

Calibration of an Optical Condensate Measurement Technique Using Indirect Static Headspace Gas Chromatography

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Abstract

Researchers in the Department of Mechanical Engineering seek to obtain a means to measure less than 3 mg of H₂O that adheres to a metal surface as condensate. The objective is to calibrate optical reflectance measurements of an aluminum surface as a function of the condensate thickness present. Collaboration with the Hazardous Substance Research Center at Michigan State University results in the development of an indirect static headspace gas chromatographic technique capable of measuring H₂O in low-milligram quantities. The technique utilizes manual headspace sampling, a megabore capillary column, and a flame ionization detector. A correlation of $r^2 = 0.999$ is obtained for the calibration of the indirect measurement technique. The calibration of the analytical instrument demonstrates adequate precision ($< \pm 50 \mu\text{g}$ at a 95% confidence interval) for such a heterogeneous sample. The calibration samples consist of a strip of aluminum metal, H₂O, and pulverized calcium carbide to convert the H₂O to acetylene. A scaled calibration technique is used to simplify handling trace water volumes. The surface reflectance measurements are found to correlate well ($r^2 = 0.935$) with measurements of the condensate mass. This result facilitates the development of an optical mass-transfer measurement technique. This study focuses on the analytical method and its relationship with engineering research.

Introduction

Condensation on the windshields of vehicles during operation can create a significant safety hazard. Automotive manufacturers use numerous design tools including computational fluid dynamics (CFD) programs to model this complex flow field. These programs use models to simulate complex phenomena such as turbulent flow coupled with heat and mass transfer. Obtaining accurate experimental measurements of the transient mass-transfer phenomenon is essential for the validation of these analytical models. Pilot experiments indicated that the reflectance of the surface changed as condensation formed. The relationship between local condensate thickness and reflectance over a surface area of interest was then explored.

A simple film model of the condensation indicates that the reflectance is exponentially related to the condensate thickness because of the absorption property of the material (1). It has been shown that the reflectance of an aluminum surface is dependent on the amount of liquid water present on the surface (1,2). A calibration of the surface reflectance as a function of the condensate thickness was sought. An independent method to measure the mass, volume, or thickness of the water condensate on the aluminum surface was required. The infrared (IR) detector used to measure the surface reflectivity was sensitive to radiation wavelengths from 8 to 12 mm. The spectral absorptivity of water and the sensitivity of the IR detector primarily determined the dynamic range of the technique. For the IR camera, the model indicated that the dynamic range of the optical condensate thickness measurement would be limited to approximately 0 to 10 mm if a thin film model proved accurate. Thus, the mass of water present on a 1- × 3-cm area target would be approximately 3 mg or less.

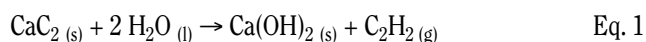
A gravimetric mass measurement of H₂O was ruled out as a possibility because of two considerations. Mounting the reflectance target on a scale would prove impractical because condensate would form on the chilled target holder, thus preventing an independent measurement of the condensate on the target. To further complicate the measurement, the target temperature was below the ambient dew-point temperature and thus the target must be removed from the target holder and quickly isolated from the environment to prevent further condensation from occurring. These two limitations provided the impetus to identify a measurement technique capable of measuring the mass of water to an accuracy of 100 μg and a method to isolate the target. Gas chromatography (GC) provided an indirect measurement of the mass of water present, and the methodology required the specimens to be sealed in a headspace (HS) vial, thus meeting both measurement requirements.

Static HS capillary (C) GC is most often used for conducting trace volatile organic (VOC) analysis for aqueous samples such as drinking, surface, and ground water. EPA Method 5021 is a rela-

tively recent adaptation of HS-C-GC as it is applied to soil matrices (3). The Hazardous Substance Research Center (HSRC) laboratory has determined traces of VOCs using HS-C-GC for well over a decade. A few years ago, the HSRC was asked to develop a method that would quantitatively determine H₂O in several soil samples (6). It was presumed that the soil samples would be relatively dry and contain water below 1% by weight. Conventional elemental analysis with a detection limit of approximately 1% for hydrogen such as using a Model 2400 CHN Analyzer (PerkinElmer, Shelton, CT) proved inadequate because of this limited sensitivity. A literature review led us to modify a method first published by Loeper and Grob whereby water reacts with calcium carbide (CaC₂) to produce acetylene (C₂H₂) in the HS (4,5). The HS is sampled and injected into a capillary column connected to a flame ionization detector (FID). Because FIDs are highly sensitive to hydrocarbons, a method detection limit (MDL) for water via its conversion to C₂H₂ enables an indirect measurement of H₂O in the low-milligram range. In other words, a small quantity of H₂O, when placed in a sealed HS vial, can yield a concentration of C₂H₂ that can be HS sampled and subsequently injected either manually or automatically into a C-GC-FID. The modification of the approach taken by Loeper and Grob to an automated HS-C-GC and its successful application to soils was first reported along with a review of the literature on the determination of water in references 6 and 7. In addition to the significant findings in these works, the need to establish a method blank with a low enough water content resulting from the extremely sensitive FID detection of C₂H₂ confirmed Loeper and Grob's statements concerning high method blanks. If the method blank can be minimized, then a very low MDL can be realized.

The focus of this study was to demonstrate that a total amount of water, present as condensate on aluminum metal in the low-milligram range, can be quantitated precisely. The method is seemingly universal and extends the previous work with soils.

Some descriptive chemistry concerning carbides serves to rationalize the indirect measurement of water. Historically, CaC₂ has been used to generate C₂H₂ gas for lighting purposes, whereby 1 kg of carbide yields approximately 300 L of C₂H₂ (8). The heavy metal carbides are thermodynamically unstable and, when dry, may explode by heat or shock. Silver carbide explodes at 140–150°C in contrast with sodium carbide, which is stable up to 400°C. CaC₂ melts without decomposition at 2300°C and reacts with water according to reference 9:



CaC₂ itself is industrially prepared by reacting coke with lime in an electric furnace held at 2500°C and is readily available from chemical suppliers. It is a relatively hard solid and must be pulverized prior to use in this analytical method.

Experimental

Calibration of the HS-C-GC-FID is necessary to correlate the instrument peak area response to C₂H₂ with the amount of H₂O

injected. As developed earlier (7), one approach to calibration is to treat H₂O as a solute in the same manner as VOCs.

Only H₂O was added to the HS vials. The density of H₂O at ambient temperature is approximately 1 mg/μL. The use of conventional 22-mL HS vials was abandoned because it is experimentally difficult to transfer 0.5- to 3-μL aliquots of H₂O precisely using liquid-handling glass syringes. The use of 125-mL HS vials with crimp tops enabled the volume of H₂O to be increased by a factor of approximately 5.7 while maintaining the concentration of H₂O at the level that would typically be found if the more conventional 22-mL HS vial was used. HS vials were dried in an oven at 110°C for 24 h and then stored in a desiccator. Aluminum test targets (10 × 32 × 0.8 mm) were polished with a fiber-free pad, cleaned with acetone, and allowed to soak in the ambient atmosphere for at least 1 h. The targets were carefully placed in a 125-mL HS vial.

The following procedure was used to calibrate the HS-C-GC-FID: 5.68, 11.36, and 17.04 μL of H₂O were added to each 125-mL vial with a 20-μL Pipetman (Gilson, Middleton, WI). It should be noted that these volumes produce equivalent C₂H₂ concentrations compared with 1, 2, and 3 μL of H₂O in a 22-mL HS vial. A stoichiometric excess of CaC₂ was then added and each vial was immediately sealed and shaken vigorously. The specimens were then stored for 24 h at approximately 10°C. Three blanks were prepared for each calibration run to establish a baseline. The blanks consisted of an aluminum target and CaC₂, but no H₂O.

The samples were analyzed by sampling the HS of each 125-mL HS vial using a 100-μL Pressure-Lok gas-tight syringe (Precision Sampling, Inc., Austin, TX) connected to an Autosystem GC (PerkinElmer). The analog output from the GC-FID was connected to a PC via a 600 interface (PE-Nelson, San Jose, CA). The PC used the Turbochrom (PE-Nelson) for chromatographic data acquisition and data reduction. The control settings for the HS-C-GC-FID are presented in Table I. The peak area measurement was obtained and the blank average subtracted from each run. This was performed to eliminate the effect of variable atmospheric humidity levels between test dates.

A technique to obtain quantitative measurements of condensate mass or volume on aluminum was sought. Optimally, this technique would be optically based in order to avoid physical interference with the surface. The reflectance of an aluminum

Table I. HS-C-GC-FID Control Settings

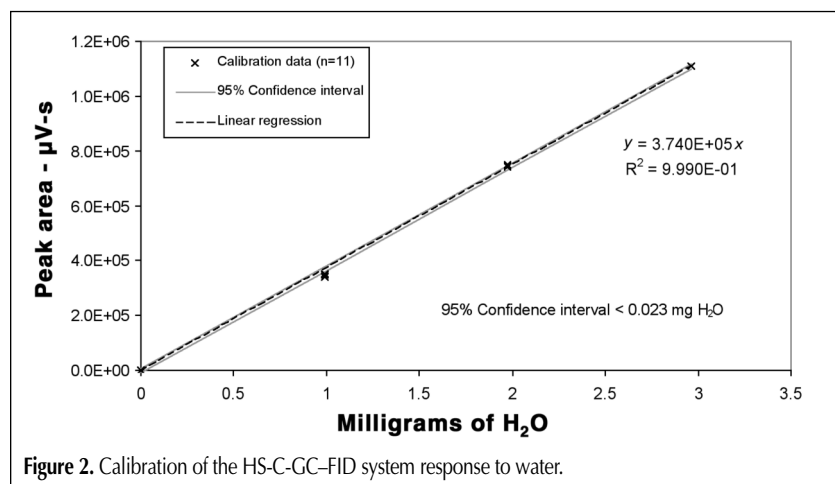
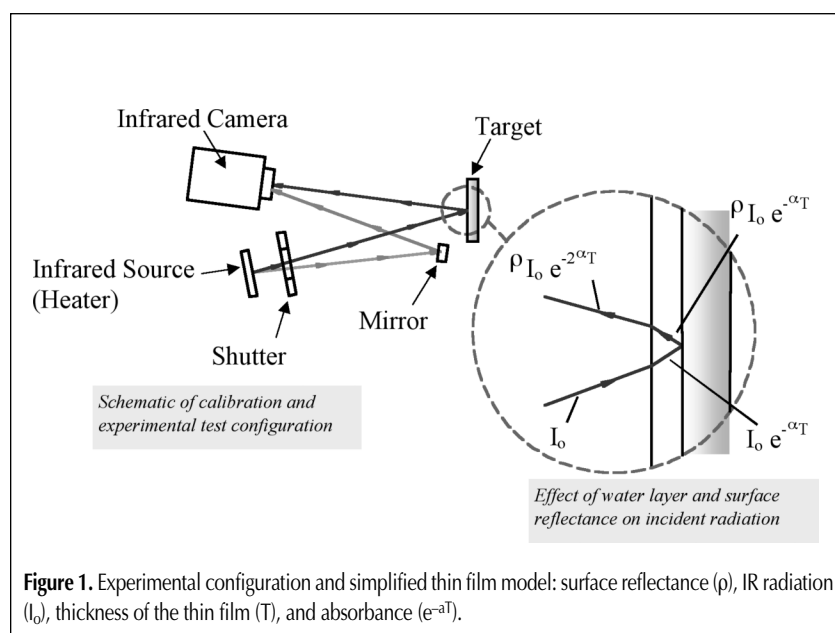
GC parameter	GC conditions
Column	30-m × 0.53-mm PE-624 (PerkinElmer)
Oven temperature	40°C
Isothermal time 1	4 min
Injection volume	25 μL
Injection port temperature	250°C
Detector temperature	250°C
Equilibrium time	0.5 min
Thermostating time	0 min
Carrier gas (N ₂) flow rate	10 mL/min
H ₂ flow rate	30 mL/min

surface was found to vary as condensation developed during pilot studies. An experiment was then designed to calibrate the reflectance of the surface as a function of the thickness of the condensate present in order to develop an optical condensate thickness measurement technique. A schematic of the experiment is presented in Figure 1 with a detail showing the absorption phenomenon in a thin condensate film. The surface was illuminated with IR radiation and the total energy reflected was a product of the surface reflectance of the aluminum and the absorbance as the radiation passed through the thickness of the thin film. The details of the thin film model are presented in reference 1.

The IR reflectance calibration experiment used an aluminum target ($10 \times 32 \times 0.8$ mm) fixed mechanically to an aluminum block. The aluminum block was thermally bonded to a CZ1-1.0-127-1.27 Peltier device (Tellurex Corp., Traverse City, MI). The Peltier device was thermally bonded to a copper heat exchanger. A chilled nitrogen gas flow cooled the copper heat exchanger. This configuration allowed the aluminum target to be cooled rapidly below the ambient dew point, and the Peltier device provided the necessary control to maintain the aluminum target

above the freezing point. The aluminum target temperature was then reduced until condensation formed. An 8-bit 600L IR camera (Inframetrics, Portland, OR) imaged the aluminum target, which was alternately illuminated every 2.5 s by two different IR sources (a heater at 48°C and a shutter at ambient, approximately 22°C). Using the two IR sources allowed the reflectance of the aluminum target to be measured independent of surface emittance. The spatial uniformity of the condensate will be discussed in the next section. The IR camera used was sensitive to radiation wavelengths of 8 to $12\ \mu\text{m}$. Nine images were averaged from each measurement to reduce random noise effects. The target was allowed to soak for various lengths of time in order to allow different quantities of condensate to form.

At the end of the experiment the aluminum target was captured in a 22-mL static HS vial. A stoichiometric excess of CaC_2 was then added and the vial was capped. The HS vial was then shaken vigorously and stored at approximately 10°C for 24 h in order to insure sufficient diffusion time for the reaction to proceed to completion. The total exposure of the aluminum target to atmosphere was limited to less than 10 s after the end of the test.



Results and Discussion

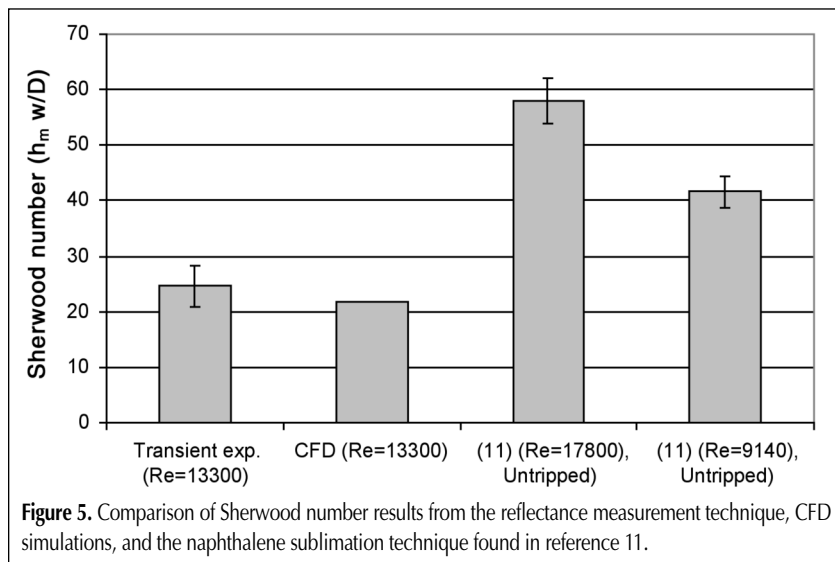
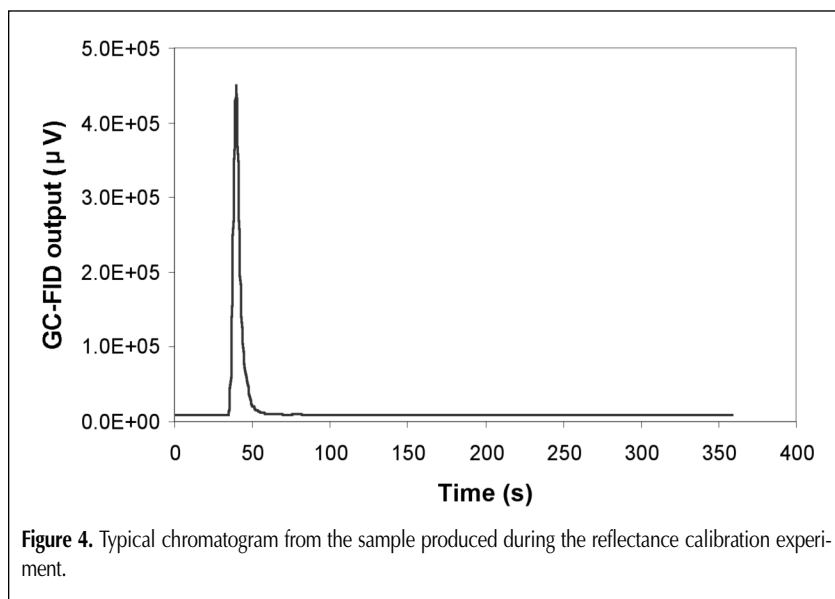
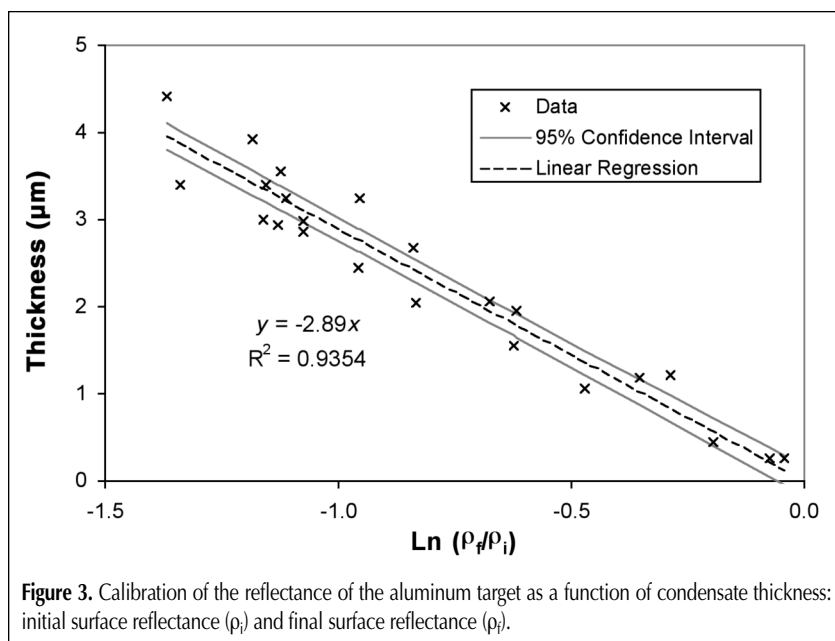
The results of the HS-C-GC-FID calibration to H_2O (C_2H_2) are presented in Figure 2. The results show an excellent linear correlation ($r^2 = 0.999$) and a narrow 95% confidence region indicated by the solid light-gray lines. This result then allowed for the calibration of surface reflectance as a function of condensate thickness to begin in earnest.

The HS-C-GC-FID was then used to measure the mass of water present in the HS vials from the reflectance calibration experiments. The volume of water was calculated using the results presented in Figure 2 and the density. An assumption was made that the condensate was uniformly distributed on the surface of the aluminum targets. This assumption was justified by three reasons.

The first reason was that the measured temperature of the aluminum target surface varied spatially by less than 1°C , thereby providing an acceptably uniform concentration gradient to drive the condensation mass transfer. This temperature was measured with the IR camera on a blackened (0.95 emissivity) aluminum target.

The second reason was that the 8-bit gray scale values of the IR images changed in a uniform fashion as condensate developed. The bias and random (noise) error was captured in the standard deviation of the image gray scale values. The average coefficient of variation of the image intensities was 3.4% and never greater than 5.6%, which was deemed acceptable.

The third reason was that the condensate nonuniformity (typical dimension approximately



20 μm) was orders-of-magnitude smaller than the optical resolution of the IR camera (approximately 2 mm), thus the IR camera effectively averaged the condensate thickness over each measurement pixel.

This assumption allowed for an estimate of the thickness to be calculated by dividing the volume of water in the vial by the exposed surface area of the aluminum target. The resulting calibration of the reflectance as a function of condensate thickness is presented in Figure 3. The solid light-gray lines in the figure represent the 95% confidence region of the linear regression model.

The thickness estimate was obtained by dividing the mass of H_2O obtained from the HS-C-GC-FID calibration in Figure 2 by the target surface area and the density of water. A typical chromatogram is presented in Figure 4. It should be noted that this peak was identified as C_2H_2 by running a known C_2H_2 sample, which presented an identical retention time.

The calibration of the reflectance as a function of condensate thickness was applied in a flow of engineering interest. A wind tunnel at Michigan State University (MSU) was used to produce a wall jet flow over an aluminum thermally active test surface. Tunnel details are provided in reference 10. The surface reflectance that was measured as the surface temperature was reduced below the ambient dew point. The resulting reflectance measurements were converted to condensate thickness with the correlation presented in Figure 3. The mass-transfer coefficient (h_m) at one location on the plate (details discussed in reference 1) was calculated from the local temporal development of the condensate thickness. A comparison of the Reynolds number as a function of the Reynolds number is presented in Figure 5. Figure 5 also contains computational results (1) and published results (11) obtained by a steady-state naphthalene sublimation from a test surface. The error bars represent the 95% confidence interval for the measurements.

Figure 5 shows the optical condensate measurement result during transient tests, the result from the CFD software, and results from steady-state tests conducted with a naphthalene sublimation technique (11). The results from reference 11 were determined at different flow velocities and conditions than the current work and showed significantly different results. The transient experimental result obtained with the optical condensate measurement technique did not agree with the result anticipated from the steady-state result. This is possibly because of the thermal transient that the surface was undergoing. The CFD result differed significantly from reference 11, but agreed to within the 95% confi-

dence region with the optical technique transient results. This highlighted the need to obtain experimental data in this and other flow regimes in order to accurately calibrate the analytical models used in the computational codes and further understand the phenomenon. This study's results did not agree with reference 11 and it is not clear whether the limiting steady-state case will adequately represent the initial transient condensate development because of factors such as surface energies, thermodynamic nonequilibrium, and development of noncondensable gas in the boundary layer.

Further data are currently being obtained to determine the dependence of the optical condensate measurement technique on the angle and distance to the target specimen. Also, because the width of the confidence regions are dependent on the reflectance calibration, further experiments to extend the calibration range and investigate the nature of the experimental variation may refine the resolution of the result. Current literature indicates that 15- μm -thick condensate is sufficient to obscure driver vision (12). Initial tests conducted indicate that lighting can affect this result substantially, and studies of optical clarity will be conducted with this new technique to verify this information.

The optical condensate measurement technique provides a new tool for engineering research and is the direct result of interdisciplinary cooperation providing tools such as the HS-C-GC-FID to nontraditional applications. A novel, optically based mass-transfer tool has been developed as a result of this collaboration.

Acknowledgments

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