators C were supported by a wooden structure, and tilted an angle of 30 degrees. Type A and B were fixed using horizontal metal rods and tilted 60 and 50 degrees, respectively. As a safety precaution, a board covered with black paper was put behind the insulators, hindering the laser beam to propagate further.

### 3. Results

LIF spectra were obtained from characteristic points on the insulators. A typical region with thick, green growth located on a shed of one of insulators C gave the spectrum shown in Figure 2. As seen, there is a large peak located around 680-690 nm, corresponding to the well-known fluorescence peak of chlorophyll $a$ at 685 nm [23]. Further, the shoulder on the right probably corresponds to another smaller fluorescence peak of chlorophyll at 735 nm.

Comparison of the obtained spectra gave that the fluorescence peak of chlorophyll around 685 nm is significant for the region covered by growth. The parts
of the insulator, which are not covered by algae, show a low and decaying fluorescence above 600 nm. The spectra obtained from measurements on insulators of type B were more difficult to interpret due to several reasons. First, these insulators were covered by fungi, which do not utilize photosynthesis, and thus not contain any chlorophyll. Second, the growth was more or less evenly distributed over the surface in the form of small isolated spots. As the spatial resolution of the measurements was in the order of 20 mm, spectra could not be obtained from regions completely without growth or regions totally covered by growth. However, comparison of typical spectra from a clean reference insulator and from insulators with growth shows that the total fluorescence of the contaminated insulator is lower, compared to the clean insulator, Figure 3. Further, if the amplitudes are normalized, it is revealed that the contaminated insulator has a slightly higher relative fluorescence in the wavelength band 520-600 nm.

As the aim was to study distributions of biological contamination, the dome was programmed to scan a window covering a substantial part of the insulator surface. The data were presented as gray level images where the intensity was proportional to the intensity of the fluorescence light within a specific wavelength band. The result of a scan of one of the insulators C is presented in Figure 5, together with a photograph (left) taken from the roof of the truck using a system camera equipped with a 300 mm telephoto lens. In the center image, depicting the average overall fluorescence intensity, it can be seen that the supporting wooden structure has a strong fluorescence (black) compared to the other materials present. However, when only studying the fluorescence peak of chlorophyll, i.e., the intensity in a range from 670-700 nm, the chlorophyll becomes clearly visible (right). As stated above, this is interpreted as presence of algae cells on the surface of the insulator.

In order to improve sensitivity and avoid incorrect classification of regions, the obtained spectral data were processed. Average intensities were calculated

![Figure 2](image-url)  
**Figure 2.** Typical spectra obtained from a region with green growth on one of the insulators C.

![Figure 3](image-url)  
**Figure 3.** Spectra from clean reference insulator B (dashed) and an insulator B with growth (solid).

Measurements on insulators A revealed that these had a low fluorescence compared to the other insulators studied. As the insulators of type B, the intensity of fluoresced light was much lower from regions covered by growth, than from clean regions, Figure 4. Further, regions covered by growth showed an increased fluorescence in an interval around 685 nm. However, the difference was very small compared to the insulators of type C. The reason for the low response was probably that the algae had died, due to desiccation and lack of sun radiation, when stored in laboratory.

![Figure 4](image-url)  
**Figure 4.** Spectra from a region covered by growth (solid) and a region without visible growth (dashed), on one of the type A insulators.

![Figure 5](image-url)  
**Figure 5.** Type C insulator with algae on the right side. Left to right: Photograph, mean intensity in 400-800 nm band and in 670-700 nm band.
for two different wavelength bands, \( B_1 \) and \( B_2 \), and the intensity ratio \( I(B_2)/I(B_1) \) were formed. The main advantage of these types of dimensionless ratios is that they eliminate the influence of geometrical artifacts, i.e. intensity differences due to different directions of studied surfaces [21]. An example is shown in Figure 6. Image a) shows a photograph taken from close distance, b) shows the average fluorescence intensity in the 410-500 nm band, while c) shows the average intensity in the 670-690 nm band. The ratio of the light fluoresced in the two bands is shown in d), where the dark areas are well corresponding to the regions covered by green growth.

![Figure 6](image_url)

4. Discussion and Conclusions
In comparison with photography, LIF can be used to get a higher sensitivity, especially when there is a large difference in fluorescence between insulator material and contamination. Further, as collection of fluorescence light only is performed under a short period of time, ~100 ns, measurements are not affected by sun radiation.

Comparison of the obtained spectra shows that the fluorescence peak of chlorophyll around 685 nm is significant for the regions covered by algae, while regions with no algae showed low fluorescence in the same wavelength interval. Presence of growth without chlorophyll, i.e. fungi and bacteria, did only cause small changes in the shape of the spectra, compared to the ones of clean surfaces. The most apparent difference here was an amplitude reduction. However, it is not unlikely that a good detection sensitivity of growth without chlorophyll can be obtained using other excitation wavelengths and more extensive data analysis. In conclusion, it has been shown that remote LIF measurements can be used to detect and measure distribution of biological contamination on composite insulators.

5. References

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Fluorescence lidar imaging of fungal growth on high-voltage outdoor composite insulators


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Abstract

Remote fluorescence imaging of fungal growth on polymeric high-voltage insulators was performed using a mobile lidar system with a laser wavelength of 355 nm. Insulator areas contaminated by fungal growth could be distinguished from clean surfaces and readily be imaged. The experiments were supported by detailed spectral studies performed in laboratory using a fibre-optic fluorosensor incorporating an optical multi-channel analyser system (OMA) and a nitrogen laser emitting radiation at 337 nm.

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1. Introduction

Modern society is increasingly dependent upon electric power and a reliable electric power transmission is of paramount importance. Thus, when developing new high-voltage outdoor insulators, for instance for support of power lines, these must be proven to withstand the impact from the surrounding environment and have a sufficient lifetime. Over the years, the use of polymeric materials in outdoor insulation has increased steadily [1]. One of the advantages of the polymeric, or composite, insulators over traditional ceramic ones is their light weight, making them easier and cheaper to store, transport, handle and install [2]. Another major advantage of these composite insulators is their low surface-free energy, making their surface hydrophobic and thereby, suppresses the development of a continuous layer of water on their surfaces. Such water layers can trigger a process leading to a surface flashover, which will lead to disconnection and possibly a power outage. As a consequence, a composite insulator has superior electric withstand performance compared to ceramic ones in polluted environments [2].

However, composite insulator performance can possibly be affected by biological growth, such as algae, fungi or lichen, which have been found to colonize insulators all over the world [3]. The presence of algae and fungi have, for instance, been found to decrease wet flashover withstand voltage [4]. Chlorophyll fluorescence from algae on insulators has been investigated remotely in earlier studies [5]. Algal growth, exhibiting a characteristic fluorescence peak due to chlorophyll $a$ at about 685 nm, could readily be detected from a surface by a frequency-tripled Nd:YAG laser generating radiation at 355 nm. The imaging of algae on insulators [5] followed similar previous investigations, such as fluorescence imaging of vegetation status [6] and the monitoring of vegetation on historical monuments [7,8]. In the present paper, we report on remote fluorescence studies of the fungal growth on insulator surfaces.

2. Instrumentation

A mobile and self-contained light detection and ranging (lidar) system [9], based on all solid-state laser technology and housed in Volvo F610 truck was used. Although the system has multi-wavelength excitation capabilities [10], the present fluorescence experiments were conducted at a single wavelength. The light source used was a frequency-tripled Nd:YAG laser operating at 355 nm with a pulse energy of about 12 mJ. The laser light pulses had a duration of about 4–5 ns and were delivered at a 20 Hz repetition rate.

The light was sent out from the lidar truck, by a roof-top transmission and receiving an optical dome that could be horizontally rotated at $360^\circ$ using a computer-controlled stepper motor with a resolution of 0.0035°. Similarly, a folding mirror could handle the vertical directionality of the light in the range of $-10^\circ$ to $+55^\circ$ with a resolution of 0.011 deg. That corresponds to a resolution of 3.7 and 12 mm, respectively, at the target insulators which were mounted at a 60 m distance.
from the lidar system. The beam diameter at the target was 3 cm as adjusted with a Galilean transmitting telescope and the separation between adjacent measurement points was 3 cm. The change in position of the laser beam at the target due to mechanical instability of the whole truck was estimated to be about 1 cm. The transmitter, dome and light receiving unit are illustrated in Fig. 1.

Part of the laser-induced fluorescence light was captured by a 40-cm-diameter Newtonian telescope via the roof-top transmission and receiving an optical dome and focused into an optical fibre. A BG 385 coloured-glass cut-off filter was inserted in the optical path to block the elastically scattered laser light while passing most of the fluorescence light for wavelengths longer than 385 nm. An optical fibre with a 600 μm core diameter and a numerical aperture of 0.22 guided the fluorescence light to an optical multi-channel analyser system (OMA), consisting of a crossed Czerny–Turner spectrometer, a time-gated image intensifier, and a charge-coupled device (CCD) camera. The Peltier-cooled detector had a CCD array of 1024 x 128 pixels where the 128 vertical pixels were binned. The resolution of the OMA system, set by the 100 μm slit width, was 2.2 nm, and the spectrum could be recorded up to 805 nm. A time gate of 40–50 ns was utilized during the experiments.

![Fig. 1. Transmitter, dome and light receiving unit.](image-url)
to suppress ambient light. The time gate was delayed with respect to the transmission of the laser pulse, to match the arrival of the fluorescence burst, some 400 ns later. Spectra from the OMA system were gathered by a data collection computer that stored the spectrum together with information about the measurement coordinates.

The OMA system could also be used separately, without the lidar system, and in that case a nitrogen laser, generating radiation at 337 nm was used as an excitation source. An optical fibre led the light to the target and also guided the fluorescence light back to the OMA system. This set-up has enabled the detailed laboratory studies of fungal growth on the small pieces of silicone rubber insulator material.

The extent of fungal growth on the material samples were estimated using a Jeol JSM-5400 scanning electron microscope (SEM) at an acceleration of 10 kV. Samples were dried in vacuum over night and sputtered with palladium/gold (60%/40%) for 30 s under an argon pressure of 0.5 kp/cm² (49 kPa) and a loading of 45 mA before the analysis.

3. Measurements, analysis and results

Several measurements have been performed, both remotely outdoors using the Nd:YAG laser-equipped lidar system combined with the OMA system and locally using the nitrogen laser-equipped OMA system in the laboratory. First small material samples (diameter ~5 cm) of silicone rubber, where one side of the samples was heavily colonized by fungal growth, were studied in the laboratory. It was observed that the intensity of the fluorescence light was substantially higher from clean surfaces compared to surfaces covered by fungal growth. This observation was previously noticed in an attempt to estimate fungal coverage [5]. However, the absolute intensity recorded in remote measurements is dependent on several factors such as laser pulse energy, laser spot size compared to the area of the sample studied and angle between the studied surface and incident laser beam. Thus, absolute intensity can be difficult to utilize for retrieving an unambiguous information. A more promising approach is to use the spectral shape of the fluorescence spectrum.

An example from the laboratory measurements is displayed in Fig. 2, where it can be seen that the fluorescence spectrum from a fungus-covered sample surface is much wider than the spectrum from a clean sample surface. Only a small variation in the spectral shapes between more or less fungus-covered areas (determined by the naked eye) was observed, indicating that the fluorescence imaging can reveal additional information compared to photographic imaging. Some parts of the rubber surface looked clean, but still showed the response of a fungus-covered area. When these parts were studied under SEM it was found that the studied areas were still infected. This shows that a fungus-covered surface can be partly cleaned but still show the same spectrum, even if it looks clean to the naked eye.

The difference between the fluorescence spectrum of a fungus-covered surface and a clean sample surface is smaller in the remote measurements made by the frequency-tripled Nd:YAG laser-equipped lidar system than in the case of the laboratory measurements, as can be seen when comparing Fig. 3 with Fig. 2. This is probably
Fig. 2. Spectra from a clean; (a) and fungus-covered; (b) sample surface, respectively. The mixed culture originated from an insulator installed in Gothenburg, Sweden, and consisted of Epicoccum nigrum (34%), Cladosporium cladosporides (26%) and Microsphaeriopsis l (20%) [11]. The spectra are normalized to have the same intensity around 430 nm. The experiment has been performed by using the nitrogen laser-equipped OMA system.

Fig. 3. Spectra from a clean sample surface and a fungus-covered sample surface can easily be distinguished due to the difference in fluorescence fall-off for longer wavelengths. The wider spectrum originated from the fungal growth. The experiment has been performed by using the lidar system together with the OMA system. Data was obtained by averaging over 200 laser pulses for each sample.
due to the relatively large beam spot size (≈3 cm) from the lidar system, which will capture the fluorescence from both clean and fungus-contaminated areas simultaneously. Moreover, the intensities of fluorescence light from the colonized areas are lower than the corresponding intensities from the clean areas, which means that the clean areas are given a higher weight in the surface average. It should also be noted that there was a difference in the excitation wavelength between the laboratory and the remote measurements, which also might have an influence on the spectral shape.

To focus on the interesting spectral features of the fluorescence spectra, these have to be intensity normalized in an appropriate way. The fluorescence spectra shown in Figs. 2 and 3 are normalized to have the same intensity in a 10 nm broad interval around 430 nm. However, this is a somewhat arbitrary choice and to more objectively study the spectral shape, a principal component analysis (PCA) [12, 13] was performed.

To imitate a real-field measurement, naturally aged insulators were placed at a 60 m distance from the lidar system and fluorescence spectral recordings and imaging were performed remotely. The insulators that were covered by fungal growth were made of silicone rubber (SIR) and ethylene–propylene–diene monomer (EPDM) rubber.

In the PCA, one of the principal components could be used to distinguish a clean surface from a fungus-covered surface. That principal component mainly captures the difference in the fluorescence fall-off towards longer wavelengths between areas with and without fungal growth. However, this fall-off is different for different materials. This means that an obtained spectrum has to be compared to reference spectra from a clean surface and a fungus-covered surface of the same material in order to make it possible to discriminate between fungal growth and clean surface.

Results from imaging fluorescence measurements are presented in Figs. 4 and 5. Fig. 4 shows a fluorescence image of the insulators where the fungus-covered
insulators made of SIR and EPDM are located as the third and the fourth from the top-left. Here, only the average intensity is displayed outlining the insulators. Mean normalized fluorescence spectra obtained from three insulators utilizing the lidar system and spectra collected in the laboratory from clean surfaces (rinsed by water) are shown in Fig. 5. It was found that it was possible to image the fungus-covered insulators using a soft independent modeling of class analogy (SIMCA) classification analysis to assess the presence of fungal growth [13,14].

To calculate the change in the spectra, PCA data from the fungus-covered SIR insulator and clean surfaces was mean normalized and mean centered. Each spectrum can then be expressed as a sum of the average spectrum, shown in Fig. 6, and the contribution of a principal component, corresponding to the deviation in the spectral shape, shown in Fig. 7. A spectrum from a fungus-covered surface is expressed by a negative contribution of the principal component, but a spectrum from a clean surface adds a positive contribution.
Fig. 6. The average spectrum calculated from all spectra obtained from the clean surface and the fungus-covered SIR surface.

Fig. 7. The principal component which corresponds to the change in the spectral shape.

4. Discussion and conclusions

The main goal with this experiment has been to extract information about a potential method for remotely assessing the fungal coverage of insulators. It was found that a fungus-covered surface could be readily detected, imaged and distinguished from a clean surface. Future experiments will include both
algae- and fungus-covered insulator surfaces in the investigations aiming at finding the excitation wavelength giving the best demarcation between algae and fungal growth. The final goal is to perform remote fluorescence imaging in order to get a full status of the insulators and possibly identify the signs of future insulator failure.

Acknowledgements

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References

Image analysis and laser induced fluorescence combined to determine biological growth on silicone rubber insulators

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Abstract

High-voltage outdoor insulators made from silicone rubber are sometimes reported to be colonised by microorganisms. When the hydrophobic polymeric surface is covered by a hydrophilic biofilm, the electrical properties of the insulator are altered. In this work, mixed biofilms, similar to those formed on the surfaces of polymeric insulators in the field, were successfully grown on five types of silicone rubber substrates in the laboratory, using specially designed microenvironment chambers. Photography and digital image analysis were utilized to estimate the areas covered by the growth. It was found that direct UV-light exposure hindered growth of the biofilms. Further, growth was also hindered on samples where zinc borate had been added as flame retardant. In contrast, addition of ATH did not influence the growth. In parallel, LIF spectroscopy was explored as a tool for detection of biofilms on silicon rubber samples. Experiments revealed that even weak traces of growth, not visible to the naked eye, could be detected. Finally, it is believed that LIF spectroscopy in combination with image analysis can be used for field diagnostics of biological growth on insulators in service.

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Keywords: Silicone rubber; Biological growth; Biofilm; Image analysis; LIF; Insulators

1. Introduction

Silicone rubber has a variety of characteristics that make the material particularly suitable for high-voltage applications [1]. Among those is the resistance of the material to biological growth. In spite of this, reports from all over the world tell that silicone rubber insulators are colonised by microorganisms [2–8]. A mixed biofilm, consisting of microorganisms such as small unicellular green algae, moulds and bacteria, is formed on the surfaces of the insulators [9]. When the insulator surface is covered by biological growth the hydrophobicity of the surface is reduced. This can affect the electrical flashover characteristics of the insulator [2–4]. It is therefore important to find reliable methods to measure the extent of growth in order to be able to clean or replace infected insulators.

A majority of utilities inspect insulators in service periodically. However, until now no standardised or widely used inspection technique is available, and most utilities still inspect their composite insulators visually from the ground or from towers [10]. In parallel, some also utilize IR thermography, night vision observations or electric field measurements to evaluate the state of insulators in service [11]. Of these techniques, visual inspection is best suited when extent of biological...
growth is to be estimated. However, manual inspection is time consuming and the inspector needs to be experienced in insulator designs and used materials, as well as their likely modes of failure.

In this study two techniques, digital image analysis and laser induced fluorescence (LIF), are applied to evaluate the status of different silicone rubber materials infected by biological growth. LIF-surface spectroscopy has been used in a variety of fields of scientific investigation since it allows detection of features not visible to the naked eye or characterization of different substances by means of their fluorescence spectral signatures [12, 13]. Due to its surface specific nature and potential to be used for remote measurements, LIF spectroscopy has been explored within the field of composite insulator diagnostics [14, 15]. Furthermore, digital image analysis has also been used in studies of high-voltage insulator materials, for the estimation of hydrophobicity of polymeric surfaces [16], and characterization of distributions of biological growth on insulator surfaces [17].

2. Experimental

2.1. Materials

Silicone rubber with 20% SiO₂ filler and di-(4-methyl benzoyl)peroxide added as crosslinker was mixed with aluminium trihydrate (ATH) and/or zinc borate as stated in Table 1.

Materials were kneaded in a 12 rpm Brabender internal mixer for 15 min prior to curing. The curing was performed in a Schwabenthan Polystat press at a temperature of 180 °C and a pressure of 10 MPa. The resulting discs had a diameter of 200 mm and a thickness of 2 mm. Samples were post-cured for 4 h in hot air oven at 200 °C before use.

2.2. Microorganisms

The microorganisms used were isolated from silicone rubber high-voltage insulators collected from Sweden, Sri Lanka and Tanzania [9]. Algae in association with bacteria and fungi were used for inoculation of the silicone rubber samples, as stated in Table 2.

2.3. Microenvironment chambers

Discs of each material were cut into plates shaped as a quarter of a circle with a radius of 10 cm. The plates were washed with 70% ethanol and dried in sterile airflow overnight. When dry three plates of each material were hung in inclined positions using nylon thread, as can be seen in Fig. 1. The lowest plate of each material was divided into two sections. One was mechanically aged with sandpaper; the other was aged with oxygen plasma just before inoculation with microorganisms. The oxygen plasma aging was carried out in a Plasma-finish device from Siemens. Half of the plate was covered while the other half was exposed to plasma at a pressure of 28 Pa, an oxygen gas flow of 50 ml/min and an electric power of 100 W for 180 s.

The assemblies of the five studied materials were placed in four closed microenvironment chambers as shown in Fig. 1. Three chambers represented the studied countries. The fourth was a reference chamber with control specimens. All chambers maintained a temperature of approximately 25 °C and a relative humidity of ≥ 85%. A daylight lamp with a cycle of 12 h light and 12 h darkness was used to provide the necessary UV-light exposure.

---

Table 1
Type and amount of flame retardant added to the silicone rubber materials tested

<table>
<thead>
<tr>
<th>Material</th>
<th>Flame retardant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>No flame retardant added</td>
</tr>
<tr>
<td>Base + ATH</td>
<td>100 pph ATH</td>
</tr>
<tr>
<td>Base + ATH + zinc</td>
<td>90 pph ATH + 10 pph zinc borate</td>
</tr>
<tr>
<td>Base + zinc borate</td>
<td>10 pph zinc borate</td>
</tr>
<tr>
<td>Commercial mix</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

Table 2
Microorganisms used for inoculation of silicone rubber samples

<table>
<thead>
<tr>
<th>Country</th>
<th>Fungi</th>
<th>Algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweden</td>
<td>Epicoccum nigrum</td>
<td>Chlorella saccharophila + 6 bacterial strains</td>
</tr>
<tr>
<td></td>
<td>Microsphaeriopsis</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cladosporium cladosporiodes</td>
<td></td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>Fusarium semitectum</td>
<td>Chlorella vulgaris var. Autotrophica + 5 bacterial strains</td>
</tr>
<tr>
<td></td>
<td>Polyscytalum fecundissimum</td>
<td>Stagonospora</td>
</tr>
<tr>
<td>Tanzania</td>
<td>Curvularia lunata</td>
<td>Chlorella vulgaris var. Autotrophica + 2 bacterial strains</td>
</tr>
<tr>
<td></td>
<td>Cladosporium tenuissimis</td>
<td></td>
</tr>
</tbody>
</table>

---

Fig. 1. Schematic drawing of microenvironmental chamber.
Thirty days old mixed cultures grown from the different biofilms were harvested from BG11 [18] agar by pouring 10 ml of BG11 liquid broth on the agar surface and gently scraping the microorganisms with a sterile platinum wire. Three suspensions were prepared, one for each country. Plates were inoculated with a solution of microorganisms from the specific country by a sterile atomiser. All specimens were reinoculated with microorganisms suspended in water once a week during the first five months of the experiment, to create a self-sustaining biofilm. Reference samples were sprayed with sterile BG11 liquid broth.

After six months, image analysis and LIF were used to determine the extent and type of growth on the different samples.

2.4. Image analysis

All samples were photographed using a standard Canon IXUS V3 digital colour camera. Photographs were taken from a distance of approximately 1 m and at an angle where the sample surface normal was anti-parallel to the direction of observation. A blue paper sheet was used to create a homogeneous background. The images were transferred to a computer where the subsequent image analysis was performed in Matlab®. In the computer, each image was represented as a set of three matrices, containing intensity values of the red, green and blue components, respectively. The procedure applied to estimate the area covered by growth is described below. First, the sample is identified in the image. This is done through Otsu’s thresholding [19], in the normalised blue component, i.e. the blue component divided by the sum of three colour components. The result is a black and white (BW) image depicting the sample. Thereafter, possible influence of shading at the sample edge is removed through erosion [20] of the obtained image by a circular element, removing object pixels at its boundaries. Multiplication of the original colour image by the BW image results in an image depicting the identified sample on a black background. In the next step, the image of the sample is divided into a set of sub-images, in which the maximum values are identified, and these are subsequently used for compensation of global illumination variations.

The blue component of the compensated image is used for segmentation of the sample into covered and non-covered areas. Blue is selected since the contrast between the rubber and the biofilm showed to be highest in this component. Similar to above, segmentation is accomplished through Otsu thresholding, and again the result is a BW image, in this case depicting regions classified as growth on the sample. Finally, the covered area is calculated by counting the number of pixels classified as growth. However, to avoid the need for calibration, the covered area was always related to the area classified as sample surface.

2.5. Laser induced fluorescence

A compact point-measuring fluorosensor was used for the detection of fluorescence. A pulsed (3 ns, 15 Hz, \( \sim 1 \) μJ) nitrogen laser (wavelength 337 nm) produced excitation light that was guided through a single 600 μm in diameter fused silica optical fibre to the sample under investigation. The distal end of the fibre was located about 1 mm above the sample.

The fluorescence light, induced typically on a nanosecond time scale, was spatially emitted in all directions. A fraction of it was collected by the same fibre. A coloured-glass cut-off filter was inserted in the optical path to block the elastically scattered laser light while passing the fluorescence light at wavelengths longer than 385 nm to a spectrometer. An image-intensified charge coupled device (CCD) camera was used to record the fluorescence spectra up to approximately 800 nm with a spectral resolution of about 2 nm. Each spectrum was accumulated from 100 laser pulses and stored by a PC, which was used to control the acquisition. The resulting LIF spectra were analysed by using a multivariate method called principal component analysis (PCA) [21].

3. Results and discussion

The problem with biological growth on silicone rubber insulators is complex in nature. Type and amount of biological growth varies between insulators depending on climate factors, handling of the material and composition of the rubber. This is a problem when effects of biological growth on the performance of silicone rubber insulators are to be evaluated. Research is often performed on insulators used for several years in an outdoor environment. Information obtained from this type of observations is valuable but suffers from lack of properly stored reference material and climate control [5,22].

Different kinds of standardised test methods that give control over material composition and climate have also been used to evaluate the effect of biological growth on silicone rubber materials [4,23]. However, microorganisms used in these experiments are often those prescribed by the standards and therefore not of the type infecting insulators in power systems. Previous research has shown that silicone rubber insulators are infected by a complex biofilm, consisting of a mixed culture of algae, fungi and bacteria [9]. Standard test procedures seldom prescribe mixed cultures of this type; instead monocultures or standard mixtures are used.

To overcome these problems, microenvironment chambers with a climate ideal for biological growth
were constructed and used in this study. Silicone rubber samples of different composition were distributed in the chambers and inoculated with mixtures of algae, fungi and bacteria isolated from silicone rubber insulators situated in Sri Lanka, Tanzania and Sweden, respectively. After a few months mixed biofilms similar to those formed on the surfaces of insulators in the field had developed on the samples.

Five different silicone rubber materials were tested under the influence of the three biofilms to evaluate how the type and amount of flame retardant affected biological growth. After six months, samples were photographed and the resulting digital images were subjected to image analysis in order to determine the extent of growth on the different materials. Generally, digital image analysis is used for extracting information from images using computer programming. However, in this report, the image analysis has mainly been used for intensity based segmentation of photographs, i.e. segmentation of photographs into regions of similar chromatic appearance. A typical result obtained through application of the described segmentation technique is shown in Fig. 2, where regions classified as growth have been marked by red. As seen, the highlighted regions correspond well to the growth, except for one of the holes, which, due to a low intensity of reflected light, has been falsely characterized as growth.

As can be seen in Fig. 3, results from the image analysis clearly showed that the flame retardant zinc borate hindered the development of the biofilm, while ATH had no hindering effect on the growth. On the contrary, results indicate that ATH might even support the biofilm. However, further studies are needed to confirm this effect. Another effect observed was that the biofilm originating from Sri Lanka developed faster on the commercial material tested when compared to the other two biofilms under study. This might be due to the composition of the biological growth. The biofilm from Sri Lanka contained a larger proportion of fungi compared to the biofilms isolated from Tanzania and Sweden. Earlier studies have shown that some commercially used silicone rubber materials support fungal growth [3,23].

Another observation made was that direct UV-light exposure effectively hindered growth of the biofilm. In Fig. 4, it can be seen that all of the samples that hung high in the microenvironment chambers, near the daylight lamp, are almost completely free from growth. On the middle plates, that are partly shaded, growth develops much better. This effect can also be seen at high-voltage insulators in service, where growth develops quicker at shaded parts of the insulators [2,5,6].

The lowest hung plates should, according to theory, be the worst infected samples, since they are partly shaded and hydrophilic [24]. However, this cannot be concluded from the results given. This is probably due to...
Fig. 4. Effect of UV-light on the extent of microbiological growth on the silicone rubber substrates.

Characterizing parameters such as covered area can be estimated by manual inspection. However, manual estimations are not objective and the use of digital image analysis may thus improve accuracy and repeatability of the estimations significantly. Recent studies point out that image analysis can be used for estimating the area and distribution of growth on both material samples and complete insulators [17]. Nevertheless, the technique has its drawbacks. For instance, the method cannot discriminate between biological growth and other coloured pollutants on the insulator surface. To overcome this problem, and possibly increase sensitivity compared to photography, LIF spectroscopy was explored as a tool for detection of growth.

Fluorescence is the spontaneous emission of radiation by which an atom or a molecule relaxes from an upper energy level to ground state level. In LIF-surface spectroscopy, the surface under study is irradiated with monochromatic light from a laser. The molecules at the surface absorb the photons and become excited. The fluorescence light is emitted when the molecules spontaneously de-excite. Earlier studies have shown that intensity of the fluorescence light can be substantially higher from clean surfaces compared to surfaces covered by biological growth [25]. However, the absolute intensity is dependent on several factors such as laser pulse energy, area of excited region, and angle between the surface under study and the laser beam. Thus absolute intensity can be hard to utilize for getting unambiguous information from the samples. A more promising approach is to use the spectral shape of the normalized fluorescence spectrum. The fluorescence spectrum from a fungi covered silicone rubber sample surface can be much wider than the spectrum from a clean sample surface and if algae are present on the surface an additional peak around 685 nm is formed from chlorophyll fluorescence [15]. These effects were clearly seen when samples from the microenvironment chambers were studied. Effects were more pronounced on samples heavily covered with biological growth when compared to cleaner samples. The algae peak

Fig. 5. Results from LIF-surface spectroscopy. (a) Spectra collected from an ATH-filled silicone rubber infected by a dense biofilm. The spectrum from the infected sample is wider than the corresponding reference spectrum and the algae peak is clearly visible. (b) Spectrum from a zinc borate filled rubber infected with microorganisms. The sample looked clean to the naked eye, since no mature biofilm had formed. The spectrum is only slightly broader compared to the reference spectra and there is no peak corresponding to chlorophyll fluorescence.
disappeared completely on samples with zinc borate added as can be seen in Fig. 5. From the measurements, it is concluded that LIF-surface spectroscopy can be used for detection of biofilms on silicone rubber surfaces.

In addition, LIF-surface spectroscopy turned out to be a very sensitive method for detection of microorganisms; areas that looked clean to the naked eye sometimes gave response as if contaminated. When these areas were studied under microscope it turned out that weak traces of biological growth were present. This indicates that LIF-surface spectroscopy could be used to detect a microbiological attack on a silicone rubber insulator before a mature biofilm, visible to the naked eye, has formed.

When a silicone rubber sample infected by biological growth is subjected to both LIF-surface spectroscopy and photography in combination with image analysis, a lot of information is gained. While LIF-surface spectroscopy can be used to decide the type of contaminant and reveal information of contaminants invisible to the naked eye, image analysis can be used to estimate the severity of the growth. Both methods have the potential to be used as in-service diagnostic techniques. However, by utilizing LIF for creating images depicting certain spectral properties, so-called imaging measurements, a combination of LIF and digital image analysis is probably even more interesting for future applications.

Today, there already exist mobile and self-contained light detection and ranging systems that could be used for field measurements. Further, work in the field of digital image analysis, directed towards studies of insulator before a mature biofilm, visible to the naked eye, has formed. Mixed biofilms, similar to those formed on polymeric insulators in field use, were grown on five different silicone rubber materials, using specially designed microenvironmental chambers. LIF-surface spectroscopy and image analysis were used to measure the biological growth. While the LIF measurements gave useful information about the composition of the biofilm and revealed information of contaminants invisible to the naked eye, image analysis was used to estimate the severity of growth. Results showed that the development of a biofilm is hindered if the sample surface is exposed to direct UV-light or if zinc borate is added to the silicone rubber.

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References


Fungus Covered Insulator Materials Studied with Laser-Induced Fluorescence and Principal Component Analysis


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A method combining laser-induced fluorescence and principal component analysis to detect and discriminate between algal and fungal growth on insulator materials has been studied. Eight fungal cultures and four insulator materials have been analyzed. Multivariate classifications were utilized to characterize the insulator material, and fungal growth could readily be distinguished from a clean surface. The results of the principal component analyses make it possible to distinguish between algae infected, fungi infected, and clean silicone rubber materials. The experiments were performed in the laboratory using a fiber-optic fluorosensor that consisted of a nitrogen laser and an optical multi-channel analyzer system.

Index Headings: Fluorescence; Polymeric insulators; Fungal growth; Lidar; Remote sensing.

INTRODUCTION

One of the basic needs of modern society is a reliable supply of electric energy. This need forces manufacturers of equipment for power generation, transmission, and distribution to develop better and more reliable components. One such component is the outdoor high-voltage insulator. These insulators have traditionally been made of porcelain or glass, but are now successively replaced by ones made of polymeric materials.1 The new insulator materials make the insulators lighter, shatterproof, and easier to handle. However, their main advantage is their better electrical withstand performance, especially during foul weather conditions.2 The better performance is due to the surface properties: a polymeric surface is hydrophobic (water-repellent), whereas water films are formed on a porcelain surface. Severe environmental conditions can, however, alter the surface properties of polymer surfaces, thereby decreasing the wet flashover withstand voltage.3 Therefore, it is important to develop methods that can be used to identify polluted insulators. Today, there are no standardized or widely used techniques capable of detecting microbiological growth on the surfaces of silicone rubber insulators for field use. However, laser-induced fluorescence spectroscopy4 is known to be a method that is both non-intrusive and capable of giving detailed information about the properties of the surface under study. Algal growth, for example, exhibits a characteristic fluorescence peak due to chlorophyll a at a wavelength of about 685 nm and can readily be detected at a surface illuminated by excitation light of, e.g., 355 nm wavelength generated by a frequency-tripled Nd:YAG laser.5-7 However, fungal growth detection is a more demanding task. The fluorescence spectrum of silicone rubber covered by fungal growth has been shown to have a larger full width at half-maximum (FWHM) than the spectrum of a clean surface, but this effect is not always easy to determine without a more careful analysis of the spectrum.

In this study a combination of laser-induced fluorescence (LIF) and principal component analysis (PCA)8,9 is used in an attempt to develop an easily applicable method to detect fungal growth on silicone rubber. The method developed should be possible to use independently of the choice of silicone rubber and the type of fungal strain infecting the material.

EXPERIMENTAL TECHNIQUES

Materials. Silicone rubber with 20% SiO2, filler and di(4-methyl benzoyl)peroxide added as a crosslinker was used as a base. For some samples the base was mixed with the flame retardants aluminum trihydrate (ATH) and zinc borate, as stated in Table I. Materials were kneaded in a 12 rpm Brabender internal mixer for 15 min prior to curing. The curing was performed in a Schwabenthan Polylstat press at a temperature of 180 °C and a pressure of 10 MPa. The resulting discs had a diameter of 200 mm and a thickness of 2 mm. Samples were post-cured for 4 h in a hot air oven at 200 °C before use.

Microorganisms. The microorganisms used were isolated from silicone rubber high voltage insulators collected from Sweden, Sri Lanka, and Tanzania.10 The eight fungal cultures described in Table II were grown on malt extract agar for 28 days in room temperature before use.

Inoculation of Samples. Fungal spore suspensions were prepared by pouring 20 mL of the nutrient medium, described in Table III, on the agar surface of each of the cultures. The surfaces of the wetted cultures were scraped gently with a flame-sterilized platinum wire. The liquid was then slightly agitated and the suspensions were filtered through thin layers of glass wool into 100 mL glass-stoppered Erlenmeyer flasks prepared with 30 mL of nutrient medium and ten solid glass beads. The flasks were...
shaken and the suspensions were sprayed onto the silicone rubber samples according to Table II. All samples were incubated for 45 days at 27 °C and 95% relative humidity before measurements were conducted. In these experiments fungal infected and clean samples could normally be differentiated by eye.

**Instrumentation.** The fiber-optic fluorosensor that has been used in the experiments consisted of a nitrogen laser, optics, a probe, and a detection system. The laser generated radiation in pulses (3 ns, ~15 Hz, ~1 μJ) at a wavelength of 337 nm. The laser light was guided via a telescope through a fused silica optical fiber (600 μm in diameter, numerical aperture of 0.22) to the sample under investigation. The tip of the fiber was placed about 1 mm above the sample. The laser-induced fluorescence was spatially emitted in all directions and a fraction of it was collected by the same fiber and guided back to an optical multi-channel analyzer system (OMA) consisting of a crossed Czerny–Turner spectrometer, a time-gated image intensifier, and a charged-coupled device (CCD) camera. The Peltier cooled detector had a CCD array of 1024 × 128 pixels, where the 128 vertical pixels were binned. The resolution of the OMA system, set by the 100 μm slit width, was 2.2 nm, and the spectrum could be recorded up to 805 nm. The gatewidth of the intensifier was about 100 ns and could efficiently suppress the ambient light by a factor of about 10^5. A compact housing contained all the electronics and optics, and a personal computer was used to control the fluorosensor and to store the fluorescence data. A detailed description of the fluorosensor is given in Ref. 12.

**Analysis.** Laser-induced fluorescence spectra, acquired by the nitrogen-laser-equipped OMA system, were accumulated from the silicone rubber materials and the fungal cultures in order to build one separate model (a PCA model) for each class of spectra (see Table II). Each spectrum was accumulated from 100 laser pulses and 20 spectra were used to build each of the models.

Prior to PCA, data were pre-processed by mean normalization and mean centering. The data set obtained was then simplified with a PCA that decomposes the data set into a structure part, containing the maximum amount of variation, and a noise part. The first principal component (PC) is the combination of variables that experiences the greatest amount of variation. The second PC describes the second greatest amount of variation orthogonal to the first PC and so on. An arbitrary spectrum can be reconstructed by adding a linear combination of the PCs to the average spectrum. The PCs are orthogonal and therefore uncorrelated. Higher order PCs correspond to small variances and can be seen as noise.

**RESULTS AND DISCUSSION**

The main purpose of this study was to evaluate a potential method that combines laser-induced fluorescence and principal component analysis to detect fungal growth on silicone rubber insulator materials. The purpose was also to decide what kind of a score plot, which is a scatter plot of the value of several principal components in the same plot, is best suited for the detection of fungal growth. A score plot can contain spectra of all materials and all biological growth but is then very difficult to utilize due to the formation of many groups of spectra that cannot be resolved. The PCs are dependent on the spectra analyzed, which makes it difficult to express too many groups of spectra by using only two PCs. A simplified score plot, which is based on only one variation, is easier to handle and capture by a PCA and can contain two well-separated groups of spectra. The fluorescence spectra of the four clean silicone rubber materials tested in this study are shown in Fig. 1. The different spectra are very similar in shape. However, a simplified score plot, based on the spectra of the insulator materials, still formed four different classes, as can be seen in Fig. 2. Ninety-five percent (95%) of the new clean material objects (spectra) have successfully been assigned to the existing classes by a soft independent modeling of class analogy (SIMCA) classification.10,11 The classification is based on classical statistics, and the object-to-model distance and the distance of the object to the model center are both crucial to which classes the new objects belong. SIMCA catches the similarities between members of the same class and a new sample will not be rejected if it is similar enough.

Figure 3 shows typical fluorescence spectra, captured by the nitrogen-laser-equipped OMA system in the laboratory, of eight different fungal cultures grown on silicone rubber filled with ATH. Spectra obtained from the

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**TABLE I.** Type and amount of flame retardant added in parts per hundred (pph) resin to the silicone rubber materials tested.

<table>
<thead>
<tr>
<th>Material</th>
<th>Flame retardant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>No flame retardant added</td>
</tr>
<tr>
<td>Base + ATH</td>
<td>100 pph ATH</td>
</tr>
<tr>
<td>Base + ATH + zinc borate</td>
<td>90 pph ATH + 10 pph zinc borate</td>
</tr>
<tr>
<td>Base + zinc borate</td>
<td>10 pph zinc borate</td>
</tr>
</tbody>
</table>

**TABLE II.** Microorganisms used for inoculation of silicone rubber samples.

<table>
<thead>
<tr>
<th>Country</th>
<th>Fungi</th>
<th>Base + ATH</th>
<th>Base + ATH + zinc borate</th>
<th>Base + zinc borate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweden</td>
<td>Epicoccum nigrum</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>Microspalteriopsis</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>Cladosporium cladosporoides</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>Fusarium semitectum</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>Polyscytalum fuscium</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>Stagonospora</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Tanzania</td>
<td>Curvularia lusae</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>Cladosporium tenuliroides</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Reference</td>
<td>Clean materials</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
</tbody>
</table>

**TABLE III.** Nutritive solution.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH₂PO₄</td>
<td>0.7 g</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>0.3 g</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>0.5 g</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>2.0 g</td>
</tr>
<tr>
<td>KCl</td>
<td>0.5 g</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>0.01 g</td>
</tr>
<tr>
<td>Sucrose</td>
<td>30 g</td>
</tr>
<tr>
<td>Water</td>
<td>1 L</td>
</tr>
</tbody>
</table>
fungus-covered samples have larger FWHM than the spectrum of the clean ATH-filled silicone rubber material and are located further to the left in the score plot (see Fig. 4). However, for some samples these effects are small and hard to detect in the spectra obtained. Results are easier to interpret from a simplified score plot of the sample set. As can be seen in Fig. 4 spectra of samples infected by fungal growth are spread out to the left in the score plot compared with the spectra of the clean material. The spread is due to the combination of fluorescence from the fungal growth and the material. A heavily contaminated sample is likely to end up further to the left in the score plot when compared with a cleaner sample. When results are displayed as a simplified score plot it is easy to differentiate a sample infected by fungal growth from a clean material. The different fungal cultures studied all followed the same trend in the simplified score plot, which is desirable for the development of a general inspection technique for composite insulators.

However, a useful method must be applicable to different materials as well as to different fungal cultures. In Fig. 5, fluorescence spectra of four different insulator materials are compared with spectra of samples of the same materials covered by fungal growth. Simplified score plots of the sample sets show that spectra of a fungus-covered material are spread out to the left in the score plots for the clean materials in all cases studied. The method seems to give the same general response regardless of the composition of the silicone rubber under study. A typical principal component is shown in Fig. 6. Spectra of all eight fungal cultures grown on the ATH-filled silicone rubber material and spectra of the clean ATH-filled silicone rubber, as shown in Fig. 4, have been analyzed. PC 1 describes the change between the spectra. By adding a negative contribution of PC 1 to the average spectrum, the resulting spectrum will have a larger FWHM.

FIG. 1. Fluorescence spectra of the silicone rubber materials. The materials are presented in Table I.

FIG. 2. Score plot of the four silicone rubber materials. For each of the four materials measurements were carried out at 10 different positions.

FIG. 3. Fluorescence spectra of all eight fungal cultures on the ATH-filled silicone rubber material. The fluorescence spectrum of the fungus culture Stagonospora shifts most to longer wavelengths.

FIG. 4. The score plot contains a group of spectra of the clean ATH-filled silicone rubber material located within the circle. Spectra of all eight fungal cultures grown on the ATH-filled silicone rubber material are shown to the left. For each group measurements were carried out at 10 different positions. Outliers have been removed.

FIG. 5.
The PCs for the spectra in Fig. 5 have been shown to be similar. Laser-induced fluorescence in combination with principal component analysis is a promising method to detect fungal growth on silicone rubber materials. Contaminated silicone rubber samples analyzed with these methods give the same general response regardless of the composition of the silicone material and type of fungal contaminant under study. However, it is desirable to find the mechanism behind the responses observed. The signature of algae growth is a characteristic peak in the LIF spectrum due to chlorophyll \( a \) at a wavelength of about 685 nm. It would be an advantage if a similar relation between the laser-induced response of a fungal culture and some molecular component of it could be found. Nevertheless, it is possible to differentiate between algae, fungi, and...
clean surface by using a PCA (see Fig. 7). The fluorescence from pure fungal growth (see Fig. 8) is shifted to longer wavelengths and it is likely that the fungi signatures in combination with the fluorescence from clean materials can describe the larger FWHM from fungus covered materials. Future studies may include an investigation of aged insulator materials with a combination of laser-induced fluorescence and principal component analysis.

CONCLUSION

Laser-induced fluorescence in combination with principal component analysis proved to be useful as a tool to detect fungal growth on the surface of a silicone rubber material. The ability of the detection method to discriminate between clean and fungi infected samples was shown to be independent of the composition of the silicone rubber material as well as the type of fungal culture grown on the surfaces of the samples. This indicates that the method studied can be used as a general technique to inspect microbiological contaminations on high-voltage insulators made of silicone rubber. For field use fluorescence lidar techniques will be useful. Then spectra of the type discussed in the present paper can be recorded remotely, and remote fluorescence imaging can also be performed.

ACKNOWLEDGMENTS

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Remote laser-induced breakdown spectroscopy for the detection and removal of salt on metal and polymeric surfaces

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Abstract

The detection of contamination such as salt in outdoor high-voltage insulator systems and its subsequent removal are vital for a reliable transmission of electric power. Remote detection of salt on a copper metal surface was carried out by using a mobile LIBS Lidar system with a laser wavelength of 355 nm. Detection of salt on a polymeric high voltage insulator was obtained when an additional lens was inserted into the beam path, and the number of photons that was detected could be calculated by using a calibrated white light source. Ablative cleaning could readily be carried out with LIBS and was verified by observing the disappearance of the sodium D-line emission.

Keywords:  lidar; polymeric insulators; libs; remote sensing

Introduction

In high voltage applications, polymeric insulators are replacing traditional insulators made of porcelain or glass. The insulators made of polymeric materials have a variety of qualities that make them appropriate to use [1]. Their better performance in outdoor environments is due to the surface properties; a polymeric surface is hydrophobic (water-repellent) whereas water films can be formed easier on a porcelain surface. A general threat to the insulation properties of a high-voltage insulator is surface contamination. In sea environments salty water can spread with the wind (seaspray) and form salt layers on
insulator surfaces. When such salt layers are formed, certain insulators, in particular in switchgear stations, must be cleaned if natural rain is not sufficient. Thus, it is important to find reliable methods to detect the salt in order to clean affected insulators. In particular, a remote detection method together with a remote cleaning process possibly also involving fungi and algae deposits would be most advantageous since they can be performed on a live line, that is, the power line can be energized during the detection and cleaning.

Laser Induced Breakdown Spectroscopy (LIBS) [2] can be used for this purpose. In this laser technique, a laser pulse is focused onto the sample, the material is vaporized, and a plasma is formed at the surface. When the plasma cools, resonant fluorescence radiation is emitted when excited electrons and ions relax back into their ground states. LIBS is a spectroscopy method to analyze the chemical composition of a material. It has been widely applied in analytical chemistry. LIBS can be applied remotely as demonstrated by Palanco et al. [3], Rohwetter et al. [4] and Grönlund et al. [5]. In a parallel development at the Department of Physics, Lund Institute of Technology, remote LIBS is now being developed for remote ablative cleaning of cultural heritage, e.g. of paintings or statues [6]. Ablative cleaning with a velocity of approximately $10 \text{ cm}^2/\text{minute} \left(17 \times 10^{-6} \text{ m}^2/\text{s}\right)$ has been obtained at a distance of 60 m.

Polymeric insulator materials covered with microbiological growth have been studied with laser-induced fluorescence (LIF) [7-10]. For example, a fluorescence Lidar system was utilized to remotely detect the growth, and LIF imaging of the growth was carried
out also including principal component analysis (PCA) [11]. In the present paper we study the possibility to detect and image salt by using a remote LIBS Lidar system, and to perform ablative cleaning of metal samples and high voltage insulator surfaces.

**Experimental techniques**

**Materials**

The main objective of the work presented is to study salt contamination on outdoor high-voltage insulators. The high-voltage insulation systems also contain bare metal electrodes. We have thus performed experiments to detect and to remove salt deposits on both types of surfaces. The surface materials chosen were the electrode material copper and the high-voltage insulator material silicon rubber.

**Instrumentation**

A Lidar system, which was recently up-graded [12], was utilized in the present study. The target was mounted at a 60 m distance from the Lidar system. A frequency tripled Neodymium-doped Yttrium Aluminium Garnet (Nd:YAG) laser emitted laser pulses that were directed to the target via a specially designed 10 cm diameter refractive transmission telescope placed coaxially with the receiving 40 cm diameter reflective Newtonian telescope. The transmission and receiving beam paths were folded via a roof-top 40x80 cm first surface aluminized mirror, which was controlled by stepper motors for
precision scanning of the target. The laser beam was expanded and transmitted through a low-aberration telescope designed with the aid of a ray-tracing program (Linos Photonics, WinLens 4.3) as described in [6]. One planoconcave and two planoconvex lenses with focal lengths of -25, 500 and 1000 mm and spaced by -20 and -25 cm were employed. The aluminized folding mirror limited the laser pulse energy and in order to avoid optical damage we normally employed 180 mJ, 4-5 ns long pulses at 355 nm, generated by a Spectra-Physics Model GCR-290 Nd:YAG laser. The focal spot diameter at the target was about 5 mm. The lower limit for LIBS breakdown at a metal target was about $1.5 \times 10^{12}$ W/m$^2$.

A part of the plasma light was captured by the receiving unit of the Lidar system and guided to an optical fibre with a 600 μm core diameter and directed to an optical multi-channel analyser system (OMA), consisting of a crossed Czerny-Turner spectrometer (Oriel Corporation MS125, 400 lines mm$^{-1}$) equipped with an Andor DH50125U-01 gated and intensified CCD detector. The Peltier cooled detector had a CCD array of 1024x128 pixels where the 128 vertical pixels were binned. The resolution of the OMA system, set by the 100 μm slit width, was 2.2 nm, and the spectrum could be recorded up to 805 nm. A timing window of 150 ns was selected to observe the emission lines from the plasma.
Analysis

In Fig. 1 temporally resolved LIBS spectra from a copper target are shown. The emission lines have been recorded using a detection gate of 20 ns which was placed at a delay of 200 ns, 300 ns, 400 ns and 500 ns beyond the arrival of the elastic Lidar echo. Spectral lines at 427.511 nm \( (3d^9 4s(D)5s-3d^9 4s(C))5s-3d^9 4s(C))4p \), 465.112 nm \( (3d^9 4s(D)5s-3d^9 4s(C))4p \), 510.554 nm \( (3d^{10}(S)4p-3d^9 4s^2) \), 515.324 nm \( (3d^{10}(S)4d-3d^{10}(S)4p) \), 521.820 nm \( (3d^{10}(S)4d-3d^{10}(S)4p) \) and 578.213 nm \( (3d^{10}(S)4p-3d^9 4s^2) \) can be seen. The delay of 400 ns was chosen since the plasma continuum almost had disappeared and the emission lines were still strong. As a first example of remote LIBS spectra we show in Fig. 2 emission lines from a copper target, recorded 400 ns after ablation using a 150 ns detection gate to improve the detection possibilities. The vertical lines correspond to tabular values of prominent emission lines [13]. A detection limit of 7.5 µg/l for Na\(^+\) using a photodiode array detector has been reported by Knopp et al. [14] when utilizing an excimer (308 nm) pumped dye laser with laser pulse at 500 nm and pulse energy at 22±2 mJ to generate a plasma in a saline solution. When LIBS (LIBS Lidar system) was applied to a salt covered copper plate in motion the sodium D-line at about 589 nm was observed, see Fig. 3. The intensity of the sodium D-line depends on amount of salt, the temperature and density of plasma, laser beam profile, the laser pulse energy, etc. Remote LIBS measurements were tried on a salt covered polymeric insulator surface, but the fluence was too low to create a break-down spark.
To obtain breakdown in salt on a silicone rubber surface a collimated laser beam (LIF Lidar system) was utilized instead and an extra lens (focal length ~ 50 cm, diameter 10 cm) was inserted into the beam path to focus the laser light onto the salt covered insulator target (spot diameter 0.7 mm). The lower pulse energy limit for breakdown was 15 mJ/pulse. Fig. 4 shows emission lines from a saturated saline solution (~22 % salt) on a silicone rubber surface where the sodium D-line clearly can be seen. A pulse energy of 25 mJ was used for this recording. The extra lens did not only increase the laser intensity at the target but also collected more laser-induced light back to the detection system. The spot diameter was 0.7 mm with the LIF Lidar system with an extra lens. This is to be compared with the theoretical spot diameter of 0.7 mm that was calculated for the LIBS Lidar system.

As mentioned, the practical diameter achieved was 5 mm. Despite a good alignment of the optical components in LIBS Lidar system the beam shape still suffered from astigmatism implying that the beam expander lenses were not perfectly mounted or cut/polished. By using a diffraction limited optical system there would be no need for an additional lens.

The number of photons that contributed to the sodium D-line in Fig. 4 could be calculated by the following procedure. A white light source (200 W calibrated quartz tungsten/halogen lamp, Oriel 63355) was placed at the target position. About $1.0 \times 10^{16}$ photons/s, emitted by the white light source at 589 nm within 0.5 nm, was captured by the extra lens, placed 22 cm from the lamp, and directed to the OMA system and a
conversion factor of $6.4 \cdot 10^9$ photons/count was derived. Thus $6.1 \cdot 10^{13}$ photons in the plasma contributed to the sodium D-line in Fig. 4. Fig. 5 shows a typical spectrum in this study of the sodium D-line captured by a single laser pulse.

Ablative cleaning of an insulator surface was also performed by using LIBS as verified by the disappearance of the sodium D-line, see Fig. 6. Imaging of salt can readily be performed in a similar way as the imaging of the metals which has been carried out at Lund Institute of Technology by using the LIBS Lidar system [6]. For an insulator surface the velocity of salt removal was faster than 10 cm$^2$/minute ($17 \cdot 10^{-6}$ m$^2$/s).

Results and discussion

The main goal with this paper was to demonstrate the possibility to detect salt by observing the sodium D-line emission with a Lidar system, and to clean a salt-covered insulator surface. It was easy to detect salt on a metal surface but it was harder to do it on a silicone rubber surface. In the case of using a metal as a target, the salt could be vaporised in the plasma that was created on the metal surface. The intensity of laser light required to obtain breakdown in salt on a silicone rubber surface could be estimated by inserting an additional lens into the beam path. To calibrate the detection sensitivity and estimate the number of photons emitted from Na on the insulator surface an intensity calibrated white light source was utilized to calibrate the detection system.
It is likely that LIBS can be utilized to measure the high salt concentrations on the switchgear stations. LIBS trials performed on saline solutions with different NaCl concentrations did not give any LIBS signal. This is due to the low absorption of laser light in the water. However, when water droplets were formed on the insulator surface and measurements were carried out on a saturated saline solution on an insulator surface (both in the water droplet and beside it) the sodium D-line could readily be detected.

A drawback of the LIBS technique has been the difficulty to quantify low concentrations of elements. A possible solution to determine the salt concentration on an insulator surface could be to utilize calibration curves compared to a standard, and to compare new spectra with the calibration curves.

Ablative cleaning could be carried out, and by observing the sodium D-line emission it could be verified remotely if the surface under study was clean or not after a LIBS measurement. Based on the experience also from Ref. [6], it seems to be likely to utilize LIBS to remove not only salt but also other possible pollutants without damaging the insulator surface during ablative cleaning.

**Acknowledgements**

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Figure 1. LIBS spectrum from a copper target. The spectrum was obtained by averaging over 100 laser pulses with a detection gate of 20 ns. Upper left: Delay of 200 ns. Upper right: Delay of 300 ns. Lower left: Delay of 400 ns. Lower right: Delay of 500 ns.
Figure 2. Remote LIBS spectrum from a copper target. The spectrum was obtained by averaging over 500 laser pulses. The solid lines designate spectral lines at 427.511 nm, 465.112 nm, 510.554 nm, 515.324 nm, 521.820 nm and 578.213 nm.
Figure 3. Remote LIBS spectrum from a salt covered copper target in motion. The spectrum was obtained by averaging over 200 laser pulses. The sodium D-line is visible at about 589 nm. Spectral lines at 510.554 nm, 515.324 nm and 521.820 nm can be seen.
Figure 4. LIBS spectrum (LIF Lidar system with an extra lens) from a saturated saline solution on a silicone rubber target. The spectrum was obtained by averaging over 200 laser pulses. The sodium D-line at about 589 nm can clearly be seen.
Figure 5. LIBS spectrum (LIF Lidar system with an extra lens) from a salt covered silicone rubber target. The spectrum was obtained from one laser pulse.
Figure 6. LIBS spectrum (solid line) (LIF Lidar system with an extra lens) from a saturated saline solution on a silicone rubber target. The spectrum was obtained by averaging over 200 laser pulses. The removal of salt is verified by the disappearance of the sodium D-line emission (dashed line).