Coating Drierite with Methylene blue for Oxygen Indication

Minjae Kim[1*], Gina Kim[2*], Bonmin Gu[3*], Jaerin Kim[4+], Younchan Nam[5+], Younbok Abraham Kang[6+], Yountae Kim[7+], Hoyeon Kim[8+], Hoseong Yoo[9]

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Chemical indicators are used throughout the chemistry industry to differentiate between toxic and safe compounds and to detect the presence/absence of chemicals. There are many types of indicators such as pH indicators, peroxide indicators, and enzyme detectors. Oxygen indicators, however, use mainly sensors to detect the presence of oxygen and are not readily available commercially making them hard to access. Using Drierite and Leucomethylene blue as an oxygen detector can create a more accessible and affordable oxygen detector. Drierite is used as an indicator by numerous chemists because it can detect and absorb water. By spraying Leucomethylene blue onto the drierite, the color of methylene blue returns as the Leucomethylene blue solution oxidizes due to the oxygen in the surrounding atmosphere. Soaking drierite in the methylene blue solution dissolved the drierite in the process, leaving less of the indicator to work with. So, by spraying the methylene blue solution instead, the detection quality of the dye is still utilized without losing any of the drierite. We used a Leucomethylene Blue solution to spray onto the Drierite in order to test the oxygen detection levels of the solution and drierite. After spraying the solution onto drierite, the color changing was recorded in intervals. The study showed that the solution and drierite can function as an oxygen detector through the color change to blue from white. Drierite coated with Leucomethylene blue can serve as an indicator that detects both water and oxygen simultaneously, making it an excellent indicator for environments such as glove boxes where materials sensitive to air and water vapor are handled.

Introduction

Chemical indicators are staples in science, detecting toxic compounds, harmful substances and presence of chemicals. Indicators are designed to respond with either chemical or physical change, which can then detect the presence of specific chemicals[1]. Common examples are peroxide indicators, pH indicators, specific enzyme indicators, and presence of acetone in urine indicators[2]. However, indication of oxygen is not simple. Existing oxygen indicators rely on sensors or detectors, making them limited in availability not commercially accessible at affordable prices[3]

Glove boxes maintain desired atmospheres by circulating high-purity gasses and filtering them. However, they contain air and moisture sensitive materials such as calcium sulfide, iron (II) sulfide, and barium sulfide, which react explosively with oxygen. Detecting oxygen in the glove box will help identify damage due to exposure to air. Simultaneously detecting both oxygen and moisture presents a unique challenge due to the differing chemical properties and sensing mechanisms required for each.

Oxygen detectors are also used for food packaging to ensure freshness and high-quality products. The exposure to oxygen for food may lead to discoloration, over-ripening, and rotting. The products during oxidation exposes the gut to inflammatory conditions such as bowel disease. For people who package or prepare their own food, an affordable oxygen detector reduces the risk of oxidation[4].

Many chemicals are reactive when they come into contact with oxygen including the alkali metals[5]. Some of these reactions can lead to combustions or simple oxidation[6]. Not only could oxygen be a danger in certain environments, but the oxidation of chemicals reduces the shelf life of these alkali metals as well. Thus, detecting trace amounts of oxygen is crucial in chemistry because exposing it to other chemicals or elements could lead to a harmful reaction, and can deteriorate their effectiveness.

Methylene blue, the positively charged dye used for staining, can be reduced into a colorless solution called Leucomethylene blue through a hydrogenation reaction in a reducing environment. The colorless solution returns to the original blue color of the methylene blue dye when exposed to an oxidizing environment[7]. Methylene blue ($C_{16}H_{18}N_3SCl$) is a heterocyclic aromatic compound, existing in a form containing three water molecules. When reduced, it forms Leucomethylene blue ($C_{16}H_{19}N_3S$), gaining an electron and an additional hydrogen atom. The oxidized form contains conjugated double and single bonds, while in the colorless form, the delocalized electron systems are isolated.

Leucomethylene blue ($C_{16}H_{19}N_3S$) is a solution that is reduced from the methylene blue. It is a colorless solution but turns into a deep dark blue color when it is oxidized. It is one of the classes of phenothiazines where the ring hydrogens at positions 3 and 7 have been replaced by dimethylamino groups.

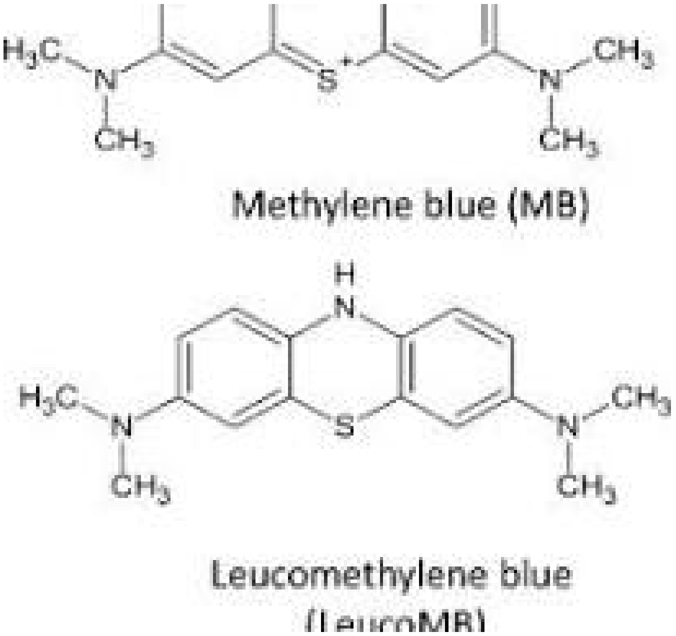

Fig. 1 Molecular structure of methylene blue and leucomethylene blue[8]

There are other color-changing indicators for other gases such as CO_2 indicator ink films that use pH indicator dyes[9]. The thin polymer film covers a carbon dioxide sensitive aqueous solution that detects dissolved CO_2. However, this indicator detects carbon dioxide through the creation of acids after the carbon dioxide has dissolved in water, not the gas itself. To detect oxygen without a sensor, you could use a uv lamp to see a color change in WO3 membranes[10]. However, many oxygen detectors use sensors because the process of detecting oxygen without a sensor in this way requires nanoparticles and redox dye inside polymer nanofibers for the colorimetry[10].

On the other hand, drierite, composed of calcium sulfate ($CaSO_4$), is a hygroscopic, odorless white powder used to detect and absorb water. It dries air, gasses, refrigerants, solids, and liquids, controlling dry atmospheres in glove boxes, desiccators, and commercial packages. The blue hue indicating drierite turns pink when exposed to moisture. While it only detects water, coating white drierite with Leucomethylene blue allows for the simultaneous detection of both water and oxygen. The drierite coated with leucomethylene blue shows signs of detecting oxygen through the oxidation reaction which turns the white leucomethylene solution blue.

Therefore, we hypothesized that coating drierite with Leucomethylene blue can simultaneously detect both moisture and oxygen.

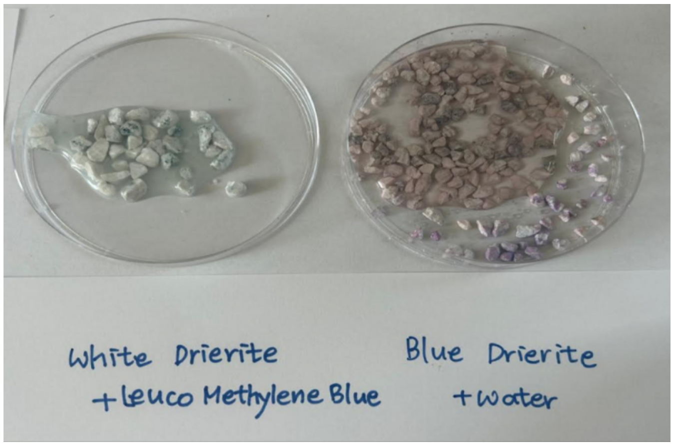

Fig. 2 Leucomethylene blue added white drierite and water added blue drierite

Results

Soaking vs Spraying method

When the coated drierite is exposed to the air, we can see the color change of the drierite to indicate that there is oxygen in the atmosphere. We tested two methods in coating drierite with Leucomethylene blue solution: soaking and spraying. In the soaking method, drierite was immersed in the solution, while in the spraying method, the solution was sprayed 10 times using a bottle sprayer.

The drierite composed of $CaSO_4$ is occasionally soluble in water. With an abundant amount of solute and absorption of moisture, this solubility of drierite sometimes leads the drierite to dissolve in water, hence distracting the observations.

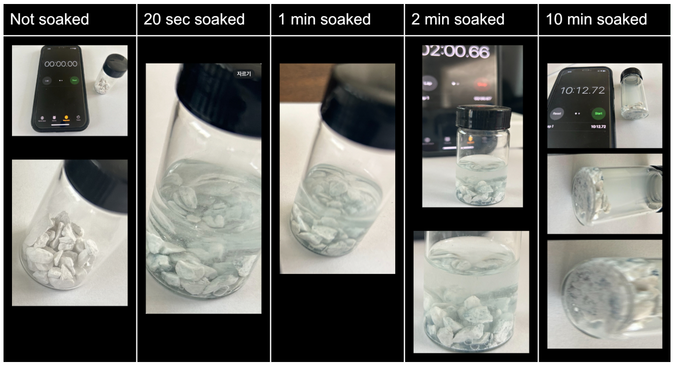

Fig. 3 Time-dependent changes in drierite soaked in Leucomethylene blue solution

Spraying the Leucomethylene blue solution onto the drierite allowed for the color to change to blue over time.

These results indicate that Leucomethylene blue-coated

Drierite can be an effective oxygen indicator under the condition that is coated using the spraying method, which is more durable and freer from outside variables impacting the results. Since drierite has the ability to absorb moisture rapidly, the leucomethylene solution sprayed onto the drierite will be absorbed rapidly as well. The absorption of the solution allows the coated drierite to be an affordable oxygen indicator due to the accessibility and cost-effectiveness of drierite.

Time-Dependent Color-Change

After we applied Leucomethylene blue using the spraying method, we measured the change of color over time in different intervals and recorded the data. At 10 seconds, the drierite mostly retained a colorless appearance, and a subtle blue tint had developed at 5 minutes. But in 13 minutes, we were able to observe a drastic color change to blue.

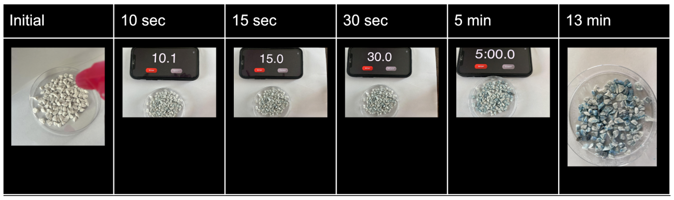

Fig. 4 Time-dependent changes after spraying Leucomethylene blue solution on white drierite.

For the control group, the white drierite sprayed with the leucomethylene blue solution was kept in an oxygen free environment. The changes in color were recorded.

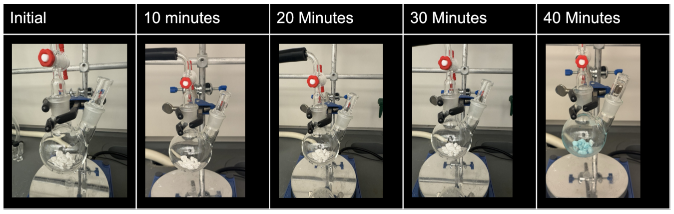

Fig. 5 Time-dependent changes after spraying Leucomethylene blue solution on white drierite in an oxygen-free environment.

After 40 minutes, the same white drierite coated in leucomethylene blue solution was introduced to oxygen.

This time-dependent color change demonstrates the gradual oxidation of leucomethylene blue back to methylene blue in the presence of oxygen. The rate of the color change correlates with the amount of oxygen exposure, confirming the coated drierite's effectiveness as an oxygen indicator. However, the drierite coated in the leucomethylene blue solution only detects if there is oxygen in the environment, not the amount of oxygen, limiting the oxygen detection to the presence of oxygen.

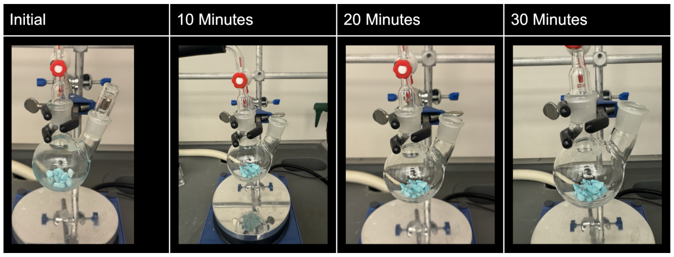

Fig. 6 Time-dependent changes after spraying Leucomethylene blue solution on white drierite after exposure to oxygen.

Effect of Reagent Concentrations on Reaction Rate

The leucomethylene blue solution was prepared using varying concentrations of methylene blue, Vitamin C, and hydrochloric acid to determine the optimal conditions for rapid and complete reduction. UV-Vis spectroscopy was used to monitor absorbance changes in the solution over time (Figure 1).

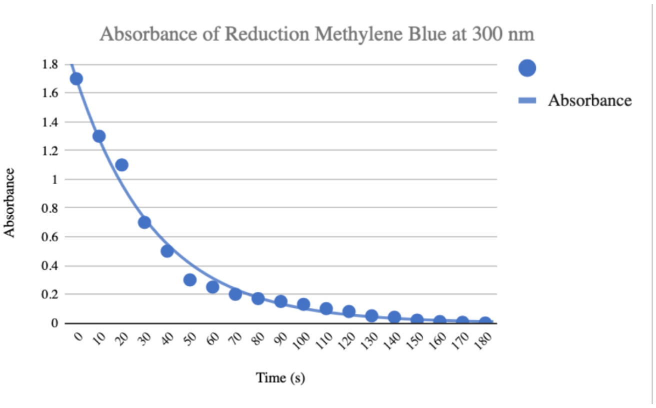

Fig. 7 Absorbance of reduced methylene blue over time

The results showed that higher concentrations of Vitamin C and HCl resulted in faster reduction of methylene blue to leucomethylene blue. This demonstrated that the choice of reagent concentrations directly impacts the reaction rate. Optimized conditions ensure the leucomethylene blue solution is prepared efficiently, making it suitable for coating applications.

Discussion

The difference between soaking and spraying methods for applying Leucomethylene blue to Drierite was shown through our experiment. The soaking method resulted in the dissolution of Drierite, especially at extended immersion times, which made it impossible for us to determine if the experiment was successfully conducted. This showed possible downsides of it being an effective oxygen indicator. The spraying method had a better result in the application of Leucomethylene blue across the drierite surface, preserving its functionality as an effective oxygen detector and allowing us to apply without significant change of the shape of the drierite. As such, spraying methods offer substantial benefits as opposed to soaking, both in terms of reliability and control— making it an effective method to serve Calcium Sulfate as an oxygen detector.

Originally, the time measurement unit for the experimental process was set to minutes. However, it was changed to seconds to more accurately show the experiment's fast reaction time. A minute is a relatively long unit of time than a second and may not be precise enough to record short, rapid changes like chemical reactions. As in this experiment, precise time recording in seconds is essential when measuring short intervals.

The original solution of Leucomethylene blue contained excessive amounts of vitamin C, which interfered with the expected chemical reaction. The initial combination of methylene blue that we used contains the following components: 4 ml of 0.1g of methylene blue is dissolved in 500ml of water, 1 ml of water, 0.1 g of vitamin C(1000mg), and 1 ml of 2 mol Hydrochloric acid solution. The excess amount of vitamin C, however, distracts the oxidation of Leucomethylene blue, which requires significant time. Accordingly, we decided to subtract the mass of vitamin C.

However, excess amounts of Vitamin C could interfere with the expected chemical reaction. The reaction time of the methylene blue solutions were measured.

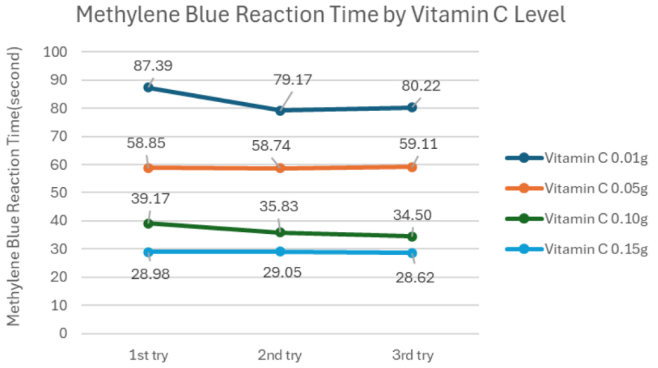

Fig. 8 Graphs of Methylene Blue reaction time based on vitamin C levels.

To minimize the possibility, using green tea extract as the reducing agent instead could improve the chemical reaction.

Compared to established methods, the Leucomethylene blue's usage to detect oxygen has longer durability and is portable. Galvanic or Polarographic electrochemical sensors are one of the common ways of oxygen detection, but it requires membrane and electrolyte solution replacement every few weeks, requiring management at least every month. Another frequently used method is titration, especially the Winkler method. This too requires frequent management due to the need of replenishing chemicals used in the detection. Furthermore, as it requires a lot of equipment like flasks, reagents and syringes, making it hard to carry around.

While this study addressed the potential of coated Drierite as an oxygen indicator, several aspects remain for further exploration. Future work could focus on quantitatively tracking the color change of the material over time to better understand its sensitivity, and investigating how other parameters such as oxygen concentration thresholds and environmental conditions affect its performance would provide deeper insights. Exploring the material's reusability, particularly whether it can be regenerated through heating like silica gel desiccants, would enhance its practical value. Lastly, developing alternative form factors, such as pH paper for easy and portable oxygen detection, may broaden its applicability across various fields.

The drierite coated in leucomethylene blue cannot be reused due to the oxidation of leucomethylene blue into methylene blue. As described previously, the blue solution of methylene blue turns into a white color due to a reduction reaction. As the leucomethylene blue becomes oxidized, the drierite cannot be used again.

Materials and Methods

1. Preparation of Methylene Blue Solution
   A methylene blue solution was prepared by dissolving 0.1g of methylene blue (ALDON, 25 g, model #IS22075) in 500 mL of water, creating a 0.00062529 M solution. 4 mL was transferred to a 20 mL plastic cap vial (Cadbibe, model #20 mL plastic cap vial-50pcs) containing 1 mL of water. The concentration of 0.00062529M was chosen to standardize the amount of methylene blue available for reduction. The 4 mL transfer and 1 mL of water dilution help maintain consistent reaction conditions for all experiments. The use of a 20 mL vial provides a controlled environment for the reaction and ensures uniformity between trials.

2. Addition of Reducing Agent (Vitamin C) and Acid (HCl)
   To the 5 mL methylene blue solution in the vial, 0.2 g of Vitamin C (It's Just!, model #JVITC) and 1 mL of 2M Hydrochloric acid (ALDON, model #IS17019) were added. The mixture was hand-shaken for 5 minutes until the solution turned colorless, indicating the conversion of methylene blue to leucomethylene blue.
   Vitamin C was chosen as it acts as a reducing agent that facilitates the conversion of methylene blue to leucomethylene blue. Its ability to donate electrons makes it effective for this reduction reaction has made it an optimal choice. The Hydrochloric acid provides the necessary acidic conditions to enhance the reduction process and stabilize the

1) 4 ml of 0.1g of Methylene blue is dissolved in 500ml of water 2) 1 ml of water 3) 0.1 g of vitamin C(1000mg) 4) 1 ml of 2 mol Hydrochloric acid solution					
1st	39.17 sec	2nd	35.83 sec	3rd	34.50 sec

Table 1. Original solution ratio and reaction time for Leucomethylene.

Volume of Vitamin C: 0.01 g of vitamin C(1000mg)					
1st	87.39 sec	2nd	79.17 sec	3rd	80.22 sec
Volume of Vitamin C: 0.05 g of vitamin C(1000mg)					
1st	58.85 sec	2nd	58.74 sec	3rd	59.11 sec
Volume of Vitamin C: 0.15 g of vitamin C(1000mg)					
1st	28.98 sec	2nd	29.05 sec	3rd	28.62 sec
The higher the volume of vitamins, the faster the reaction speed.					
Volume of Hydrochloric acid solution: 0.5 ml of 2 mol Hydrochloric acid solution					
1st	1′14″51(74.51sec)	2nd	1′13″43(73.43 sec)	3rd	1′14″07(74.07 sec)
1.14.51 sec 1.13.43 sec					
Volume of Hydrochloric acid solution: 1.5 ml of 2 mol Hydrochloric acid solution					
1st	27.68 sec	2nd	27.34 sec	3rd	28.12 sec
The higher the volume of Hydrochloric acid, the faster the reaction speed.					
No Vitamin C					
1st	sec	2nd	sec	3rd	sec
No Hydrochloric acid solution					
1st	3′07″76(187.76 sec)	2nd	2′55″54(175.54 sec)	3rd	3′05″42(185.42 sec)

Table 2. Reaction time for varying the volume of Vitamin C and Hydrochloric acid from the original Leucomethylene solution.

leucomethylene blue. The 2M concentration ensures efficient and reproducible reduction.

3. Coating Drierite Using Spray Method
The prepared leucomethylene blue solution was applied to drierite (Hammond, model ASIN B0017UDTEQ) using a bottle sprayer (DilaBee, model STSSPR31). The drierite was sprayed 10 times in a consistent manner to coat the surface uniformly.
We were able to standardize the spraying technique through the use of a single sprayer model and limiting the application to 10 sprays across trials, minimizing variability and improving reproducibility.

4. Observation of Color Change
The coated drierite was observed for color changes at specific time intervals (10 seconds, 15 seconds, 30 seconds, and 1 minute) using a cell phone timer.

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