A stable black-refractive-index-matching liquid for optical CT scanning of hydrogels

Kevin Jordan and Jerry Battista
London Regional Cancer Program, London Health Sciences Centre and Department of Medical Biophysics, University of Western Ontario, London, ON, Canada
kevin.jordan@lhsc.on.ca

Abstract. The calibration of optical CT scanners often involves referencing of transmission values to surrounding refractive index matching liquid. Often these liquids suffer from wavelength dependencies or can degrade during the course of a scan. In this paper, we describe a black liquid that serves as a stable reference for attenuation measurements. An optically stable, refractive index matching liquid for optical CT scanning of hydrogels was developed. The solution contains: water, glycerol, surfactant and carbon black. Sequential transmission measurements demonstrated less than 5% variation in transmission during a two week storage period at room temperature. Black solutions are expected to minimize spectral beam hardening artefacts associated with polychromatic light sources.

1. Introduction
Refractive index matching liquids are valuable for optical computed tomography (CT) scanning. Their use minimizes refraction and reflection of the imaging light and associated image artefacts. Radiation sensitive hydrogels and plastics (Presage™) have refractive indices in the ranges 1.34-1.37 and 1.52-1.54, respectively. This report focuses on optimizing the refractive index matching reference liquids for optical CT scanning of hydrogels. Currently, commercial optical CT scanners are equipped with either monochromatic lasers or narrow bandwidth light emitting diodes (LED). Often coloured compounds are added to the refractive index matching liquid in order to control the range of optical transmission by making the attenuation coefficient in the liquid similar to that of nonirradiated gel. Effectively this approach nulls out the base attenuation of the nonirradiated gel. However, if the absorption spectra of the added coloured compound changes over the spectral range of the LED source, transmission values through the hydrogel may be negatively affected. Specifically radiochromic gels such as ferrous-xylene orange, crystal violet and malachite green have absorption peaks between 570 and 630 nm. Unless the light source is matched precisely to these absorption peaks, there is the potential for producing spectral hardening artefacts in the transmission CT images. This spectral hardening problem may occur with LED light sources with spectral bandwidths that span a range where the absorption spectrum of the samples is changing.

Water is the best choice for the base liquid since the gels are primarily water and the refractive indices are very similar. Water is also, convenient, nontoxic, inflammable, inexpensive and it has a low vapour pressure. Often, glycerol or propylene glycol are added to water in order to match the hydrogel refractive index. Other solutions based on dissolved NaCl and sucrose can be readily prepared with appropriate refractive indices. However, during experiments liquids often come into
contact with other surfaces. Sucrose solutions are sticky as they dry and NaCl solutions are corrosive to many metals. Often the CT scanner aquarium contains machined plastic materials. Solvents such as alcohols can lead to hazing and fracturing of these machined surfaces and premature failure. The solutions are open to the atmosphere and scanning is often performed in an enclosed room where volatile, flammable solvents such as ethanol could be a safety hazard. Dust from the air accumulates in the liquids and periodic filtration is required to restore optical clarity of the liquid. Many coloured materials will adhere to paper filters leading to an increased transmission following filtration. Generally if mixtures of dyes are used then one dye will preferentially diminish during filtration leading to a change in their composite transmission spectrum. Still other types of coloured compounds are sensitive to pH and their spectra change as the pH is lowered by dissolution of carbon dioxide. Dissolved oxygen often plays a direct role in gradual degradation of coloured materials. In practice, we have found that patent blue violet and nigrosin dyes dissolved in water or propylene glycol aqueous solutions are reasonably stable over periods of days. However, these solutions form floating gelatinous particles over weeks in propylene glycol solutions. Nigrosin slowly adheres to plastic surfaces lowering the solution concentration. Gelatinous moulds, algae and bacteria also grow in these solutions unless preservatives are added. In brief, stable and user friendly liquids are necessary for reference liquids in quantitative optical CT scanning.

Black solutions are optimum for scanning with non-laser CT scanners since spectral hardening is limited only to the hydrogel. Black ink solutions have been reported in evaluation of laser CT scanners\(^1\). Previous investigations, within our lab tested several black inks but most were determined to be mixtures of several dyes, with crystal violet as a common ingredient. This work, evaluated surfactants as a method of preparing black, transparent, aqueous solutions with refractive indices matched to hydrogels. This initial study has identified a promising approach to preparing stable solutions that will simplify and improve the calibration and accuracy of optical CT scanning of hydrogels by wavelength-independent stable referencing.

2. Materials and methods

Crude carbon black was prepared by collecting soot from a candle flame onto metal foil. The carbon black was dissolved in a dilute aqueous solution containing liquid dish soap (Sunlight, Lever Ponds). The clear solution was brownish grey in colour. Several black inks were dissolved in similar soap solutions but only the drawing ink from Staedtler Mars had a similar visible colour. The absorption spectra of these two samples were recorded with a spectrometer (Hitachi Perkin-Elmer model 139). Subsequent studies were performed with this ink assuming that carbon black is the principle coloured ingredient in this product.

Triton X-100 (Sigma) a non-ionic surfactant and a commercial detergent (‘Simple Green® house and siding cleaner’, Sunshine Makers Inc, product code 18201) which contains non-ionic surfactants (polyethylene glycol ether derivatives) were chosen since both were clear and colourless. Combinations of solutions containing 10% glycerine or propylene glycol with either 2% Triton X-100 or ‘Simple Green®’ were prepared. Ink was added dropwise to obtain solutions with an estimated linear attenuation coefficient of 2 cm\(^{-1}\). These samples were much darker than would be typically required for optical CT scanning. Samples were observed for precipitate formation over several days and then filtered with 5 micron paper to test for adhesion to paper fibers.

Plastic cuvettes were filled with the samples containing 10% glycerine and sealed with wax paper. These samples were stored at 295 K. Transmission images were recorded through the cuvettes over a period of 500 hours with an Apogee AltaU47+ 16 bit CCD camera. The reference image was air for this experiment.
3. Results

Figure 1 shows the visible attenuation spectra of aqueous dishsoap solutions (Sunlight) containing carbon black from candle flame soot and black drawing ink. Note that the spectrometer filter switches at 600 and 650 nm, resulting in added structure to the smoothly increasing transmission spectrum. These spectra are similar those reported data for carbon black dispersed in mineral oil[2].

![Figure 1](image_url)

**Figure 1.** Transmission spectra for aqueous soap solutions of carbon black: candle flame soot (circle) and black drawing ink, Staedtler Mars (square). The similarity if the spectra confirm that Staedtler Mars ink is acceptable. The discontinuity at 600 nm is due to the switching filters in the spectrometer.

Figure 2 is a transmission image through cuvettes containing water and the black solutions with the surfactants Triton X-100 and Simple Green® house and siding cleaner. Mean values of a region of interest (2x10 mm) through the centres of the cuvettes referenced to air were recorded as a function of time. Water provided a reference liquid for this three week experiment. Table 1 lists the sample transmission as a function of time. The Triton X-100 sample transmission increased continuously. After four days a slight amount of black precipitate had settled in the cuvette and the sample was beginning to scatter light more than the Simple Green® solution. By 21 days, the Simple Green® sample was also developing a measurably greater transmission and transparency was beginning to degrade. Both samples were supporting mould or algae growth. Future experiments will identify a suitable anti-microbial agent that is effective and does not significantly alter the sample absorption spectrum.
Figure 2. Transmission image at 590 nm of carbon black, 10% glycerine 2% surfactant aqueous solutions: water (left), Triton X-100 (middle), ‘Simple Green®’ (right) in 1 cm pathlength cuvettes.

Table 1. Transmission of carbon black solutions as a function of storage time at 22°C.

| Time(hours) | H₂O Transmittance | Triton X-100 Transmittance | “Simple green” Transmittance |
|------------|--------------------|--------------------------|----------------------------|
| 48         | .936               | .296                     | .384                       |
| 72         | .936               | .305                     | .387                       |
| 98         | .923               | .327                     | .383                       |
| 144        | .908               | .374                     | .393                       |
| 216        | .917               | .412                     | .398                       |
| 360        | .924               | .475                     | .405                       |
| 528        | .923               | .547                     | .424                       |

4. Conclusions
Carbon black is a relatively inert material and stable transparent aqueous solution with refractive index of 1.36 have been successfully prepared with a surfactant. For this example the commercial product ‘Simple Green® house and siding cleaner’ which contains predominantly a non-ionic surfactant was used. A solution with a transmission of 40% per centimetre demonstrated a stable transmission for approximately 400 hours. It is anticipated that storage times for these solutions can be dramatically increased with the addition of appropriate antimicrobial agents. These stable black solutions will simplify quantitative optical CT scanning by minimizing the potential spectral changes for narrow band light sources and providing accurate attenuation coefficients from LED type scanners similar to those obtained with laser scanners.

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References
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