Poly (N-isopropylacrylamide) Microgel-Based Etalons for Determining the Concentration of Ethanol in Gasoline

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Abstract:

A device composed of a poly (N-isopropylacrylamide)-based microgel layer sandwiched between two thin gold layers was used as a platform for determining the amount of ethanol in gasoline (octane number of 87). This device, also known as an etalon, has unique optical properties, which depend on the diameter of the microgels that make up the device. We show that the optical properties of the device depend on the concentration of the ethanol in gasoline samples. Specifically, as the reflectance peaks shift to higher wavelength, the visual color of the device changes from green to red up to 12% (v/v) ethanol. We show that the response was consistent from sample to sample and that the devices are reusable at least three times. We went on to show that the response did not depend on the source of the gasoline, and that the etalon's response is specific to ethanol compared to other common solvents found in gasoline. The performance of these devices make them useful for detecting ethanol in gasoline at the time of gasoline purchase, to determine if the gas being purchased has been adulterated.

Introduction

Gasoline (gas or petrol) is a mixture of multiple hydrocarbons, which is mainly produced via fractional distillation of petroleum [1]. As is well known, gasoline is essential for worldwide commerce, supporting many economies around the world,

and playing a vital role in transportation, shipping, and a number of other industries. Due to its importance, monetary value, and the massive volumes used by consumers, gas "adulteration" is a common occurrence, especially in developing countries. "Gas adulteration" is the addition of inexpensive (relative to gas) organic solvents to gasoline as a diluent, thereby making a given volume of the adulterated gas less valuable to the consumer, while raising dealer profits [2]; some common adulterants include kerosene [2], ethanol [3], and/or hexane [1]. One of the most common adulterants is ethanol, this is due to the fact that most countries allow (and regulate) this practice, and many cars can operate on ethanol-diluted gasoline (also known as gasohol) [3]. However, the amount of ethanol in gasohol is restricted to a specific range, regulated by various government agencies [4]. While this is the case, sampling and analyzing gasohol is only done periodically, so detecting cases of adulteration is not very efficient. This allows for vendors to very easily take advantage of consumers to gain more profits by adding excess amounts of ethanol to gasoline at times of the year when a given volume of ethanol is significantly less expensive than gasoline. In addition to the impact of gas adulteration on consumers, it can also have dire implications on the environment by emitting toxic combustion products such as nitric oxide and hydrocarbons [5]. Finally, the addition of high ethanol content gasohol to certain cars will cause damage to engines, leading to an increased economic impact on consumers, and can lead to certain safety concerns, potentially impacting human lives. For these reasons, a device that is capable of analyzing gas content at the time of purchase, using an inexpensive, and easy to use device would be highly advantageous.

Previously, several techniques have emerged to accomplish this. The most common of these include gas chromatography (GC) [6], high-performance liquid chromatography (HPLC) [7], conducting polymer-based sensors [8-10], fuel sensors based on refractive index measurements [11], flame emission spectroscopy [12] and organic microfibers [13]. These techniques have the ability to produce specific responses to different solvents, such as methanol [8], hexane [1], ethanol [3] and

benzene [9] usually used to dilute gasoline. While this is the case each approach has its drawbacks. For example, the use of GC, HPLC, Flame Emission Spectroscopy can provide accurate results, but professional technicians are needed for operation, as well as complicated equipment, therefore making these approaches useless to the everyday consumer. For these reasons, a device that is easy to use, and is able to detect ethanol level both qualitatively and quantitatively at the time of gas purchase would be highly desirable.

In this submission, we fabricate a polymer-based device that exhibits visual color, which depends on the environment that it is exposed to. Specifically, we previously reported on such devices that are constructed by sandwiching poly (N-isopropylacrylamide) (pNIPAm)-based microgels between two thin gold layers (see Figure 1(a)) [14]. The device's two gold layers act as "mirrors", while the space between two mirrors (the microgel layer) acts as dielectric cavity. When light strikes the etalon, some passes into the dielectric cavity and resonates between the two Au layers, leading to constructive/destructive interferences, as shown by Figure 1(b). This leads to certain wavelengths of light being reflected, resulting in visual color and multi-peak reflectance spectra, as in Figure 2. The position of the peaks in the spectra can be determined using the following equation:

$$m\lambda = 2nd\cos\theta \qquad\qquad (1)$$

Where λ is the maximum wavelength for the peak(s), m is the peak order (an integer), n is the refractive index of the dielectric cavity, d is the distance between two mirrors, and θ is the angle of incidence relative to the normal.

These devices are constructed from pNIPAm-based microgels, which are temperature responsive hydrogel particles. PNIPAm is one of the most commonly used and studied responsive polymers [15-22], which undergoes a swollen (random coil) to collapsed (globule) transition in water as its temperature is raised above pNIPAm's lower critical solution temperature (LCST) of 32°C. Likewise, pNIPAm-based microgels undergo a swollen (large diameter) to collapsed (small diameter) transition if the temperature of the water they are in is increased to above

the LCST [23]. Therefore, pNIPAm-based microgels afford the etalons color as a function of solution temperature; this is a direct result of the etalon's cavity thickness being modulated by the temperature-dependent solvation state of the microgels in the etalon, changing its optical properties as can be predicted from equation 1. Specifically, if the water temperature is > LCST, the microgels in the etalon's cavity collapse bringing the etalon's metal layers close together and vice versa. This leads to what is called a blue shift (reflectance peaks shift to shorter wavelengths), and red shift (reflectance peaks shift to longer wavelengths), respectively. We have also made these devices responsive to the presence of a variety of different species such as DNA [24], proteins [25], and glucose [26].

In another previously published study, we showed that the spectral properties of the etalons depended on the amount of methanol (MeOH) dissolved in water [27]. This was a result of what is known as cononsolvency, where the microgels are fully solvated (and large) in both pure MeOH and water, but not fully solvated in certain mixtures of the two. Furthermore, it has been shown that the solvation state of microgels is dependent on the addition of a number of other solvents to water [28]. In the current submission, we exploit the ability of the microgels to change solvation state in different solvent mixtures to detect ethanol in gasoline. Specifically, we determined that indeed gasoline is capable of solvating the microgel layer in the etalon, leading to distinct optical properties as discussed above. We showed that the optical properties of the devices depended on the amount of ethanol added to three gasoline samples. We also show that the devices are reusable, and can exhibit distinct colors in gas samples of different ethanol compositions, making detection of adulterated gas samples as simple as observing a color change.

Experimental:

Materials: N-Isopropylacrylamide was purchased from TCI (Portland, Oregon) and purified by recrystallization from hexanes (ACS reagent grade, EMD, Gibbstown, NJ) prior to use. BIS (99%), and ammonium persulfate (APS) (98+%) were obtained from Sigma-Aldrich (Oakville, Ontario) and were used as received. All deionized water

was filtered through a Milli-Q Plus System (Millipore, Billerica, MA) to have a resistivity of 18.2 MΩ • cm. Chromium/gold annealing was done in a Thermolyne muffle furnace from Thermo Fisher Scientific (Ottawa, Ontario). Anhydrous ethanol was obtained from Commercial Alcohols (Brampton, Ontario). Toluene was obtained from Fisher Scientific (Ottawa, Ontario). Hexane was obtained from Sigma-Aldrich (Oakville, Ontario). Fisher's Finest glass coverslips were 25×25 mm and obtained from Fisher Scientific (Ottawa, Ontario). Chromium was 99.999% and obtained from ESPI as flakes (Ashland, OR), while Au was 99.99% and obtained from MRCS Canada (Edmonton, AB).

Microgel synthesis: All the pNIPAm-microgels used here were medium size (~1 μm) and composed by 95% NIPAm and 5% BIS. Microgels were synthesized via free radical precipitation polymerization as described previously [29]. The monomer, NIPAm (12.33 mmol) and BIS (0.703 mmol), were dissolved in deionized water (99 mL) with stirring in a small beaker. The mixture was filtered through a 0.2 μm filter affixed to a 20 mL syringe into a 100 mL 3-neck round-bottom flask. The beaker was rinsed with ~10 mL of deionized water and then filtered into the pNIPAm solution. The flask was then equipped with a temperature probe, a condenser and N_2 outlet, stir bar, and a N_2 gas inlet. The monomer solution (~100 mL total volume) was purged with N_2 gas for about 1 h, with stirring set to a rate of 450 rpm, while the temperature was allowed to reach 70°C. Then, 0.0456g of APS in 1 mL of deionized water was delivered to the monomer solution with a transfer pipet to initiate the reaction. The reaction was allowed to proceed at 70°C for 4 h, and the resulting suspension was allowed to cool overnight. The resultant solution was then filtered through a Whatman #1 filter paper to remove any large aggregates. The coagulum was rinsed with deionized water, and the solution was diluted to about 120 mL (diluted approximately two times from the original microgel solution concentration). Aliquots of these microgels (12 mL) were centrifuged at a speed of ~8400 relative centrifugal force (rcf) at 23 °C to produce a pellet at the bottom of the centrifuge tube. The supernatant was removed from the pellet of microgels, which was then re－suspended to the original

volume (12 mL) using deionized water. This process was completed a total of six times to remove any unreacted monomer and/or linear polymer from the microgel solution.

Etalon Fabrication: The details of the paint-on technique used to fabricate microgel etalons for these experiments have been reported previously [30]. Briefly, 25×25 mm glass coverslips were rinsed with ethanol and dried with N_2 gas, and 2 nm of Cr followed by 15 nm of Au were thermally evaporated onto them using a Torr International Inc. model THEUPG thermal evaporation system (New Windsor, NY). The Au coated substrates were annealed at 250 °C for 3 h and then cooled to room temperature. An aliquot of about 12 mL of microgel solution was centrifuged for 30 min to pack the microgels into a pellet. A Cr/Au substrate was placed onto hot plate set to 30°C. 40 μL aliquot of the concentrated microgels was deposited onto the substrate and then spread toward each edge using the side of a micropipet tip. The microgels were allowed to dry completely on the substrate for 2 h with the hot plate set to 35°C. After 2 h, the dry film was rinsed with deionized water to remove any excess microgels not bound directly to the Au. Next, the film was placed into a deionized water bath and allowed to incubate overnight on a hot plate set to ~30°C. Following this step, the substrate was again rinsed with deionized water to further remove any microgels not bound directly to the Au substrate surface. The substrate was subsequently coated with another layer of 2 nm Cr followed by the desired Au overlayer thickness. These assemblies, now formally etalons, were soaked in deionized water overnight on a hot plate set to 30 °C and subsequently used for experiments.

Gasoline Samples: Three tanks of regular gasoline (octane number = 87) were purchased from three different local gas stations. The same three samples of gasoline were used throughout all the experiments.

Experimental setup: All experiments were performed within a temperature-controlled chamber (fabricated in house). The etalon was secured in the chamber, and a

reflectance probe inserted into the chamber used to collect reflectance spectra. The etalon was fixed on the bottom of the chamber, while the R400-7-VIS-NIR optical fiber reflectance probe shine light directly onto it at fixed angle (90° relative to the normal). The reflected light from the etalon was collected via the USB 2000 detector and to be converted into a reflectance spectrum. A USB 2000 detector and the R400-7-VIS-NIR probe were both purchased from the Ocean Optics.

Etalon response to ethanol in gasoline: 95% pNIPAm + 5% BIS microgel-based etalons were soaked in deionized water prior usage. Each etalon was then dried using N_2 gas and placed onto a hotplate (set to ~60°C) for ~10 min in order to encourage drying. The etalon was then added to the chamber and 20 mL of gasoline added. The gasoline was held 23° C. An iphone 5 (Apple, California, United States) was used to photograph the etalon. The etalon was allowed to stabilize in the gasoline for 1 h, after which 200 μL of ethanol was added into the chamber, followed by mixing. 15 min was allowed for the etalon equilibration, and a spectrum recorded. Ethanol was added to the gasoline until the ethanol volume reached about 12%. After all the ethanol additions, an iphone 5 was used to photograph the etalon. The above procedure was repeated for all experiments. The same procedures were also used for determining the etalon response to hexane and toluene.

Gas Chromatographic analysis of gasoline: Each gas sample was analyzed using gas chromatography mass spectrometry (GCMS, Bruker SCION TQ with 456-GC). Each gas sample was injected into the GCMS in order to obtain a chromatogram. Based on the chromatogram, the components of the gas sample can be identified -- based on retention time. The peak area of each component was compared to the total peak area to calculate the percentage of each component in the gas sample. A library search was performed in order to identify the retention time of toluene and hexane.

Result and Discussion:

In order to determine if the pNIPAm microgel-based etalons can be used to determine the amount of ethanol in gasoline, it was essential to show that gasoline

could swell the etalon's microgels allowing it to function as an optical device (etalon). To do this, an etalon was secured in a temperature controlled chamber and 20 mL of gasoline added. After stabilization, we determined that the etalon was able to function, as determined by its characteristic multipeak reflectance spectrum, as can be seen in Figure 2. Following this, aliquots of ethanol were added and mixed into the gasoline, and the position of the reflectance peaks monitored as a function of time. In each case, the reflectance peaks red shifted as a function of increasing ethanol concentration. The red shift is a result of microgel swelling, which may be from the ethanol hydrogen bonding with pNIPAm's amide group. It can also be a result of the ethanol interacting with pNIPAm's isopropyl group through hydrophobic interactions. Regardless, the etalon 's response to the addition of ethanol to gasoline was a red shift. The magnitude of the red shift was plotted as a function of volume percent ethanol (volume of ethanol/volume of gasoline) added to gasoline, as can be seen in Figure 3(a). As can be seen, upon the addition of 2400 μL of ethanol to gasoline (12% v/v ethanol in gasoline) the reflectance peak shifts about 45 nm. It can also be seen that the device's response is linear in the range of 0 - 3% ethanol.

Since we showed that the etalons are responsive to the amount of ethanol in gasoline, we went on to determine how reproducible the etalons responses are, and if individual etalons can be reused multiple times. To determine reproducibility, we performed these experiments in the same manner as above, using three separate etalons. Figure 3(a) shows the responses for three different etalons to ethanol in gasoline. As can be seen, they all exhibit similar responses to the same concentration of ethanol in gasoline. Next, we performed the same experiment three times using the same etalon to investigate its reusability. Figure 3(b) shows that the average cumulative peak shift from three repeated experiments is about 45 nm, which is consistent with the cumulative peak shifts observed from a single use. Hence, microgel-based etalons exhibit good sample-to-sample reproducibility and are reusable.

In order for an etalon to be considered as reusable, it has to respond to ethanol in gasoline in a similar manner with every use. Figure 4(a) shows that as the same etalon was used multiple times, the wavelength of the reflectance peak increased. What this means is that the microgel diameter is not returning to its initial diameter with each use, i.e., the microgels are getting larger in diameter with every use. We hypothesize that this is a result of incomplete removal of ethanol from the microgel layer prior to reuse. What's interesting is the magnitude of the etalon's response in consistent from use to use. Importantly, as can be seen in Figures 4(a, b), the type of gasoline (where it was purchased) doesn't change the optical response to ethanol in gasoline.

Further evidence of the etalons ability to function similarly in gasoline samples purchased from multiple locations can be seen in Figure 5. As can be seen, the response of three different etalons to ethanol concentration in gasoline is very similar. It is also important to point out that only three etalons were used for this experiment, i.e., one etalon was used to analyze the ethanol concentration in gasoline three separate times and the magnitude of the responses averaged. What we can see from the data is: (1) all etalons exhibit red shifts in their reflectance peaks upon the addition of ethanol to gasoline; and (2) all etalons (including reused etalons) exhibit similar cumulative spectral shifts (~45 nm)

Response specificity:

We also investigated whether the etalon response to ethanol in the gasoline is specific. To evaluate this, hexane and toluene (12% (v/v)) were added separately into 20 mL of gasoline at 25°C, and the etalons response recorded according to the experimental section. Toluene and hexane were chose because they are common solvents found in gasoline, and can also be used as diluents. Figure 6(a) shows that etalons reflectance peaks blue shift (~10 nm) in response to hexane addition, while they red shift (~10 nm) in response to toluene, as can be seen in Figure 6(b). From this result we determined that the etalons response is minimally affected by these other common solvents.

Figure 7 shows the GCMS analysis of the three different gasoline sample used in

this study. In this case we were interested in the variability in the solvent composition of the gasoline from station to station. As can be seen, the solvent composition is slightly variable from station to station. What's important is the fact that the etalons response to ethanol in gasoline is not affected by the initial solvent composition.

Detection of ethanol in gasoline visually:

Ultimately, a hand held device that is capable of exhibiting different visual colors in the presence of gasoline with different ethanol compositions is desired. To prove that this is a possibility we immersed an etalon in gasoline and took photographs before and after the addition of ethanol. Figure 8 clearly shows that the etalon exhibits a bright green color in the absence of ethanol, but turns red once ethanol is added.

Conclusion:

Microgel-based etalons were fabricated, and were shown to exhibit their predicted optical properties in gasoline samples, i.e., multipeak reflectance spectra and visual color. We have shown that the optical properties of the etalon depend on the concentration of ethanol in a gasoline sample (tested in gasoline samples from three independent stations), reproducibly showing ~ ~45 nm spectral shifts after bringing the concentration of ethanol in a gasoline sample to 12% (v/v). We also showed that the etalons can be reused multiple times, although the response is somewhat degraded with each use. Finally, we show that the microgel-based etalons are surprisingly selective for ethanol over other common solvents found in gasoline. We feel that the microgel-based etalon has great potential for crudely analyzing gasoline composition before purchase. Not only is the device selective for ethanol, but it is inexpensive (~0.05 CAD/inch^2) and easy to use, making it even more attractive for this application.

Acknowledgements:

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Figure Captions:

Figure 1. (a) Basic construct of a microgel-based etalon. A 2 nm Cr layer was used for adhesion of Au to the glass/microgel layer. (b) A cartoon illustrating light resonating in the etalon cavity.

Figure 2. Multipeak reflectance spectrum for an etalon in gasoline

Figure 3. Etalon response to increasing volume of ethanol in regular gasoline purchased from one gas station. In this case, the y-axis is the difference between the initial position of the peak prior to adding ethanol and the final position after adding ethanol and stabilization. (a) Three separate etalons were tested under the same experimental conditions (etalon in 20 mL gasoline at 23°C); (b) One etalon was tested under the same experimental conditions three times (etalon in 20 mL gasoline at 23°C). Each data point is the average from the three measurements, while the error bars are the standard deviations.

Figure 4. Three separate etalons were placed in three separate gasoline samples purchased from different gas stations (the different symbols on the plot). Each etalon was analyzed in the same manner three times in each specific gasoline sample. (a) Initial peak position at 0% ethanol as a function of the number of times the specific etalon was used; and (b) Cumulative peak shift as a function of the number of times the etalon was used. In this case the cumulative peak shift was for ~12% ethanol addition.

Figure 5. The magnitude of peak shift as a function of ethanol addition to gasoline purchased from three different gas stations (the three different symbols). In this case, the y-axis is the difference between the initial position of the peak prior to adding ethanol and the final position after adding ethanol and stabilization. Each data point is the average from the three measurements, while the error bars are the standard deviations.

Figure 6. (a) The response of an etalon in gasoline to (■) ethanol and (●) hexane; and (b) The response of an etalon in gasoline to (■) ethanol and (▲) toluene.

Figure 7. GCMS analysis of the composition of (■) ethanol, (●) hexane, and (▲) toluene in gasoline purchased from three different gas stations.

Figure 8. Photograph of an etalon in gasoline (left) before and (right) after addition of

ethanol to gasoline to bring the concentration up to 12%.