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# A Holographic Alcohol Sensor

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**A simple liquid-phase alcohol sensor based on a reflection hologram distributed throughout the volume of a cross-linked poly(hydroxyethyl methacrylate) film is described. The sensor is interrogated optically through the back of the film, by measuring the peak wavelength of the narrow-band reflection spectrum when the hologram is illuminated with white light. This procedure makes it possible to measure thickness changes in the film with great precision. The presence of alcohol in the sample medium causes the polymer film to swell in a concentration-dependent manner, whence the alcohol content can be determined by measurement of the wavelength of the reflected spectral peak. The sensor exhibits a wide dynamic range, which can easily be tuned for specific applications, and is unaffected by highly colored and turbid samples, since the light path does not pass through the sample. The sensor is relatively insensitive to pH in the range 3–6.5 and is highly stable, both in use and in storage. The performance of the sensor was demonstrated by measuring the alcohol contents of a wide range of alcoholic beverages such as wines and beers, with no sample pretreatment. Most alcohol concentrations were determined to be within approximately  $\pm 0.3$  vol % of their stated values.**

A substantial number of chemical and biological sensors, based on a variety of different optical transduction principles, have been reported in the literature. Many are reconfigurations of existing spectrophotometric methods involving the production or consumption of colored compounds, directly or indirectly, by a (bio)-chemical reaction, or involve competition assays set up between chromogenically labeled and unlabeled analytes or receptors. Such devices are generally either irreversible or require reconditioning in a number of regeneration solutions prior to reuse. An alternative approach is to design a chemical or biological receptor molecule that incorporates an analyte-sensitive chromophore in its structure.<sup>1</sup> Binding of the analyte causes a change in the spectral properties of the attached chromophore that can be monitored directly. Such devices often have the advantage of reversibility, but problems with photobleaching can be encountered, making it necessary to use more complex techniques such as dual-wavelength ratiometric methods or fluorescence lifetime measurements to overcome this intrinsic instability.

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During the past few years a number of new optical sensor principles have been introduced, which rely on diffractive or interferometric techniques rather than absorption and emission to generate the sensor signal and thus do not suffer the problems outlined above. These techniques include systems based on reflectometric interference spectroscopy (RIFS),<sup>2–4</sup> metal island coated swelling polymer over mirror (MICSPOMS),<sup>5</sup> polymerized crystalline colloidal arrays<sup>6,7</sup> and volume holograms.<sup>8–11</sup> Each of these techniques has particular strengths and weaknesses: RIFS has been demonstrated in both gas and liquid phases, is sensitive enough to detect low-molecular-weight analytes binding at surfaces, but requires complex instrumentation and high-quality films. The introduction of MICSPOMS is an attempt to increase signal strength compared with RIFS, but the technique suffers from poor spectral peak shape, making measurement more complex, and requires very precise deposition of the thin films. Polymerized crystalline colloidal arrays generate very bright narrow-band diffraction spectra and make visually perceptible sensors a possibility. The preparation of the crystalline colloidal arrays is rather exacting, however, and the nature of the supporting polymer hydrogel is limited by the need for a nonionic structure that does not disrupt the packing of the charged nanospheres. This places some constraint on the design of the recognition elements in the structure. Volume holograms also offer the opportunity for direct visual readout of the sensor and mass production at very low cost. The theoretical background to using holograms as sensors has been discussed previously.<sup>10</sup> Until recently, the scope of the holographic technique was seriously constrained by the range of materials in which suitable holograms could be recorded. With the introduction of new methodology,<sup>12,13</sup>

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however, it is now possible to record silver halide volume holograms in a variety of synthetic polymers and hydrogels that were previously unusable for holography. These developments have opened up many new opportunities for the rational design of holographic sensors.

The measurement of ethanol is of great importance in many industrial, pharmaceutical, and food industry processes, as well as in the fermentation and process monitoring of alcoholic beverage production. Many electrochemical and optical biosensors have been developed for ethanol measurement, mostly based on enzymes such as alcohol oxidase and alcohol dehydrogenase.<sup>14–20</sup> Such devices suffer from instability in use and storage due to the rather labile nature of the enzymes, are also adversely affected by electroactive interferences from the sample, are difficult to sterilize, and frequently do not have sufficient dynamic range to allow direct measurement in undiluted samples. To circumvent these problems and produce robust sterilizable devices for on-line monitoring, a number of chemical sensors have been developed. Some rely on fluorescence enhancement<sup>21,22</sup> or fluorescence quenching<sup>23</sup> of dyes in particular microenvironments, but these effects tend to be rather nonspecific and are affected by photobleaching. The specificity issue has been addressed by developing trifluoroacetylstilbene derivatives<sup>24</sup> that react with alcohols to produce hemiacetals, thereby causing a shift in the emission spectrum of the stilbene fluorophore. When incorporated into plasticized PVC membranes<sup>25</sup> these compounds produced sensor membranes with good stability and dynamic range, although microporous PTFE overlayers were required to isolate the fluorophore from pH and ionic fluctuations. The sensor returned erroneous responses in red wines due to the coloration, which overlapped the emission spectrum of the fluorophore and was unreliable at very low alcohol concentrations.

The work described in this paper outlines an alternative strategy to produce a simple optical sensor for alcohol based on a volume hologram. The construction of the sensor is outlined, followed by an evaluation of its properties and its performance when measuring the alcohol content of a range of beverages.

## EXPERIMENTAL SECTION

**Materials.** Hydroxyethyl acrylate (HEA), hexanediol diacrylate (HDDA), hydroxyethyl methacrylate (HEMA), ethylene glycol dimethacrylate, acrylamide, methacrylamide, isopropylacrylamide, methylenebisacrylamide, dimethoxyphenylacetophenone (DMP), methanol, propan-1-ol, propan-2-ol, butan-1-ol, 1,1'-diethyl-2-2'-cyanine iodide (sensitizing dye), and methacryloxypropyltriethox-

ysilane were supplied by Aldrich Chemical Co. (Poole, U.K.). Absolute ethanol came from Fisher (Loughborough, U.K.). All other chemicals were of analytical grade and were supplied by Sigma/Aldrich (Poole, U.K.). Aluminized 100- $\mu$ m polyester film grade MET401 was purchased from HiFi Industrial Film Ltd. (Stevenage, U.K.). Glucosyl methacrylate (GEMA) was synthesized from HEMA and methyl  $\alpha$ -D-glucoside according to a published procedure<sup>26</sup> and purified by column chromatography on silica gel. Alcoholic beverages were purchased from a local store.

**Synthesis of Polymer Films.** Glass microscope slides were boiled for 30 min in 5% (v/v) nitric acid, washed thoroughly with distilled water and propan-2-ol, and allowed to dry. The slides were laid out horizontally, coated with a freshly made 1% (v/v) acetone solution of methacryloxypropyltriethoxysilane, and left overnight at room temperature while the acetone evaporated and the silane coupled to the glass surface. The slides were washed twice with acetone and allowed to dry before use or storage (stacked in a box).

The required amounts of monomers to give 500 mg of the desired composition were weighed and mixed. Propan-1-ol (500  $\mu$ L) containing DMAP (5 mg) was added and mixed until all components were dissolved. The monomer mixture (100  $\mu$ L) was placed on a sheet of aluminized polyester supported on a glass plate and a silanized microscope slide gently lowered onto it to spread the monomer solution and produce a uniform film. The films were polymerized for 1 h at room temperature under a high-pressure mercury lamp (Spectroline SB-125/F, Spectronics Corp., New York). The aluminized polyester was peeled off, and the films were washed with methanol to remove any initiator fragments and unpolymerized monomer remaining, before being left to dry in air.

**Hologram Construction.** A film was soaked for 5 min in a 0.3 M silver perchlorate solution in propan-1-ol/water 1:1 (v/v). The surface was blotted dry and the film dried in a gentle stream of warm air from a hair-dryer. Under red safelighting, the slide was placed film upward in a shaking bath containing 50 mL of 0.3 M lithium bromide in methanol/water 3:1 (v/v) to which had been added 1.25 mL of a 0.2% (w/v) solution of sensitizing dye in methanol. The film was washed under running water and then briefly with distilled water before immersion for 30 s in sensitizing solution (0.5% (w/w) ascorbic acid adjusted to pH 5 with NaOH) and transfer to the hologram exposure bath. This comprised a plastic box containing a front surface mirror to which a glass spacer had been glued so that the slide lay at an angle of approximately 3° to the surface of the mirror. The slide was placed film side downward onto the mirror/spacer and immersed in water. A black plastic mask (6-mm-wide slots about 15 mm long, perpendicular to the long axis of the slide, with 2-mm spacers between) was placed over the slide and the whole area exposed to a single 6-ns pulse from an expanded beam (approximately 6-cm diameter) of a frequency-doubled Nd:YAG laser (Brilliant B, Quantel, France). (Note: high-energy class IV pulsed lasers such as this are potentially dangerous and appropriate protective clothing and safety glasses must be worn. The laser should be located and used according to local safety regulations.) The slide

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was removed from the exposure box and immersed for 30 s in a freshly made developer solution (1 vol of 5% (w/w) sodium hydroxide solution mixed with 1 vol of 2% (w/w) hydroquinone dissolved in methanol), followed by extensive washing under running water. The film was then fixed for 10 min, with gentle agitation, in 10% sodium thiosulfate in methanol/water 1:1 (v/v) before being washed under running water and twice in distilled water. The completed holograms were then left to air-dry.

**Monitoring Hologram Responses.** Single strips of hologram about 8 mm wide were cut from a slide and inserted into a 1-cm glass cuvette with the film side facing inward. Water (1 mL) was added and the cuvette equilibrated in the thermostated cuvette holder of a reflection spectrometer described previously.<sup>8,10</sup> The solution in the cuvette was exchanged for the solution of interest, and the contents were allowed to reequilibrate before recording the spectrum of the hologram or the peak wavelength as required. This was repeated for different holograms and test solutions. All measurements were made at 30 °C unless stated otherwise. Citrate buffers were made by mixing citric acid and trisodium citrate solutions in the required proportions to give the desired pH.

**Alcohol Analysis of Beverages.** A range of alcoholic beverages was purchased from a local supermarket. Bottles and cans were opened at random and the pH and conductivity of the contents measured immediately, after which a sample was incubated with a hologram. After equilibration and measurement, the hologram was washed twice with distilled water and twice with a 5 vol % ethanol standard solution. The wavelength for the ethanol standard was then recorded (after equilibration) before washing again twice with distilled water and twice with the next beverage before equilibration and measurement.

**Calibration Curves.** Calibration curves were recorded using standard ethanol solutions made up volumetrically in water or in Kaliber alcohol-free lager (taking care to avoid foaming). The hologram was exposed sequentially to solutions with increasing alcohol content using either the water series or the Kaliber series of standards.

## RESULTS AND DISCUSSION

The diffusion method used in this work for making the holograms is quite different from the technique normally used for preparation of conventional silver halide holographic recording materials.<sup>27</sup> The development of this technique has made it possible to record silver halide volume holograms in a wide range of previously inaccessible natural and synthetic polymer films. The details and subtleties of the method and its significance in holography are discussed elsewhere.<sup>12,13</sup> In the context of the present work, it need only be stated that despite the fact that the holographic conditions were not optimized for each material, the method described gave adequate holograms, which could be seen easily by eye and recorded in the reflection spectrometer. The reflectivity varied according to the material and the degree of cross-linking. Highly cross-linked materials had a lower tendency to swell, imbibed less silver salt, and produced less bright holograms. The colloidal silver particles present in all the holograms appeared yellowish-brown, indicating a very small particle size. All the holograms replayed at a wavelength of about

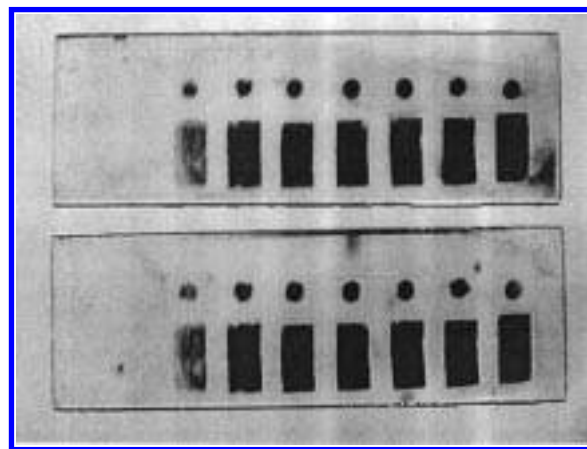


Figure 1. Photograph of sets of "sister" holographic sensors produced in polymer films attached to microscope slides.

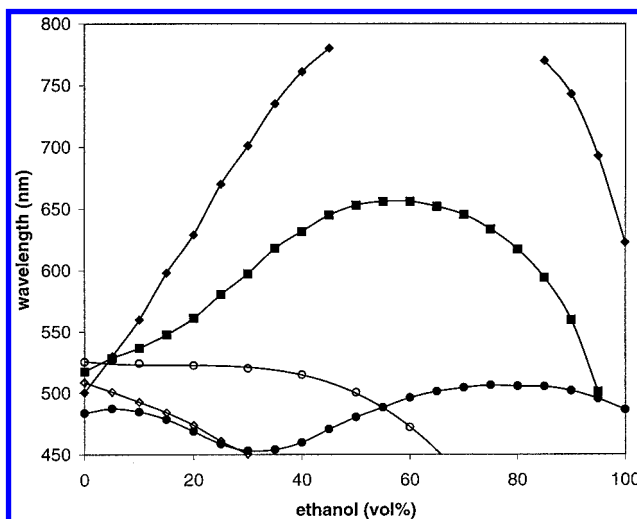


Figure 2. Curves showing the swelling of different polymer films in ethanol/water mixtures. Film compositions (in wt %): 95% HEMA/5% EDMA (◆), 96% HEA/4% HDDA (■), 94.3% GEMA/5.7% EDMA (○), 72% acrylamide/22% methacrylamide/6% methylene bisacrylamide (◇), and 72% isopropylacrylamide/22% methacrylamide/6% methylene bisacrylamide (●).

500 nm, which is consistent with the exposure wavelength of 532 nm. A slight shrinkage compared with the construction wavelength is normal for colloidal silver holograms, since some silver halide is removed during fixation and the remaining silver has a volume smaller than the silver halide present at the time of exposure. A photograph of typical strips of sensors on microscope slides, produced by a single holographic exposure through a mask, is shown in Figure 1.

A number of different polymeric materials were tested for their sensitivity to ethanol in order to select one with appropriate characteristics for use as an alcohol sensor. The response of some of these materials to ethanol is shown in Figure 2. The compositions of the polymers are summarized in the figure legend, but all contained about 5 wt % cross-linker compared to the total monomer content. The responses to ethanol are characteristic of the different types of polymer. Poly(HEMA) and poly(HEA) displayed bell-shaped curves with swelling maximums around 60% (v/v) ethanol. The top of the curve is missing for poly(HEMA) due to the range of the spectrograph being exceeded, but the overall shape was confirmed using samples with higher degrees

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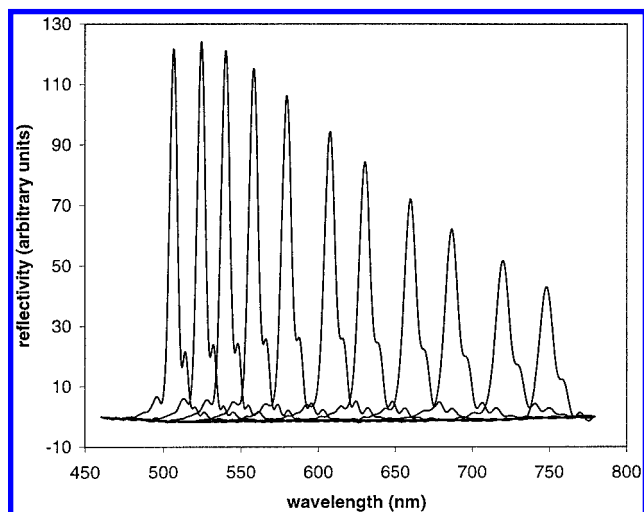


Figure 3. A series of spectra showing the peak broadening and the reduction in peak reflectivity as the hologram swells. The spectra are measured in water (lowest wavelength) and then in 2.5% (v/v) increments of ethanol in water, up to 25% ethanol (highest wavelength). The polymer contains 95% HEMA and 5% EDMA by weight.

of cross-linking, which swell less. Poly(GEMA) shows almost no response below 40% (v/v) but then contracts. Above 60% (v/v) ethanol, the response was out of the range of the instrument below 450 nm. Polyacrylamide generated very poor holograms, although a copolymer with methacrylamide produced good holograms that contracted progressively even at quite low ethanol contents (0–30% (v/v)). A copolymer of methacrylamide and isopropylacrylamide showed complex behavior, contracting on exposure to ethanol concentrations up to 30% (v/v) but then swelling again, before beginning to contract again above 90% (v/v) ethanol.

From the results of these exploratory experiments, poly(HEMA) was chosen for further study due to its large and near-linear response over a wide range of ethanol concentrations. The polymer also gave good bright holograms and tough robust films that adhered very well to the silanized glass slides, making it practical to work with.

Figure 3 shows a series of reflection spectra for a typical poly(HEMA) hologram exposed to different concentrations of ethanol. The shoulder on these particular spectra probably results from a spurious reflection during hologram construction, but does not affect the interpretation of the data in any way. The narrowest bandwidth and highest reflectivity are observed near the hologram construction wavelength at about 500–550 nm, while at longer wavelengths, band-broadening and consequent reduction in reflectivity is apparent. This effect is indicative of some loss of definition of the holographic fringes, possibly due to microheterogeneity of swelling within the polymer film. The structure of the polymer is not permanently altered, however, since the hologram can be swelled and contracted many times and always returns to the same peak shape and reflectivity. The peak wavelengths of these relatively bright reflection spectra can be defined to single pixel resolution by simple inspection, giving a precision of about  $\pm 0.3$  nm for measurement of the peak wavelength. This precision is defined by the optical arrangement of the grating spectrograph, but could be altered to give higher resolution at the expense of wavelength range, if deemed appropriate.

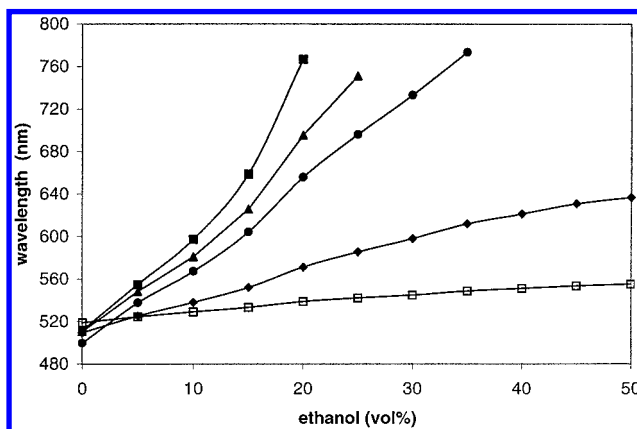


Figure 4. Swelling of poly(HEMA) holograms with increasing levels of EDMA cross-linker as a function of ethanol content. The holograms contained 2 (■), 5 (▲), 8 (●), 15 (◆), and 30% (□) EDMA by weight.

The degree of swelling of poly(HEMA) can be controlled by varying the extent of cross-linking and, hence, the elasticity of the polymer film. Results showing the peak wavelength change as a function of ethanol concentration for a range of progressively more cross-linked materials are plotted in Figure 4. As expected, the maximum degree of swelling is reduced as the extent of cross-linking is increased. This allows the dynamic range of the hologram to be tuned by varying the composition of the polymer film, depending on whether a high sensitivity over a limited range or a lower sensitivity over a broader range of ethanol concentrations is required.

Unlike chromophore-based systems, the wavelength range over which the device operates can also be altered within wide limits. This can be done in several ways: first, the polymer film can be exposed during hologram construction in any partially or fully swollen state. For example, exposing a poly(HEMA) film in an ethanol/water mixture would cause the film to swell more than in water alone. This would cause it to replay at a shorter wavelength in water, hence increasing the range of ethanol concentrations that could be measured before the hologram went out of range for any given degree of cross-linking. Alternatively, the angle of incidence of the laser beam can be altered during hologram construction. This increases the replay wavelength at a fixed angle of incidence according to the Bragg equation. A third option would be to change the laser source to one with a different wavelength, and to change the sensitizing dye to match the new laser wavelength.

The response of a poly(HEMA) hologram to different alcohols is presented in Figure 5. As anticipated for a device based on a polymer structure that shows little chemical selectivity, the hologram responds to all the alcohols tested. The ability of alcohols to penetrate the polymer structure and cause swelling increases as the alkyl chain length of the alcohol increases. The branched chain propan-2-ol is less effective in this respect than the linear propan-1-ol, presumably reflecting a reduced ability to interact sterically with the polymer backbone.

The reproducibility of the response for a series of “sister” holograms swelling in several concentrations of ethanol has been measured. “Sister” holograms are those which were produced simultaneously on the same microscope slide. In the present study, six separate holograms were tested and gave very similar

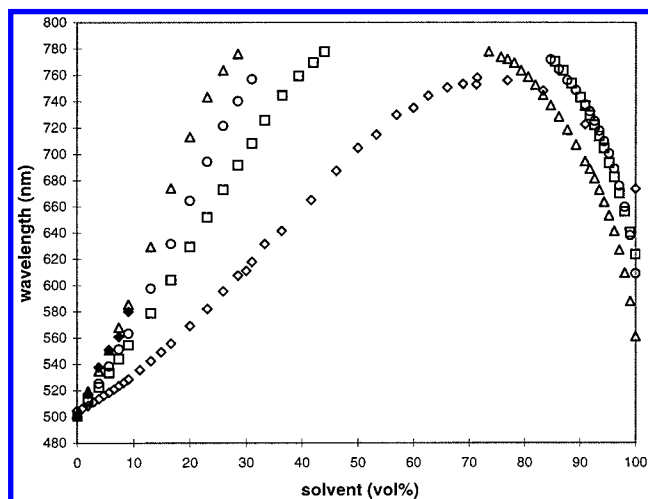


Figure 5. Swelling of a poly(HEMA) hologram containing 5% (w/w) EDMA as a function of alcohol concentration for a range of different alcohols: methanol ( $\diamond$ ), ethanol ( $\square$ ), propan-1-ol ( $\triangle$ ), propan-2-ol ( $\circ$ ), and butan-1-ol ( $\blacklozenge$ ).

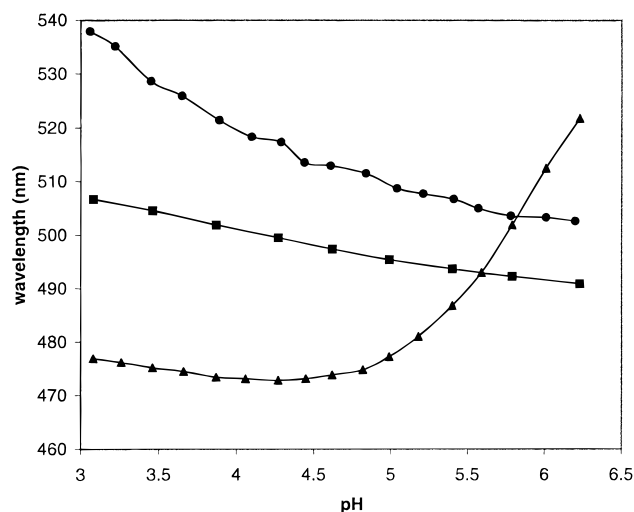


Figure 6. Swelling of poly(HEMA) holograms containing 5% (w/w) EDMA as a function of pH in 50 mM citrate buffers. The holograms were untreated poly(HEMA) ( $\triangle$ ), untreated poly(HEMA), which was treated with EDC/ethanolamine after hologram production ( $\bullet$ ), and poly(HEMA), where the HEMA monomer was treated by passage through an alumina column prior to polymerization ( $\blacksquare$ ).

responses. For each ethanol concentration checked at 0, 10, 20, and 30% (v/v), the standard deviation was about  $\pm 0.5\%$  of the mean wavelength value. The batch-to-batch reproducibility was somewhat less impressive at this stage, presumably due to small differences in film composition, polymerization conditions (temperature and UV intensity), and other physical and chemical conditions of hologram creation and processing. These parameters are not well managed in our laboratory-scale experiments but could be carefully controlled when scaled up to a production environment.

For use in real samples, it is important that the sensor shows little response to variations in pH or ionic strength. The effect of pH on the response of poly(HEMA) holograms is shown in Figure 6. In early studies, a marked response to pH was noted at higher pH values. This response was unexpected for a neutral polymer like poly(HEMA) and showed the characteristics of the presence

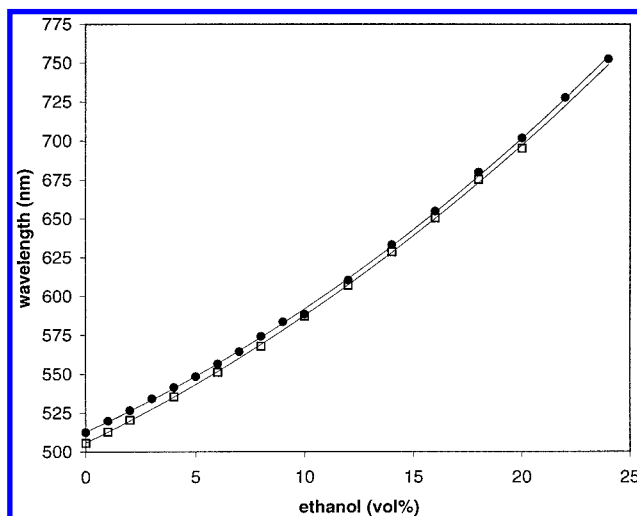


Figure 7. Calibration graphs in ethanol/water mixtures ( $\bullet$ ) and in Kaliber alcohol-free lager ( $\square$ ) for a poly(HEMA) hologram containing 5% (w/w) EDMA. The fitted quadratic function (solid line) for the Kaliber curve is described by the equation  $y = 0.1387x^2 + 6.7975x + 505.79$ . This was used for interpolation in order to calculate the measured alcohol contents of alcoholic beverages.

of a low concentration of an ionizable carboxylic acid, presumably formed by de-esterification during the alkaline development step of hologram construction. In an attempt to circumvent this problem, hologram strips were treated for 1 h with 1 M ethanolamine hydrochloride, pH 5.5, containing 0.2 M EDC. This treatment was designed to transform any free carboxylic acids into hydroxyethylamides. Reexamination of the pH response showed that the carboxylic ionization had disappeared, but an increased tendency to swell at low pH had been introduced. This consequence was also rather unsatisfactory, particularly for alcoholic beverages, which tend to be acidic. It was subsequently found, however, that the carboxylic acids were not generated during hologram development but were present as a minor contaminant in the HEMA monomer. They could readily be removed by passage of the monomer through an alumina column, and holograms made from the purified monomer showed nearly flat pH response profiles. The slight contraction with increasing pH value appears to be a specific effect of citrate buffer on polyalcohols and has been observed previously for poly(vinyl alcohol) holograms.<sup>8</sup> The poly(HEMA) holograms used in all the alcohol measurements described subsequently were fabricated from alumina-treated HEMA.

Calibration graphs for ethanol concentration in distilled water and Kaliber alcohol-free lager are shown in Figure 7. There is a small but significant displacement of the calibration line in lager compared with that in distilled water and is probably attributable to a slight increase in hydrophobic polymer backbone interactions in the presence of ions in solution, since solutions containing sodium chloride also cause a slight contraction. For interpolation purposes, the calibration curves were fitted to second-order polynomials and the coefficients used to back calculate volume percent alcohol values for a given wavelength from the appropriate root of the quadratic equation.

The poly(HEMA) holographic sensor was used to measure the alcohol content of a range of beverages based on the calibration curve in Kaliber. The wavelength in each beverage

Table 1. Stated Alcohol Content of 17 Beverages Compared with the Alcohol Content Measured with the Holographic Sensor, Together with pH and Conductivity Data for Each Beverage

beverage	alcohol (vol %)	pH	conductivity (mS/cm)	wavelength (nm)	calc alcohol (vol %)	error (vol %)
Kaliber lager (Guinness)	0.03	4.10	0.91	503.6	-0.32	-0.35
Swan Light lager	1	3.70	0.84	514.2	1.21	0.21
Steinbrau lager	3	3.95	0.79	524.9	2.67	-0.33
Heiniken lager	5	4.26	1.16	542.3	4.88	-0.12
Carlsberg Special Brew	9	4.11	0.96	575.6	8.72	-0.28
Weihenstephaner Hefe Weissbier	5.4	4.31	1.05	547.1	5.47	0.07
Woodpecker cider (Bulmers)	3.5	3.19	0.76	534.4	3.90	0.40
"Katy" strong cider (Thatchers)	7.4	3.46	0.91	563.6	7.39	-0.01
White Label Bitter (Whitbread)	1	4.01	0.66	513.5	1.11	0.11
Exmoor Gold Bitter	5	4.07	1.17	543.4	5.02	0.02
Newcastle Brown Ale	4.7	3.88	0.87	541.3	4.76	0.06
Guinness	4.3	3.91	0.99	539.2	4.50	0.20
Hoopers Hooch	4.7	2.77	0.81	536.5	4.16	-0.54
Liebfraumilch white wine	9.5	3.36	1.00	582.4	9.45	-0.05
french red wine	11.5	3.56	1.40	600.9	11.36	-0.14
french white wine	11	3.29	0.97	603.3	11.60	0.60
ruby port	20	3.55	0.69	683.2	18.85	-1.15

was recorded after equilibration and the value used to calculate the measured volume percent alcohol value. The values obtained are summarized in Table 1, along with measurements of the pH and conductivity and the stated volume % alcohol value from the packaging label of the product.

After each beverage sample, a measurement was taken for a 5% (v/v) ethanol/water standard solution. For 18 measurements of this standard, taken over a period of about 3 h, the mean peak wavelength was 549.78 nm, with a standard deviation of 0.58 nm, indicating a very high intermeasurement precision.

The beverages measured were selected to provide the toughest possible challenge to the sensor and included turbid, highly colored, and even nonfermented products. The measurements were made directly in the sample with no dilution or pretreatment (other than temperature equilibration). Under these conditions, no large discrepancies between measured and stated volume percent alcohol values were noted, with the regression line very close to the theoretical  $y = x$  ( $y = 0.964x + 0.147$ ) and a correlation coefficient of  $>0.99$ . The data are presented graphically in Figure 8, where the solid line represents the perfect fit ( $y = x$ ) and the dotted line is the calculated regression line for this data set.

Typical errors in the measured volume percent alcohol concentrations were in the range  $\pm 0.3\%$ , considerably greater than the precision of measurement (approximately 0.05%). There was no obvious correlation between the size and direction of the error in the volume percent alcohol concentration and simple variables such as pH or conductivity. The errors are probably caused by more subtle variations in the sample matrix from beverage to beverage, such as the presence or absence of particular organic carboxylates or complex compounds like tannins. The accuracy of measurement seems surprisingly high, given the variability of the samples and the fact that they were all calibrated against alcohol-free lager spiked with known concentrations of ethanol. For a particular measurement situation, where the samples are more comparable, it might be possible to construct more appropriate standard curves and hence improve accuracy.

The results achieved here for direct measurement of ethanol in real samples compare very favorably with those published for

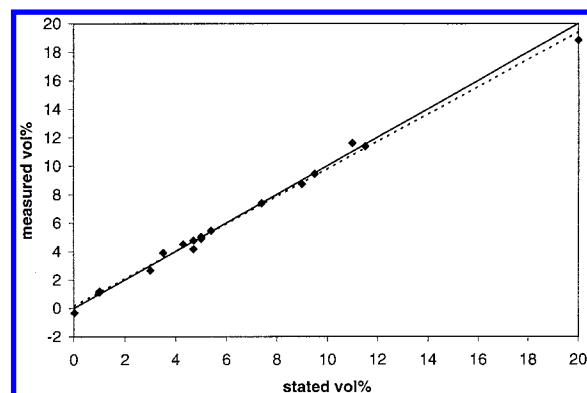


Figure 8. Comparison of the stated alcohol contents of 17 alcoholic beverages with the values determined using the holographic sensor, calculated on the basis of the Kaliber calibration graph. The solid line is the theoretical line of perfect correlation ( $y = x$ ). The dotted line is the actual regression line calculated for this data set ( $y = 0.9641x + 0.1468$ ). The correlation coefficient was 0.9944.

other alcohol sensors based both on chemical and on biological interactions.<sup>17-19,25</sup> In some of these cases, however, sample dilution was required to bring samples into range.

The response time for the holographic alcohol sensor, excluding temperature equilibration, is about 2 min, but varies slightly depending on the alcohol content and hence the degree of swelling required before equilibrium is reached. The response time could be reduced, at the expense of some hologram brightness, by reducing the thickness of the polymer film in which the hologram is recorded. The effect of this tradeoff is currently under investigation.

## CONCLUSIONS

A simple, inexpensive, and robust holographic sensor for measuring alcohol in liquids such as fermented beverages is described. The holographic format has a number of advantages compared with other alcohol sensors. Since the reflected signal is monitored through the back of the device, the sensor is unaffected by highly colored or turbid samples and can even be used in semisolid pastes. The operational wavelength range and

dynamic range of the device can be tuned to match a particular instrumental setup and application, by changing the nature and condition of the polymer film in which the hologram is recorded and/or by changing the geometry or laser source during hologram construction. The polymer film is very robust and, unlike enzyme-based sensors, can be exposed to relatively severe conditions without any loss of performance. This makes sterilization of the sensor feasible if required. The holograms can be conveniently stored in the dry state at room temperature for many months, with no deterioration of performance on rehydration. The hologram is particularly appropriate for construction of probe-type sensors, and work is underway to make a fiber-optic probe for use in process and fermentation monitoring. Due to the simple nature of the material from which the sensor layer is made, and the lack of chromophore species, the sensor should be highly stable in use and thus ideally suited to such applications. This

remains to be demonstrated in practice, however, and will be the subject of a future study. While the precision of the present device was good, it could be further improved by optimizing the composition of the polymer membrane in which the hologram is recorded. Alternatively, suitable membrane overlays could be used to prevent penetration of interfering species and more appropriate calibration solutions could be selected for specific applications.

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