



THE DEVELOPMENT OF A SAMPLER-SENSOR USING A VANADIUM-OXINATE-POLYMER FILM FOR THE SELECTIVE AND DIRECT DETERMINATION OF ATMOSPHERIC ETHANOL

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Summary—The development of a sensor for the direct and selective determination of atmospheric ethanol is in the initial stages. The sensor takes advantage of the selective chemical reaction between ethanol and vanadium oxinate. This reaction occurs in an organic medium where a red colored complex is the product. This reaction is determined spectrophotometrically where the absorbance maxima is 475 nm. The focus of this paper is to discuss the parameters necessary to develop a solid sorbent sampling-sensor which can be used to determine atmospheric ethanol.

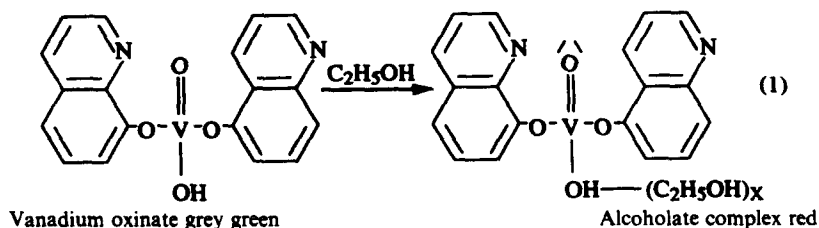
Over the course of the past 10 years, this research group has been developing sampler-sensing devices for trace gas analysis.¹⁻³ The research involves the use of chemical reagents immobilized on solid sorbents for selective surface reaction with the analyte of interest. In most cases, the reaction between the reagent and analyte on the surface results in the formation of an irreversible complex. The product yields a colored or fluorescent surface where either visual and/or an appropriate spectrochemical technique can be utilized to determine the analyte concentration. The advantages of using solid sorbents for trace gas analysis are low cost, selectivity, simplicity, high sample collection efficiency, suitable storage time, and detection limits in low ppm-ppb range.⁴

In addition to these advantages, the use of an archimedean sampler-sensor adds the dimension of direct *in situ* analysis of air pollutant. An archimedean sampler-sensor has been developed in this laboratory for the direct determination of air pollutants and has been previously described.² The novelty of this device is the elimination of instrumentation for analyte determination. The species of interest is

quantified by measuring the spiral length of color established by the pollutant reaction.

The use of sorbent material for the determination of atmospheric ethanol is not widely accepted, but there exist detector tubes available for this analysis. Sorption tubes containing activated charcoal are common for ethanol detection.⁵ Although suitable for atmospheric ethanol determination, activated charcoal tends to be nonspecific and adsorbs other organic volatiles present. In addition, humidity greater than 60% can reduce the adsorptive capacity of activated charcoal.⁶ In general, chemical sorbent chosen for atmospheric ethanol need not be very sensitive since the Federal Permissible Exposure Limits (PEL) is 1000 ppm. However, the surface reagent must be selective to ethanol due to the presence of other organics and high humidity available in environmental and industrial atmospheres.⁵

In this research, the reagent chosen for ethanol selectivity is a compound referred to as vanadium oxinate. Vanadium oxinate, a phenol ester of orthovanadic acid, reacts with ethanol to form a red colored complex (equation 1).



This reaction is characteristic of alcohols over all organic functionalities. As a matter of fact, this reagent, which is sparingly soluble in many organic solvents, has been used to remove low levels of ethanol in mixtures containing other organics.⁷ In addition this compound is completely insoluble and non-reactive with water. Because of the selectivity, the vanadium oxinate has been used to determine levels of ethanol in beers, wine, blood samples, and other solvent mixtures.⁸⁻¹⁰ The detection occurs with minimum sample preparation and the ethanol levels are quantified with basic UV-Vis spectrophotometry. Thus, because of its selectivity, vanadium oxinate appears to be a prime sorbent reagent for the selective determination of atmospheric ethanol using a sampler-sensor device.

EXPERIMENTAL

Reagent

The vanadium oxinate was prepared to adding solutions of 0.02M ammonium vandate (Fischer) to 2.5% 8-hydroxyquinoline (MC5B) in 5% acetic acid (Fischer). The resulting precipitate was soaked in an acetic acid-sodium acetate (Fischer) solution, pH 4, for 1 hr. All solutions were prepared in analytical grade deionized water. The precipitate was filtered in a sintered glass filter and allowed to dry overnight in the oven at temperatures ranging from 100 to 120°C. Reagent solutions ranging from 2.0×10^{-4} to $4.5 \times 10^{-4}M$ were tested for solubility and ethanol sensitivity in the following solvents: (1) toluene, (2) 2,4-dichlorotoluene, (3) cyclohexane, (4) acetonitrile, (5) benzene, and (6) chloroform. The chloroform had to be washed with analytical grade deionized water to remove residual ethanol. The effectiveness of these reagent solutions were tested in contact with solutions of ethanol at concentrations (V/V) ranging from 0.001 to 10%. The ratio of organic to aqueous phase was 1 to 2, and analyses were carried out in 25 ml test tubes. Reaction times were varied from 20 min to 3 hr depending on concentration and temperature. The colored product in the organic phase was analyzed spectrophotometrically at 475 nm.

In addition to various solvents, several polymers were also investigated as a matrix for vanadium oxinate immobilization. The following polymers were explored: (1) polyvinyl acetate, (2) polymethacrylate, (3) cellulose acetate, (4) polyethylene oxide, and (5) poly-

vinyl alcohol. The polymer films were formed by dissolving 10 mg of vanadium oxinate and 2 g of polymer in 60 ml of solvent. An aliquot of 2 ml was placed on a polypropylene disk (7.5 cm diameter) where the solvent would evaporate, leaving a caste film. These polymer films were tested for the mechanical stability, capacity to immobilize the reagent, and interaction with atmospheric ethanol.

Instrumentation

UV-Vis spectra of the various solutions were obtained on either a Perkin-Elmer Lambda 5 UV/Vis Spectrophotometer or Hewlett Packard 8452A Diode Array Spectrophotometer. The sample was placed in a 1 cm quartz curvette. These spectrophotometers were also used to analyze atmospheric ethanol collected on the various polymer surfaces. The complex was recovered in an appropriate solvent for analysis. Calibration gas standards were prepared from a VICI Dynacalibrator Model 230-50-2. A 5 mm diffusion vial (VICI metronics) with 100% ethanol was inserted into the instrument chamber and concentration was controlled by adjusting the gas flow rates. The atmospheric ethanol entered a reaction chamber where reaction with the vanadium-oxinate polymer film occurred.

RESULTS AND DISCUSSION

Solvent test

Initial research was devoted to determining the best solvent for the dissolution of the vanadium compound. Ideally the solvent should meet several criteria. The ideal requirements are as follows: (1) totally immiscible with water, (2) possess a low dielectric constant, (3) be able to dissolve sufficient amounts of the vanadium-oxinate, (4) non-hazardous to users, (5) ability to dissolve a polymer-reagent mixture for the film formation, and (6) have a high volatility. Furthermore, the reaction with ethanol in the aqueous or gas phase has to be rapid, have a large formation constant to yield sensitivity, and must be selective. It is to be noted that none of the solvents tested fulfilled all the criteria. The advantages and limitations of each of the solvents in contact with ethanol solutions is listed below.

Toluene. Toluene meets many of the ideal specifications for choosing a solvent. It has a low dielectric constant, immiscible with water, and non-hazardous to potential users. Never-

theless, vanadium-oxinate is sparingly soluble in toluene limiting the effectiveness to determine low levels of ethanol. Reagent solutions ranging from 2.0×10^{-4} to $5.0 \times 10^{-3} M$ were tested. Levels of 0.5% (5000 ppm) and 1% (10,000 ppm) were detected at the saturated reagent concentration. This is insufficient for the required PEL (1000 ppm) needed for atmospheric ethanol.

2,4-Dichlorotoluene. 2,4-Dichlorotoluene was chosen to investigate possible substituent effects of the chlorine on improved solubility. Results for this solvent, however, had identical detection levels as toluene offering no advantages.

Cyclohexane. In terms of the criteria, cyclohexane has similar properties to toluene. However, the vanadium oxinate is completely insoluble in cyclohexane; therefore, no color formation occurred in the organic phase with ethanol solution.

Acetonitrile. This was the only water miscible solvent investigated; thus it is in essence undesirable. In addition, acetonitrile is more hazardous than the previous solvents mentioned. Nevertheless, the acetonitrile can dissolve a sufficient amount of vanadium oxinate to determine ethanol levels of 0.1% (1000 ppm).

Benzene. Benzene is the solvent most widely used to dissolve the vanadium compound, but it is the most toxic, thus, least preferred. The desirable aspect of using benzene is that ethanol levels as low as 0.05% (500 ppm) can be determined.

Chloroform. Chloroform is a compromise solvent, therefore, being the choice solvent for sensor development. It dissolves a sufficient amount of vanadium to determine ethanol at levels of 0.01% (100 ppm) and it is immiscible. The apparent disadvantage is the toxicity of this solvent; although, its toxicity is less severe than benzene and acetonitrile. Figure 1 shows the UV-Vis spectra of the vanadium solution in contact with 1 and 3% ethanol solutions. The absorbance maxima occurs at 475 nm. This maxima agrees closely to reported literature values for this complex.⁹ In addition, this solvent is capable of dissolving most of the polymers investigated. Its volatility is suitable for casting polymer films containing the immobilized reagent.

Regardless of the solvent, there was a major problem associated with dissolution of the vanadium compound. Vanadium-oxinate, as mentioned earlier, is sparingly soluble in most solvents. When this compound dissolves in an

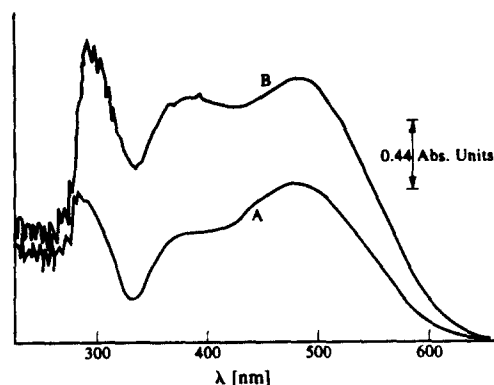


Fig. 1. Absorbance spectra of vanadium-oxinate solution in contact with (A) 1% aqueous ethanol, (B) 3% aqueous ethanol.

organic medium, it forms a dark black solution which tends to precipitate in the organic layer on standing. Thus, the reagent solution has a variation in color intensity and absorbance for a particular ethanol concentration which is time dependent. In order to circumvent this particular problem, sieving of particles and filtering of solutions were employed before analysis. However, time dependent changes persisted. This problem is carried into the second stage of polymer film development for atmospheric determination of ethanol. In conclusion, none of the above solvents fulfil all requirements of ideality. Chloroform is the choice solvent due to its ability to determine ethanol at levels of 0.01% (100 ppm).

Polymers

The next stage of sensor development was to find a polymer which can incorporate the vanadium compound in a film. In essence, the ideal polymer should have compatibility with the ethanol promoting adsorption and/or permeability, it should be soluble in organic solvents that dissolve the vanadium oxinate, it needs to be mechanically stable when cast, and the reagents should be homogeneously distributed in the film. Thus, these criteria were explored for identifying the choice polymer.

Polyethylene oxide. Polyethylene oxide had many desirable properties for immobilizing the reagent. It exhibited mechanical stability, dissolved well in chloroform, and formed homogeneous films of the immobilized reagent. It also exhibited surface reaction with ethanol solutions of 10% (v/v) and greater. However, no reaction occurred with atmospheric ethanol.

Polyvinyl alcohol. Polyvinyl alcohol had many undesirable attributes as a substrate matrix.

This polymer did not have any permeability for the ethanol. In addition, the oxine reagent was formed in non-homogeneous and irreproducible zones on the polymer surfaces. Although the surface vanadium reagent reacted with ethanol solutions, it was impossible to obtain reproducible color changes with ethanol concentration.

Polymethacrylate. The polymethacrylate behaved similar to polyethylene oxide in all regards. Surface color change reactions with ethanol solutions greater than 10% (v/v) occurred, but it was non-active to atmospheric ethanol.

Cellulose acetate. Cellulose acetate was very ineffective. As a matter of fact, this polymer film was mechanically unstable on incorporating the vanadium reagent. Thus, no further testing were performed.

Polyvinyl acetate. Polyvinyl acetate fulfilled all the necessary requirements for formation of a sensor film. It readily permeated with the ethanol and exhibited a rapid color change for both ethanol solutions and gases. Solutions of 1% (V/V) and 1200 ppm of ethanol gases were easily detected. In addition, the films were mechanically stable and uniform in terms of reagent distribution. Figure 2 shows the UV-Vis spectra of films exposed to 8300 ppm and 10,000 ppm of ethanol where the film was dissolved in chloroform. Notice the characteristic absorbance maxima of 475 nm.

In summary, polyvinyl alcohol and cellulose acetate which are hydrophilic in nature tend to precipitate the vanadium compound out as the solvent evaporates on casting the film. Polyethylene oxide and polymethacrylate films distribute the vanadium compound uniformly

on film formation. However, the ethanol does not readily permeate these films, thus, forming color changes only with ethanol solutions greater than 10% (v/v). Moreover, this inability to adsorb ethanol produces no color change for atmospheric samples. Polyvinylacetate shows both hydrophobic and hydrophilic characteristics. Thus this polymer promotes the uniform distribution of the vanadium oxinate on casting and has sufficient hydrophilicity to interact with the atmospheric ethanol. This allows the ethanol to react both at the surface and within the matrix with reagent. Response time for color formation varied from 3 to 6 hr for atmospheric samples depending on concentrations.

CONCLUSIONS

The combination of a reagent, solvent, and polymer for an immobilized surface sensor film for atmospheric ethanol determination was successfully completed. The selectivity of the vanadium-oxinate towards ethanol is excellent in both the solution and gas phase. Ethanol solutions as low as 0.01% (v/v) were determined in chloroform solvent-reagent system, and the immobilized vanadium oxinate-polyvinyl acetate substrate film can detect as little as 1200 ppm of atmospheric ethanol. However, the problem of solvent-vanadium stability gave non-reproducible color formation for each concentration of ethanol tested. This has not yet been solved. Thus, continued work must be performed on establishing stable and homogeneous reagent solutions for improved sensor data reproducibility. Once this problem is solved, the applicability of these films for use in the archimedean sampling-sensor unit can be evaluated.

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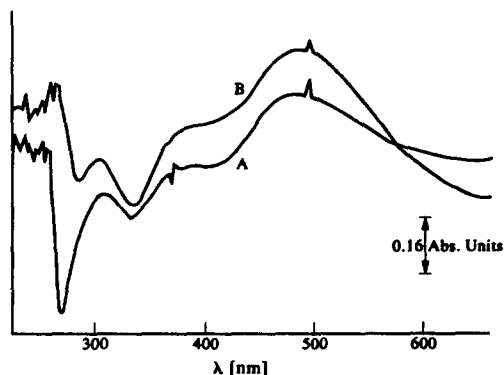


Fig. 2. Absorbance spectra of vanadium-oxinate film in contact with (A) 8300 ppm ethanol-air sample, (B) 10,000 ppm ethanol-air sample.

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