Chapter- V

Interaction of Glucose with Electrostatically Stabilized Magnetic Nanoemulsions and a Novel Application of Magnetic Nanoemulsions
5.1 Introduction

There has been an increasing demand for the selective and sensitive detection methodologies for monitoring glucose levels in body fluids, food products and biochemistry.\textsuperscript{147} The normal glucose level in human body is 4.2-6.4 mM and for diabetes mellitus it is above 7.0 mM. An elevated urine glucose concentration indicates a familial renal hyperglycemia\textsuperscript{148} or diabetes mellitus. Over the years, several methodologies have been developed for glucose detection, of which most of them are based on glucose oxidase coupled to electrochemical system where the response depends on enzyme activity or glucose mass transport.\textsuperscript{149-147} Some of the recent techniques are based on 3D Graphene-cobalt oxide electrodes,\textsuperscript{150} platinum-cobalt (PtCo) bimetallic alloy nanoparticles decorated graphene,\textsuperscript{151} dielectric properties of polymers,\textsuperscript{152} surface plasmon resonance,\textsuperscript{153} zinc oxide (ZnO) nanowires modified with gold (Au) nanoparticles,\textsuperscript{154} three-dimensional porous sensing platform using nickel foam\textsuperscript{10}, copper sulphate (CuS) nanotubes\textsuperscript{11} and opal closest-packing photonic crystals.\textsuperscript{155} Most of the reported sensors are enzyme labeled.\textsuperscript{149, 156-159} Two other issues with existing approaches that limit their practical applications are long response time and instrumentation. The notable optical sensing approaches are based on optical diffraction.\textsuperscript{147, 160-161} Some of the drawbacks of optical methodologies are non-glucose specificity, long response time and pH dependence.\textsuperscript{147} Towards exploring the use of nanoemulsion for glucose detection, the interactions of nanoemulsion with glucose of different concentrations are studied here.
Glucose is used in many food and pharmaceutical industries. The concentration of glucose in aqueous solutions largely influences the quality and shelf-life of final products.\textsuperscript{162} Sugar plays important role in stabilization of biological structures and functions.\textsuperscript{163-164} Some living organisms are able to survive in hostile environments such as extreme cold or drought conditions due to the secretion of carbohydrates.\textsuperscript{165} Also, glucose is shown to be a promising candidate for structural modification of free-standing surfactant films owing to its capability to form hydrogen bonds.\textsuperscript{166} There are also reports on the role of glucose in enhancing the stability of aqueous silica gels against dehydration.\textsuperscript{165} Therefore, the interactions of glucose with colloidal dispersions are of fundamental interest too.

The present work is aimed to investigate the possible interaction of D-glucose with surfactant stabilized emulsions by equilibrium force measurements for better understanding the role of carbohydrates in colloidal stability. The influence of glucose on the electrostatic interactions as a function of glucose concentration is probed by force measurements. The effect of glucose on the 1D droplet array spacing is also studied at different D-glucose concentrations. Towards development of some practical applications, effort is also made to develop a label free (without boronic acid derivative and enzyme) glucose detection approach and a non-destructive optical sensor for detecting buried defects in ferromagnetic structures using magnetic nanoemulsions.

\textbf{5.2. Materials and Methods}

D-Glucose anhydrous with 99.9 \% purity was purchased from E-Merck and used without further purification. The magnetically polarizable nanoemulsion used in the present study is \textit{ESD0.8} and \textit{ESD0.08}. Magnetic nanoemulsion preparation methods are discussed in Chapter II.

\textbf{5.3 Results and Discussion}
5.3.1 Effect of Glucose on 1D Droplet Array Spacing

To study the effect of glucose on the 1D array spacing, diffraction peaks are measured with different glucose concentrations by the same experimental procedure followed in 3.3.1.

**Figure 5.1** The Bragg peaks at different D-glucose concentrations in (a) *ESD0.8* emulsion at an applied magnetic field strength of 81 G and (b) *ESD0.08* emulsion at 117 G. Arrow indicates increasing concentration of D-glucose form 243 μM – 25 mM. The inset of Fig. 5.1(a) shows molecular structure of D-glucose.
**Fig. 5.1a** shows Bragg peaks measured for different D-glucose concentrations starting from 1.2 to 30 mM at an applied magnetic field of 81 G for *ESD0.8* emulsion. The molecular structure of D-Glucose is shown in the insert of **Fig. 5.1a**. Without D-glucose, nanoemulsion shows a fairly symmetric diffraction peak (\(\lambda_{\text{peak}}\)), which shifts towards higher wavelength with increasing concentration of D-glucose. **Fig. 5.1b** shows spectral response of magnetic nanoemulsion stabilized with SDS at a lower concentration of 0.08 mM (*ESD0.08*) where the diffraction peaks are recorded at an applied magnetic field of 117 G (**Fig. 5.1b**). Without D-glucose, the diffraction peak appears at \(\sim\) 840 nm and it shifted towards higher wavelength with increasing D-glucose concentration.

**Fig. 5.2** shows the \(\Delta\lambda_{\text{peak}}\) for *ESD0.8* stabilized nanoemulsion at applied magnetic field strengths of 81, 108 and for *ESDS0.08* at 117 G applied magnetic field as a function of different D-glucose concentrations. In the concentration range of 0.243 to 1 mM, \(\Delta\lambda_{\text{peak}}\) was not significant but above 1 mM, \(\Delta\lambda_{\text{peak}}\) changes linearly. The \(\Delta\lambda_{\text{peak}}\) value at 30 mM D-glucose concentration was 69 nm. At higher applied magnetic field strengths, the diffraction peak appears at a lower wavelength of 640 nm (compared to 685 nm for 81 G) due to stronger dipolar coupling. Again, the diffraction peak position moves towards higher wavelengths with increasing D-glucose concentrations. At lower concentrations, up to 4.5 mM, \(\Delta\lambda_{\text{peak}}\) was almost the same for both applied magnetic field strengths of 81 and 108 G, but above 4.5 mM, the \(\Delta\lambda_{\text{peak}}\) was higher at 81 G. The maximum \(\Delta\lambda_{\text{peak}}\) observed at 30 mM (at 108G) D-glucose was 54 nm.

The *ESD0.08* emulsion showed a better linearity in the concentration range 0.24 – 25 mM at an applied field of 117 G. As the maximum \(\Delta\lambda_{\text{peak}}\) is \(\sim\)100 nm, even naked eye D-glucose visualization of color change in the emulsion is possible. The colors seen in the emulsion
without (left) and with 25 mM D-glucose (right) at a magnetic field strength of 117 G are shown in the inset of Fig. 5.2. $\Delta \lambda_{\text{peak}}$ changes linearly with D-glucose concentrations at applied magnetic field strengths of 81, 108 and 117 G. Solid lines in Fig. 5.2 correspond to the linear fits, $y=2148.6x-3.8$, $R^2=0.968$; $y=1703.2x-16$, $R^2=0.974$; $y=3696x+3$, $R^2=0.996$. Though the emulsion showed a linear response in the concentration range of 0-30 mM, at all three magnetic field strengths, the best linearity is observed for applied field of 117 G.

**Figure 5.2** The shift in the diffraction peak wavelength with increasing D-glucose concentration at different magnetic field strengths for *ESD0.8* and *ESD0.08* emulsions. Photographic image of cell containing emulsion without (left) and with 25 mM D-glucose (right) at a magnetic field strength of 117 G are shown in the inset.
5.3.2 Effect of Glucose on Interaction Forces

![Force-distance profiles](image)

**Figure 5.3** Force-distance profiles measured at different D-glucose concentrations for ESD0.8 emulsion. Solid lines correspond to fit using Eqn. 1.30.

To decipher the observed red shift in the Bragg peak upon D-glucose addition, the interdroplet force profiles were measured. **Fig. 5.3** shows the force-distance profiles measured at different concentrations of D-glucose in ESD0.8 emulsion. Here, the force-distance profiles were exponentially decaying with the inter-droplet spacing. The force-distance profiles are fitted (solid lines) with the overlapping diffuse electric double layers force profile (Eqn. 1.30).\(^\text{48}\) From the force distance profile we have extracted the \(2 \lambda_0\), \(\kappa^{-1}\) and \(K\). Before the addition of D-glucose, the force profile decays with a \(\kappa^{-1}\) of 6.2 nm and a \(2 \lambda_0\) of 55.6 nm. The \(\kappa^{-1}\) values extracted for D-glucose concentrations of 2.38, 5.5, 16.7, 25 and 30 mM were 6.4, 6.8, 7.8,
9.3 and 10 nm, respectively and the corresponding $2L_0$ values were 58.7, 58.6, 64, 68.7 and 70 nm, respectively. In the D-glucose concentration range of 0-30 mM, the force magnitude decreases from $2.1 \times 10^{-9}$ to $4.5 \times 10^{-10}$ N.

![Graph](image)

**Figure 5.4** Force-distance profiles measured at different D-glucose concentrations for ESD0.08 emulsion. Solid lines correspond to the best fit using Eqn. 1.29.

Fig. 5.4 shows exponentially decaying force-distance profiles for ESD0.08 emulsion measured at different D-glucose concentrations. The interaction force between two spherical particles with small charge densities (extended electric double layer, $\kappa a < 5$) is represented by Eqn. 1.29 (solid lines in Fig. 5.4). From the best fit using Eqn. 1.29, the $\kappa^{-1}$ values were 18.4, 18.7, 21.6 and 24.4 nm for D-glucose concentrations of 0, 2.3, 16.6 and 25 mM,
respectively. The corresponding 2L₀ values were 102.6, 106, 110.5 and 116 nm, respectively. These results show that the force-distance profiles are dictated by the electrical double layer forces due to the adsorbed SDS molecules at the oil-water interface and the D-glucose molecules do not affect the decay length significantly. Surprisingly, in the presence of D-glucose, the onset of interaction (2L₀) increases significantly when the D-glucose molecules are introduced. Therefore, the interdroplet spacing is increased significantly upon the addition of D-glucose.

5.3.3 Proposed Interaction Mechanism

Glucose is known to form hydrogen-bonding with an organic functional group, a property that has been successfully exploited for the synthesis of mesoporous silica materials with D-glucose as a nonsurfactant pore-forming agent in the sol gel reactions,¹⁶⁷ to produce self-assembled polymer nanotubes in water,¹⁶⁸ self-assembled chiral organogels from achiral hydrogen bonded hydrazide foldamers by induction of chiral¹⁶⁹ produce self-assembled freestanding air–water interfacial ZrO₂ films.¹⁶⁶ The preparation of superior quality inorganic/organic nanostructures using surfactant-templated self assembly became popular since the emergence of nanotechnology. The crystalline metallic oxide/surfactant hybrid films prepared by surfactant-templated self assembly exhibit periodic nanostructures with different curvatures.¹⁶⁶ Earlier studies revealed that the glucose molecules are associated with SDS through hydrogen-bonding interactions.¹⁶⁶ Depending on the ratio of glucose to SDS, different architectural packings are possible. The X-ray diffraction and high resolution transmission electron microscopy studies showed that Glucose-SDS template can form lamellae structures.¹⁶⁶ The recent simulation and vibrational sum frequency studies show that at the
oil/water interface, SDS head group is surrounded by water molecules while the hydrophobic tail part is in a disordered state and partially in contact with water.\textsuperscript{141-142}

Before the introduction of glucose, the SDS molecules adsorb at the droplet surface with the negatively charged head group exposed to water. The co-ions with negative charge and the counter ions with positive charge form an electric double layer.\textsuperscript{99} For \textit{ESD0.8} with 1.3mM (30 mM) of glucose, the numbers of SDS and D-glucose molecules are $4.818 \times 10^{20}$ and $7.34 \times 10^{20}$ (1.8 x $10^{22}$), respectively. This means that even at the lowest D-glucose concentration, more than one SDS molecules/glucose is present in the system. At 5 mM D-glucose, the ratio of D-glucose to SDS molecule is 7, which increases to 37 at 30 mM. The force-distance curves show that the $\kappa^{-1}$ increases from 6 to \textasciitilde10 nm as the concentration of D-glucose is increased from 1 to 30 mM, where the magnitude of force decreases from $2 \times 10^{-9}$ to $4.5 \times 10^{-10}$ N. This means that the association of SDS with D-glucose gives rise to a more diffused overlapping double layer (i.e. less screening effect). As the minimum interdroplet spacing is much larger, the short-range forces such as Van der Waals forces and structuring forces do not have any dominant contributions to the force profiles.

Based on the observed Bragg peak shift, force-distance profile data, and the HRTEM/XRD studies on glucose-SDS complexes, the possible architecture of glucose-water-SDS at the emulsion interface is schematically shown in Fig. 5.5. The glucose molecules interact with SDS via hydrogen-bonding and the association of glucose-water- SDS leads to a stretched lamellae like structure,\textsuperscript{166} that eventually increases the inter-droplet spacing leading to a red-shift in the Bragg peak. Of course, more systematic simulation and experimental studies are necessary to fully unravel the exact architecture of the self assembled structures. As emulsion
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shows a linear change in the peak wavelength in the concentration range of 0.243 to 25 mM, it offers an ideal condition for diabetic glucose detection. Owing to the smaller droplet size, the typical response time of the emulsion is \(~\)1.5 sec, which is quite rapid compared to many solid state sensors which is another advantage of the present approach.

Figure 5.5 Schematic representation of droplet without (left) and with D-glucose bound on droplet via SDS and water molecules (right) along with the Bragg peaks and the enlarged view of glucose–water-SDS complex at interface (bottom).
5.4 Application of Magnetic Nanoemulsions in Defect Detection

Inspired from the magnetic field tunable diffraction of visible wavelengths by magnetic nanoemulsion, a novel naked eye magnetic field sensor for visualizing buried defects of different morphologies and dimensions in ferromagnetic structures is developed. Detection of defects in materials or components in a non-destructive manner is popularly known as Nondestructive testing (NDT). It is very important for many industries in ensuring safety of machines and components, productivity and unexpected shutdowns. Several traditional NDT techniques have been established, yet new ones that are user friendly, rapid, compact, non-contact, highly sensitive and cost effective are being developed. Among magnetic testing of components, magnetic flux leakage (MFL) has been one of the popular techniques for defect detection in ferromagnetic materials, due to their simplicity and ease in usage.\(^{170-174}\)

The presence of a defect or crack or inclusion causes a sudden local change in the magnetic permeability that results in a flux leakage around the defective region. To detect such defects and to quantify their features such as morphology, dimension and location within the material, the leakage field near the defect is detected by a magnetic field sensor such as Hall probe, flux gate sensor, magneto-diode, search coil, magnetic particle, Forester micro probe.\(^{175-178}\) Recently, new magnetic sensors such as SQUID,\(^ {179}\) Giant magneto resistance (GMR),\(^ {180-181}\) giant magneto impedance (GMI)\(^ {182-183}\) and anisotropic magneto resistance (AMR)\(^ {184}\) have been used to detect the defects with high sensitivity. Magneto optic (MO) sensors which work on the Faraday’s rotation change with the MFL also appear as attentive and sensitive for visualization of defects.\(^ {185-186}\) In MFL techniques, the raw data needs to be processed along with computationally intensive numerical modeling to obtain accurate
information on the defect shapes, dimension and the location within the test components. Analytical models are fast and simple but less accurate because of many approximations used in the calculations. Whereas numerical models are accurate but they are computationally expensive.\textsuperscript{187} These problems associated with conventional MFL techniques warrant the need for more reliable, simple, cost effective and sensitive techniques for detection of leakage of magnetic flux in ferromagnetic components and structures. Towards realizing this goal, here a new methodology to detect defects of different morphologies to quantify the defect shape, location and dimensions is developed. The new approach is tested and validated in specimens with artificial defects of different geometries.

5.4.1 Theoretical Background

Prior knowledge about the MFL profile of a defective region is useful for interpreting the defect features. There are several analytical and numerical models\textsuperscript{187, 195-206} to predict the magnetic flux leakage from a defective region. Although Zatsepin and Shcherbinin model,\textsuperscript{207} based on magnetic line and surface dipoles, yields reasonably good results with respect to experiments, it cannot be readily adapted for overlapping defects and defects of different morphologies. In such cases, finite element approaches are ideal for the analysis of defects of different morphologies.\textsuperscript{195, 208} We use the simple analytical approach of Uetake-Saito\textsuperscript{192} to obtain the MFL profiles for testing our experimental results. The magnetic flux leakage originates from magnetic reluctance of the defective region where the magnetic permeability is much lower than that of the sound region. According to a simple dipole model, normal components of the leakage flux from rectangular defect with depth $Y_0$ and width $l$ is given by,\textsuperscript{209}
\[ H_y = \frac{H_g}{2\pi} \ln \left( \frac{(x+l/2)^2 + (y+y_0)^2}{(x-l/2)^2 + (y+y_0)^2} \right) \frac{(x-l/2)^2 + y^2}{(x+l/2)^2 + y^2} \]  

(5.1)

where, ‘\( H_g \)’ is the field inside the defect for an applied field ‘\( H_a \)’ and is given by,

\[ H_g = \frac{2Y_0/l + 1}{(1/\mu)2Y_0/l + 1} H_a \]  

(5.2)

Here, the tangential and normal components of the leakage fluxes are calculated with an assumption that the surface charge density on the faces of the defect is a constant. The origin of the x-y coordinate axes is at the center of the top surface of the defect. It should be noted that the tangential component of leakage flux peaks at the center of the crack and falls to zero at the defect edges. Zhang et al.\textsuperscript{191} has developed analytical expressions for magnetic leakage field of two types of internal defects by taking into consideration the magnetic image effects from the spatial boundary and the defect boundary using the modified dipole model and image theory. We use the modified dipole model for adjacent parallel surface slots to obtain the leakage field profile. The schematic representation of the two adjacent defects geometry is shown in Fig. 5.6. The depths and widths of slot1, slot2 and the separation between the two adjacent slots are \( y_1, y_2, l_1, l_2, \) and \( 2l_g, \) respectively. According to the modified dipole model, the normal component of the two leakage fields from two parallel surface slots are given by,\textsuperscript{192}

\[ B_y = \frac{H_g}{2\pi} \left\{ \ln \left( \frac{(x+l_2)^2 + (y+y_1)^2}{(x+l_2)^2 + y^2} \right) - \ln \left( \frac{(x+l_1+l_g)^2 + (y+y_1)^2}{(x+l_1+l_g)^2 + y^2} \right) \right\} \]

\[ + \ln \left( \frac{(x-l_2-l_g)^2 + (y+y_2)^2}{(x-l_2-l_g)^2 + y^2} \right) - \ln \left( \frac{(x-l_g)^2 + (y+y_2)^2}{(x-l_g)^2 + y^2} \right) \]  

(5.3)
**Figure 5.6.** Schematic representation of adjacent cylindrical slots (defects).

**Figure 5.7** Calculated normal component of leakage field profile (a) rectangular slot and (b) for two adjacent cylindrical slots.

The normal component of leakage field profile for a rectangular slot defect and two adjacent cylindrical slots, calculated using **Eqn. 5.1** and **Eqn. 5.3** respectively, is shown in **Fig. 5.7**.
5.4.2 Experimental Setup

Figure 5.8 Schematic representation of typical experimental setup used for magnetic leakage field measurement and defect imaging with nanoemulsion.

Figure 5.8 shows schematic representation of a typical experimental setup for leakage field measurement and defect imaging. The specimens were magnetized using a DC magnetic yoke. The normal component of leakage flux around the defect were measured at a constant lift-off distance of 1 mm, using a hall probe. The specimen was first magnetized with an electromagnetic yoke and then the thin film sensor head was placed on the rear surface, at a constant lift of distance of 1 mm. The color pattern on the sensor was recorded using a digital camera or observed with the naked eye. The color patterns in the sensor were analyzed more carefully to assess the severity of the defects. The sensor is scanned across the specimen
surface to map the MFL profile across the entire specimen. To understand the correlation between the colour pattern and the leakage field from different specimens, the MFL values are measured with a Hall probe.

5.4.3 Sensor Head Fabrication and Specimen Details

Nanoemulsion is sandwiched between two optically transparent (microscopic) glass slides. A spacer of 300 μm thickness is used to achieve desired uniform gap. The sides of the cells are sealed to avoid seepages, moisture trapping and contamination of emulsion with foreign particles from outside.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Width/Diameter (mm)</th>
<th>Depth (mm)</th>
<th>Gap between slots 2l_s (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slot1</td>
<td>Slot2</td>
<td>Slot1</td>
</tr>
<tr>
<td>S1 (two cylindrical)</td>
<td>5</td>
<td>10.5</td>
<td>8</td>
</tr>
<tr>
<td>S2 (rectangular, cylindrical)</td>
<td>3</td>
<td>6.5</td>
<td>4</td>
</tr>
<tr>
<td>S3a (rectangular)</td>
<td>0.5</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>S3b (rectangular)</td>
<td>0.5</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>S3c (rectangular)</td>
<td>0.5</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>S3d (rectangular)</td>
<td>0.5</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>S4 (rectangular)</td>
<td>3</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>S5 (cylindrical)</td>
<td>10.5</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

**Table 5.1** Details of the specimens used in the studies. The specimen dimension in all cases (L × B × T) are 21 × 4.5 × 1 (cm).
Mild steel plates 50 mm length, 25 mm width and thickness of 10 mm with several well defined defect dimensions and shapes were fabricated for the test. The different defect geometries used for the study and their dimensions are listed in Table 5.1.

5.4.4 Nanoemulsion Sensor Response

![Schematics and photographs of specimens](image)

**Figure 5.9** Schematics of the specimens S1–S3a–d (a, c and e) and the corresponding photographic images of nanofluid sensor (b, d and f–i), respectively. (f–i) are S3a, S3b, S3c, S3d, respectively. The defective regions of each sample are encircled in the photographic images.

**Fig. 5.9 a-i** show the schematics of the specimen S1, S2, S3 (a-d) and the corresponding photographic images of the nanofluid sensor response. The sensor exhibits a natural color of brown (without MFL) due to the presence of iron oxide nanoparticles in the oil droplets. The defective region of each sample is encircled for clarity. On both sides of the defect, a color spectrum is observed due to the leakage of the magnetic flux around the defects. The centre line on the colour pattern was straight for the rectangular slot and semicircular pattern for the
cylindrical slot. **Fig. 5.9e** shows the photograph of the specimen S3 (a-d) and the corresponding sensor images are shown in **Fig. 5.9f-i**. The defects are clearly discernible from the images, though color contrasts were not very clear. This is mainly due to the lower leakage flux, owing to the smaller defects present and the larger remnant thickness of the specimens. However, the defect centre was very clearly discernible from the image.

In brief, a new approach to image and visualize defects buried inside ferromagnetic components is established. Colour pattern from MFL induced self-assembly of nanoemulsion is unique for different defect morphology which enables a user friendly and a naked eye defect detection approach. As the color pattern in the sensor is totally reversible, the sensor is reusable. This new approach will have potential applications in simultaneous inspection of large area ferromagnetic components and structures.

### 5.5 Conclusions

The optical properties and intermolecular interactions in magnetically responsive oil-in water nanoemulsions in the presence of an anionic surfactant and D-glucose is studied. The Bragg reflected light intensity from the emulsions at a fixed magnetic field strength shows that the equilibrium interdroplet distance between the emulsion droplets in the 1D array is increased by several nanometers in the presence of glucose because of intermolecular hydrogen bonding of glucose with sodium dodecyl sulphate molecules at oil-water interface. The intermolecular hydrogen bonding of glucose with sodium dodecyl sulphate molecules at oil-water interface gives rise to stretched lamellae like structures that un-screen the overlapping double layer, thereby increasing the onset of repulsion and the decay length significantly. The observed large red shift in the diffracted Bragg peak (~80 and100 nm) and the linear
response in the glucose concentration range of 0.25-25 mM offer a simple, fast and cost effective non-enzymatic approach for glucose detection.

A new approach to image and visualize defects buried inside ferromagnetic components by using magnetically polarizable nanoemulsion has been demonstrated. Leakage magnetic flux induced self-assembly of nanoemulsion, causes visible colour patterns in the sample. Defect dimensions can be quantitatively extracted from the RGB profile analysis. The extracted defect widths are in good agreement with the magnetic flux leakage measurement. As the color pattern in the sensor is reversible, the sensor is reusable and allows inspection of large area specimens.