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ON-LINE, SINGLE POINT STANDARDIZATION ANALYSIS FOR MEASURING HYDROGEN PRODUCTION BY TRANSITION METAL CATALYST IN LIGHT DRIVEN SYNTHESIS

by

Derek Joseph Pegram

A Thesis

Submitted in Partial Fulfillment of

Requirements for the Degree of

Master of Science

Major: Chemistry

The University of Memphis

August 2012

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ABSTRACT

Pegram, Derek Joseph. M.S. The University of Memphis. Conferred August 2012. On-line, single point standardization analysis for measuring hydrogen production by transition metal catalyst in light driven synthesis. Major Professor: Paul S. Simone Jr.

An automated SPS-GC-TCD has been optimized to determine hydrogen production in light driven synthesis reactions while operating in real time and being capable of multiple analysis per hour. The SPS-GC-TCD method incorporates two sample loops on a valve, one for a check standard and the other for the sample, eliminating many sources of error associated with gas sampling and allowing for automated calibration during each analytical run. Gas samples containing hydrogen in a percent volume concentration were analyzed and method detection limit (MDL), accuracy, and precision measurements have been conducted. Using single point standardization, proof of concept results for the analyzer gave an MDL of 0.73% (v/v%), accuracy of 100%, and precision of 3.7% for hydrogen. These values were comparable to results obtained by a much more intensive 5-point external calibration. The automated system gave extreme improvements in reproducibility, and a detection limit of 0.25% and precision of 1.7%.

Introduction

As populations and technologies continue to increase in this globalized world, so too does the demand for power and fuel. Massive consumption of non-renewable fossil fuels amongst developed and developing countries are leading to predicaments on local, national, and even global scales. Alternative energy is a growing field of research in response to this global energy crisis. Foreign oil dependence is a significant topic in both our political system and governments abroad. The energy crisis is being addressed in various ways. Nations such as America have provided subsidies by the federal, state, and local governments to encourage both improvements to current energy sources and the creation of new alternative energies. Some nations are looking to completely break their dependence on foreign oil, such as Sweden who has pledged to replace all energy demands with alternative sources and become an oil free nation by 2020 (Commission on Oil Independence, 2006). The answer to America's energy future may be unclear, but it will likely combine multiple innovations in alternative fuel technologies to improvements made on our current system. In a lecture on alternative energies conducted by his research group at MIT, Prof. Donald Sadoway claims, "If we're going to get this country out of its current energy situation, we can't just conserve our way out. We can't just drill our way out. We can't bomb our way out. We're going to do it the old-fashioned American way. We're going to invent our way out, working together" (Sadoway, 2012).

Among the potential sources of alternative energy, hydrogen has numerous characteristics that will make it a key contributor to breaking the domestic and global dependence on fossil fuels. Hydrogen is a clean, renewable source of energy. It is the most abundant element on Earth, and it could rather easily be integrated into the fuel-

consuming products that consumers rely on for everyday use (National Renewable Energy Laboratory, 2005).

The major disadvantage of hydrogen as a large scale fuel source is the lack of a clean, efficient means of mass production. Hydrogen can be obtained from the electrolysis of water; however energy is required to do this. Currently, mass production of hydrogen requires the consumption of fossil fuels to provide that needed energy, negating the benefits of being clean and renewable as well as contributing to its cost of production. It is for this reason that great interest has been taken to research alternative methods of production. These methods typically utilize other alternative energies such as wind, solar, biomass, et cetera, to provide the needed energy and replace the fossil fuel consumption (Milbrandt & Mann, 2007). However, the answer to this problem may be found by looking to Mother Nature instead.

The most straightforward water-splitting scheme is to have catalysts act directly on water. The objective is to develop a system for artificial photosynthesis (AP) to photochemically separate water into its constituent elements (Zhao, 2011). This AP incorporates the use of a metal catalyst in a photoelectrolysis reaction that reduces the protons in water to directly produce hydrogen gas. The initial goals of AP studies are to qualitatively find which metals can induce this photoelectrolysis, followed by refinements and directed development to find new active catalysts composed of more abundant and less expensive metals (McNamara, Holland, & Eisenberg, 2011). Once a catalyst has been found effective for proton reduction, its efficiency must then be quantitatively assessed. The expensive and inexpensive hydrogen production values are then to be compared to one another, providing information about what characteristics and

conditions are most beneficial to further develop better electrocatalysts. The ultimate goal of AP research is to identify the most efficient electrocatalyst for the cheapest cost to use in the mass production of hydrogen as an alternative energy.

To acquire this valuable data on the rates of hydrogen production, an analyzer capable of monitoring proton reduction and the presence or absence of other gaseous analytes is necessary. The instrument must be capable of separating a headspace sample into its constituent permanent gases (a term used to refer to hydrogen, oxygen, nitrogen, and carbon monoxide). Once separated, it should be able to qualitatively and quantitatively detect these gases representing the atmosphere inside the reaction vessel. The instrument should have a wide dynamic range. In other words, the instrument should detect low concentrations of the analyte while still capable of quantitative data on higher concentrations with little to no adjustments, avoiding the need of a dilution step. Additionally, it's advantageous to design and construct an instrument with on-line and real-time capabilities incorporating an automated standardization step into the analytical method.

Permanent gases are traditionally analyzed by gas chromatographic (GC) methods, using manual injection and a thermal conductivity detector (TCD) (Li & Guan, 2009). The instrument developed here uses a GC-TCD, constructed to employ automated, on-line analysis and calibration capabilities. On-line automation saves the user time, allows for lower operator skill level, eliminates numerous sources of error, gives significant improvements in reproducibility, and overall accumulates more reliable data.

Calibration of any instrumental method is always an important analytical step to consider. For any given analyzer, analytes of similar or equal concentrations can have

varied analytical signal due to changing environmental conditions in the laboratory (Skoog, 1998). Thus, it is necessary to calibrate for the analytes being tested on a daily basis. Simply having reference values of detector response from a known analyte concentration may not always account for all variables in a method. Other commonly overlooked factors affecting how reliable the accuracy of data produced can be include matrix effects, irreproducibility of manual injection, and sample preparation. Calibration methods such as standard addition or internal standardization can be used to mitigate these issues. The instrument presented here is designed to use single point standardization (SPS), which is similar to internal standardization in that it takes into account minor variations in reagent concentrations or sample loss, flow rates, and other potential sources of calibration drift over monitoring periods (Ranaivo, Henson, Simone, & Emmert, 2011).

The goal of this research is to develop a GC-TCD analyzer capable of monitoring hydrogen production in a closed AP reaction environment, by separating a headspace sample into its constituent permanent gases with on-line and real-time capabilities while also incorporating single point standardization as an additional, continuous and on-line calibration technique.

Experimental

Reagents and Consumables

All gases are purchased from Airgas (hydrogen, oxygen, nitrogen, argon, helium, and custom blends). Argon is used as the reaction's background gas. Argon and helium (UHP) are used as carrier gases. All argon used is "ultra-high purity" (UHP; minimum purity 99.999%, <1ppb O_2, <1ppb H_2O, <1ppb CO + CO_2). The SPS check standard gas

is comprised of 95% argon and 5% hydrogen, mixed by the manufacturer and bottled into a '300-volume' gas cylinder tank, with a CGA350 regulator fitting. A 95% argon and 5% methane internal standard was used for manual injection samples and method comparison. A 95% nitrogen and 5% hydrogen standard was used for SPS verification. Zero grade compressed air was used for optimization studies of flow rates and pressure settings through the standard and sample lines on the sampling valve. Custom manufactured calibration standards of various percent compositions of hydrogen in argon are purchased from Airgas. The GC consumables were purchased from Restek.

Proof of Concept and Manual Injection Method GC-TCD Analysis

Gas Standard Preparation. A gas mixture of hydrogen, oxygen, nitrogen, and argon is made in identical 100 mL vials with a fresh septum from Fisher Scientific. The vials are evacuated and filled with a desired volume of argon, hydrogen, oxygen, and/or nitrogen. The gases are extracted from the individual cylinders from a purged tygon tube fitted with a Swagelok tee using an air-tight septum placed inside the tee. A 'gastight' syringe is used to pull out the desired volume of gas and inject it into the vial. The volumes of desired analytes to calibrate for are adjusted proportionally to give different percent volume compositions at the same total volume.

Manual Single Point Standard Procedure. A proof of concept was performed to compare the viability of using the simpler SPS method as opposed to an external calibration. A SPS standard was prepared in the same manner as the external standards. Five calibration standards and a check standard were made using identical vials with fresh septa to avoid interference (Skoog, Holler, & Nieman, 1998). The check standard concentration was between the two lowest concentrations of the calibration standards.

The calibration standards were run from lowest to highest concentration and the check standard was analyzed 7 consecutive times. On the tail end of each analysis the SPS sample was injected at the 5 minute mark.

Manual Sampling GC-TCD Method. The first step for the AP research was to build a working instrument in order to start collecting data. As with any analyzer, an instrumental method was developed for the GC-TCD for minimization of error and continuity between sample analyses. The manual injection technique involved first preparing the sample and irradiating with a light source. The reaction was monitored by using a microsyringe to extract a headspace sample and inject onto the GC-TCD. The syringe was evacuated and plugged with a septum to avoid ambient air interferences, and was always removed in a manner to not expose the tip to outside air until the sample was to be injected.

The carrier gas pressure is set to 80PSI at the source, and the column head pressure is set to approximately 40PSI. The temperature program was set run isothermally at 50°C, the injector at 150°C, and the TCD at 300°C. Manual injections of 30 μL from the headspace were injected. The TCD sensitivity was put on the 'high' setting. Argon is used for the carrier gas, set at approximately 30 mL min^{-1}. The dead time is ~0.9 min and ~5min total run time (excluding the presence of gaseous byproducts from certain reactions, which would extend the run time to ~18min). Various precautions were taken to avoid column degradation. A stand-by method was developed for when the GC-TCD was not in use; raising the oven temperature to 100°C and lowering the detector temperature to 200°C. This was done to regenerate any deactivated pores in the packed column, hence helping to maintain better levels of sensitivity and column longevity.

Automated GC-TCD Single Point Standard Parameters

Flow Controlled Method. The flow controlled method will enable automated sampling from both the single point standard gas and the sample vial during the same analytical run. This method was chosen over other proposed designs after the proof of concept to give the desired functionality with the least cost and most simplicity.

Apparatus. As shown in figure 1, the on-line sampling instrument requires a custom inlet system fabricated with an arrangement of traps, valves, and flow controlling/restricting devices. There are two primary gas lines from the gas cylinders (one for the carrier & TCD reference gas and another for the check standard) and a sample line. These lines are connected to a HP 5890 gas chromatograph with a thermal conductivity detector via a micoelectrically actuated 10-port injection valve (VICI, Inc.). The GC has a packed column (Restek, molecular sieve 5Å 80/100 mesh [3.05m x 1/8in OD x 2mm ID]) and a purged-packed inlet manifold, with chemical trap. An oxygen/nitrogen trap was installed upstream on the carrier line to help stabilize the baseline. There are two electronically controlled 2-way ball valves (Omega, Inc.) to affect the standard/sample gas lines, both using two internal reducing unions from ¼'' to 1/16'' (VICI, Inc.). The 10-port valve, electronic ball valves, GC (via remote start wiring), and data processing are all automated by Peaksimple hardware/software (SRI Instruments.) The GC is run isothermally, but has the ability to sync temperature programs with Peaksimple as well.

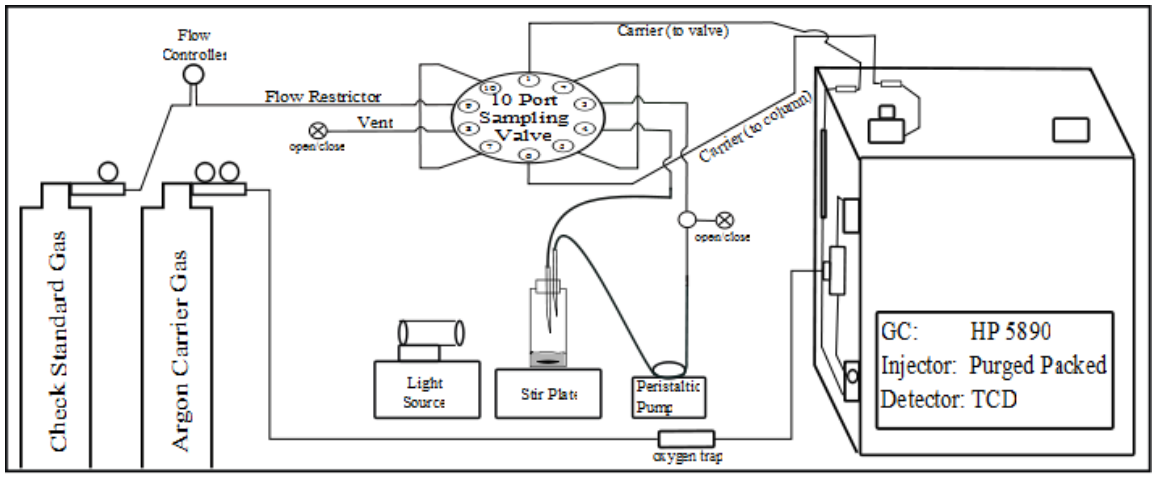

Figure 1. Flow controlled instrument schematic showing standard and sample systems.

This system is based off the traditional purge-and-trap routing of the carrier gas line. The carrier gas goes through the oxygen/nitrogen trap, then a chemical trap, and is finally split before reaching the injector. The line is rerouted to the 10-port valve (displayed in figure 2), equipped with two 50 µL sample loops (loop 1 being the sample loop, loop 2 the standard loop). The carrier gas will enter through port 1, flow through either loop then out of the valve at port 6 and on to the injector.

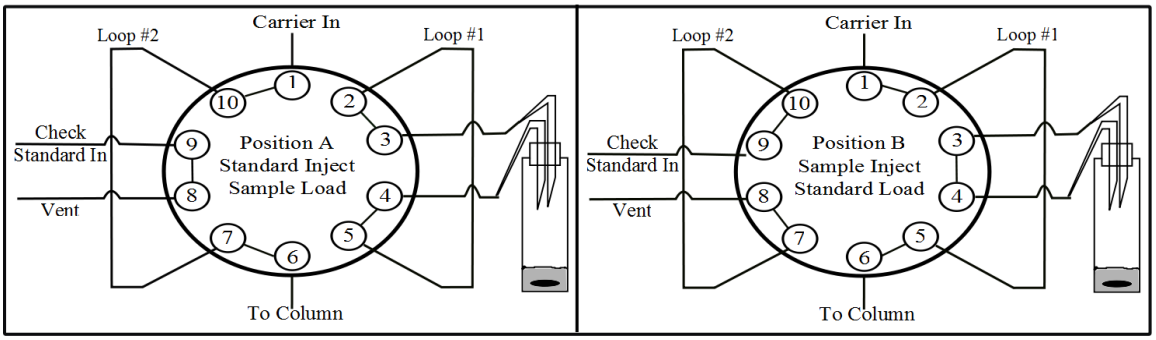

Figure 2. Schematic diagram of 10 port injection valve for sample and SPS standard

The 10-port valve will load one sample while the other is in the inject position. At the beginning of analysis, the sample injection valve is in Position "A". The reaction vessel sample is loaded into loop 1 using a peristaltic pump to pull the headspace of the

vial through the tubing. Concurrently, the carrier gas flows to the column through loop 2 and the check standard gas is set to vent. The valve then actuates to position "B" and the headspace sample in sample loop 1 is swept onto the column and the single point standard is simultaneously flowed through loop 2 at a flow rate set to mimic the conditions of the reaction vial on the basis of the ideal gas law. At 5.000 min, the valve is actuated again back to position "A". The single point standard is then swept onto the column for separation and analysis. The resulting chromatogram, presented in Figure 4, shows a sample and single point standard analysis within a single GC run.

Reaction Vessel Sampling Configuration. The sample headspace gas is flowed through the sample loop by 1/16'', 0.5 mm internal diameter (ID), stainless steel (SS) tubing on both the 'sample-in' and 'sample-out' ports of the sampling valve (ports 3 and 4). The SS tubing segments end with a length of 1/16'' tygon rubber tubing which is zip-tied down onto the SS tubing to eliminate air interference. The tygon tubing then goes to a peristaltic pump which will push/pull the headspace of the sample vial through the sample loop, ensuring that the gas sample is thoroughly mixed at an adjustable rate. The terminal ends of the tygon tubing are fitted over modified syringe needles (B-D brand, 18G, 1-1/2'') and zip-tied in place to prevent leaks or sample loss. These syringes are inserted into the sample vial before the sample is prepared, essentially making all the sample line tubing an extension of the sample vial's headspace (ie, all the volume of the tubing and the sample loop are in actual fact added to the volume of the vial). This must be done before the sample is prepared to ensure removal of ambient air from all the tubing and sample loop from entering into the reaction environment when the AP experiment is ready to begin.

Single Point Standard Configuration. The standard gas is regulated to approximately 8 PSI at the source then flows to another flow controller for fine tune flow adjustments. Immediately after the flow controller, a flow restrictor is implemented from the controller's exit to the 10-port valve 'standard-in' spot. The flow restrictor is a reduced ID SS tube, which is labeled at 4 mL/min at 30 PSI. The flow rate is measured after the standard loop and was set to approximately 0.8 mL min^{-1}. After the loop is a length of reduced ID PEEK tubing connecting the 'standard-out' port of the sampling valve to a 2-way electronically controlled ball valve with another length of PEEK tubing traversing down the instrument and venting to the atmosphere.

Sample and Single Point Standard Purging. The two systems on the valve must both be purged of ambient air in the lines before analysis can be done. Any air in the system will affect the percent composition values of the analytes being tested. Also, air in the sample's system may affect the catalyst and prevent hydrogen generation.

On the sample system, one of the SS lines is tee'd with a 3-way union which has another 1/16'' SS, 0.5 mm ID tube going from it to an electronically controlled 2-way ball valve. This ball valve is used to open the system to vent when purging the sample vial with the argon background gas. The manner in which the vial must be purged was investigated and optimized to ensure minimal contamination. The argon gas cylinder is fitted to a tube with a modified syringe. The cylinder's pressure is set at the source to be ~8 PSI (slightly above STP). The sample lines from the pump are inserted in a manner to have the "in" line (the one being pushed from the pump) inserted all the way down, and the other "out" line (the one being pulled from the pump) is inserted to a point of having the needle as close to the top of the vial as possible. The gas is first turned on to eliminate

air out of the line, then the ball valve is opened to vent. The argon line is then inserted and allowed to purge the system for approximately 15 min. The needle for this line is inserted fully into the vial at 90°. After the purging period, the argon line is first removed to avoid pressure build-up, and the electronic ball valve is immediately closed. After the system has been purged a test run is performed to ensure all air has been removed from both the sample system (the vial and sample lines) and the standard system. The test run's chromatogram should have a flat baseline during the 'sample' portion and only one peak for hydrogen during the 'SPS' portion, ensuring the system is free of interference.

Monitoring Studies of Hydrogen Producing Catalyst. The sample vial is cleaned and given a stir bar then capped with a rubber septum, which is sealed and tightened to ensure no leakage. The vial is then place on a stir plate in front of the light source. The sample line needles are inserted into the sample vial and the vial is purged with argon (as previously described). The standard line is also set to vent during the sample prep. Once the sample and standard systems have been purged, the test run is performed before introducing the sample. If any air remains after the test run then the system purge is extended and the analyst should check for any potential leaks.

The electrocatalyst solution is then carefully injected into the vial. Attention should be given to ensure no air is being injected with the sample from inside the syringe or needle (priming the needle if needed). It should be injected at approximately 90° to avoid introducing parallax error. Caution should be taken to not touch the sampling lines during this step of the procedure as it has been shown that small amounts of air can enter into the vial if they are disturbed. Once the electrocatalyst solution is in the sample vial, the stir plate is turned on and the system is covered in aluminum foil. The software is

then set for total run time, number of desired runs, and time allotted between sample run. The system is then ready for on-line autonomous monitoring studies for the given AP reaction.

Results and Discussion

Optimization of Manual GC-TCD Analyzer

Carrier Gas Optimization. Helium was initially used as the carrier gas, but there were problems with argon and oxygen co-eluting and the sensitivity for hydrogen was not acceptable. Argon (0.016 W/(m·K)) has a much greater difference in thermal conductivity than helium (0.142 W/(m·K)) does to hydrogen (0.168 W/(m·K)). Switching the carrier gas to argon increased the hydrogen sensitivity and solved for the co-elution problem as the background gas for the AP reaction was now the same as the carrier gas, hence removing the solvent peak from the chromatogram. This carrier gas change initially spurred the interest in performing a proof of concept for using single point standardization (SPS) as the means of instrument calibration because its use of the same chemical species.

The sensitivity for oxygen and nitrogen was decreased, but was acceptable as hydrogen is the primary analyte. Ambient air interference can be assessed by the presence of oxygen or nitrogen peaks, though we focus on nitrogen as it is more prevalent in air and the oxygen produced from the photoelectrolysis may react to form other byproducts during the reaction.

MDL, Accuracy and Precision of the Manual Analysis. A 5-point calibration curve was prepared and the slope and y-intercept were determined. The check standard concentration was determined using the slope and y-intercept. The MDL was calculated

by multiplying the standard deviation of the experimental concentrations of the check standard by the Student t-value at 98% confidence interval (USEPA, 1996). Accuracy is estimated by the mean percent recovery, which is calculated by dividing the experimental concentration by the theoretical concentration multiplied by 100% for each check standard and calculating the mean value. Precision is estimated by the percent relative standard deviation (%RSD), which is calculated by the standard deviation of the check standards divided by the check standards mean multiplied by 100%.

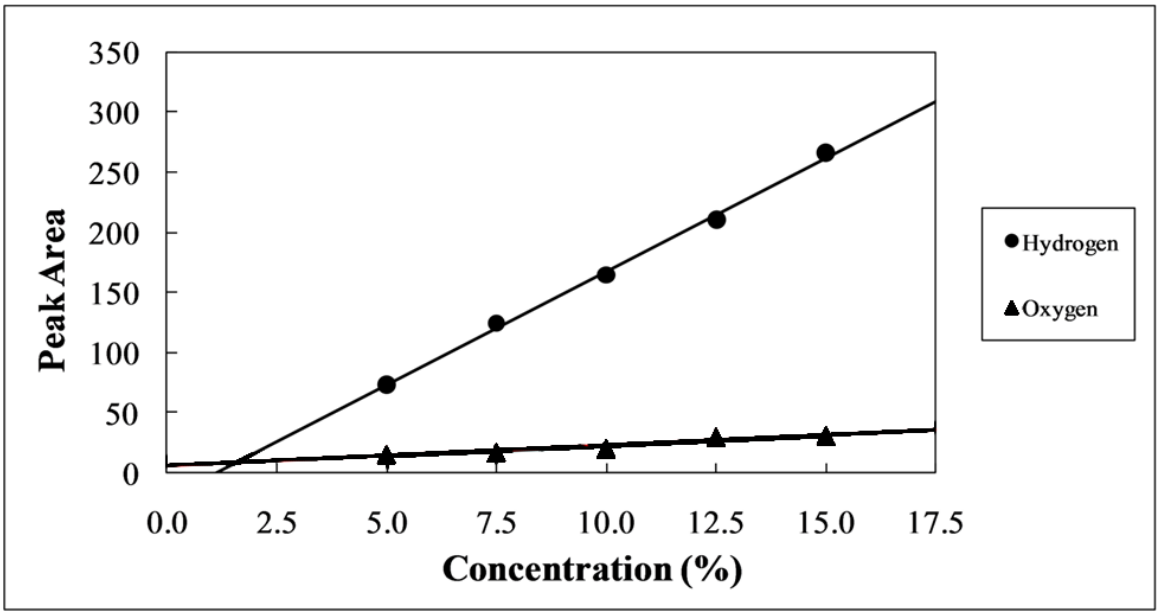

Figure 3. External 5-point calibration curve for hydrogen and oxygen, manual injection.

The GC-TCD's external calibration using the USEPA calibration protocol gave excellent results for hydrogen and oxygen. Concentrations are reported as percent composition. Volume percent composition (v/v%) is the ration parts of solute to one hundred parts of solution, expressed as a percent. Hydrogen had a MDL of 0.70% volume, accuracy of 105%, and a precision of 3.4%. Oxygen had a MDL of 9.5% volume, accuracy of 129%, and a precision of 37%.

The calibration standard concentrations ranged from 5-15% for hydrogen and oxygen gas. These standards were meticulously prepared to avoid ambient air interference. Oxygen was calibrated with the hydrogen, and the quantity of nitrogen present is proportional to the amount of experimental error due to ambient air interference from sample preparation and injection steps.

The single point standard was made at 10% volumes for hydrogen and oxygen gas. Hydrogen had a MDL of 0.73% (v/v%), accuracy of 100%, and precision of 3.7%. Oxygen had a MDL of 5.4%, accuracy of 126%, and precision of 22%. Comparing the external calibration data to that of the single point calibration showed comparable values and much promise for long-term on-line analysis of gases.

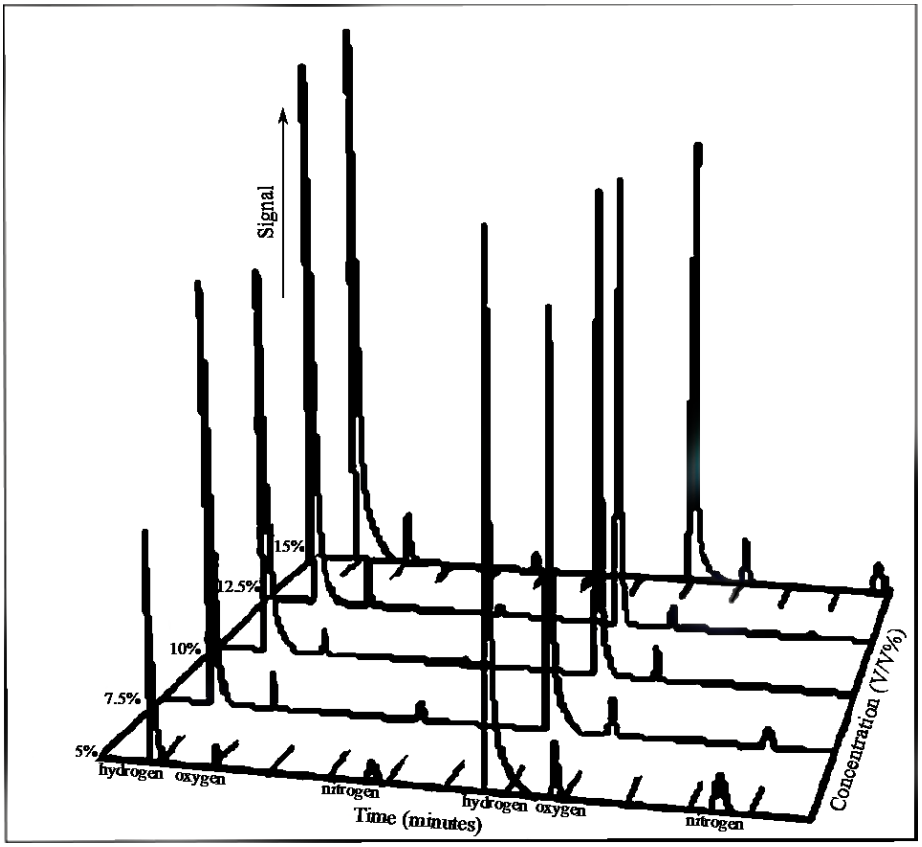

Figure 4. Proof of concept chromatogram. 10 minute run time. First half for sample (or in this case, external calibration standards), and second half for SPS standard.

It was found that quantitative analyses of gases have more potential for mistakes by manual injection technique as opposed to sampling of liquids. With each piercing of a septum during the sample preparation and analysis the potential for associated human error will increase. Standardization for the instrument also requires numerous piercing of the septa in both the making the standards (from drawing each anaylte and injecting it into the vial) and from the actual sampling of the standard itself. As shown in Figure 3, when observing the hydrogen peaks for the single point standard injected on each run; one can notice an irregularity between the 7.5% SPS injection compared to the other hydrogen-standard peaks. This supports the claim that no matter how skilled the GC analyst may be, an inherent human error associated with manual injection technique will always exist. Though this error can be reduced as the analyst becomes more precise with sample preparation and more skilled with GC analysis, the most common source of error usually results from the actual injection technique of the sample by the human analyst.

The preliminary results from the proof of concept showed a validation for why the benefits provided by developing an on-line automated sampler together with the single point calibration would be beneficial going forward. The excellent performance results from external calibration and SPS proof of concept did not come easy. They required intensive sample prep and analysis labor over more than a 12-hour-span with meticulous attention to detail to minimize interferences performed by an experienced GC analyst. Automating the instrument for on-line sampling and calibration in one step will solve numerous issues. The use of industrially prepared standards will minimize errors associated with standard preparation, and interfacing the sampling apparatus to the

reaction vial will reduce the associated sample preparation error and eliminate the injection related errors.

Mechanical automation of the instrumentation allows for the ability to perform autonomous extended monitoring studies, capable of an indefinite number of sample iterations. This will save analyst time by being able to set-it and forget-it and allow them to spend their time on other tasks. Greater instrument functionality is capable with a lower operator skill level. Having an automated instrument most importantly minimizes the human error, giving much greater reproducibility and hence more reliable data.

Single Point calibration will be used for the incorporation of an automated standardization step to the method. It is advantageous because it uses the same chemical species as the instrumental method. It can be performed on the tail end of the sample run, essentially giving two unique parts to each chromatograph; the sample half then the standard half. It provides a very easy source of data analysis to determine quantitative results. Using SPS, the concentration of the sample can be calculated by using a 'ratio and proportion' approach. The analyzed check standards can then be used to calculate an MDL, accuracy, and precision. The formula for this method is:

$$\frac{Sample\ concentration}{Standard\ concentration} = \frac{Sample\ signal}{Standard\ signal}$$

SPS accounts for minor variations in flow rates and other potential sources of calibration drift over extended monitoring periods. Most importantly, it offers the advantage of extraordinary time savings and simplicity.

Optimization of Automated Single Point Standard GC-TCD Analyzer

Single Point Standard Flow and Pressure. The conditions on both parts of the sampler must be approximately the same to ensure continuity between the concentration of the standard and the concentration of the sample to be injected. By observing the ideal gas law, PV = nRT, the pressure must be adjusted to ensure that equivalent molar volumes of the gas from each side of the valve is being injected. The sample loops are the same volume, however if the pressure of the standard gas is too high, then the molar concentration of the standard being injected will be too high. This was proven by filling a sampling vial with the check standard gas at approximately STP and comparing the peak area to that of the check standard flowed through the standard-line tubing at various pressures/flow rates. To perform method verification between sample and standard conditions, the vial is loaded with the standard in the same manner that it would normally be purged with background argon during the AP reaction. The standard gas flow rate (or source pressure if needed) is then adjusted to approximately match the peak areas on both halves of the chromatogram.

Previous ideas of how to match the method conditions included a gas-sampling-bag method in which the sample headspace and standard gas would be pulled into sampling bags then from there through the sample loop, a vacuum method which would briefly pull sample through the loop to a vent line in a manner to match that of the standard gas flow, and a pressure gauge method which would use gauges on both lines to adjust the pressure to match both sides. The flow controlled system was chosen to add simplicity, reduce analysis time, save money, and minimize potential disturbances to the reaction environment when compared to these previously proposed methods.

Purge Time Optimization. The amount of time required to vent the standard was optimized to remove all traces of ambient air interference. Air in the standard gas lines would show up if injected by the sampling valve. The presence of this air will lessen the accuracy of the SPS results. This happens because the standard is prepared as a percent volume in argon and any extraneous gas would throw off the ratio mixture. This is proven by observing the change of peak area for hydrogen as the interferent is removed from the system; as the amount of air decreases to vent, the standard side of the chromatogram gives exponentially smaller peaks for oxygen and nitrogen while giving peak areas for hydrogen that asymptotically increase towards the true value. It was found that the standard part of the system should be allowed to vent for at least 10 minutes before sampling at the set flow rate. Once the system is sufficiently purged, it was also found that pressure build up would skew the data for hydrogen's peak area. To correct for this, the method was modified to open the normally-closed valve at 0.100min and, having all relays programed to reset upon completion, the valve will close at the end of the sample run until the next programmed run in a monitoring study is initiated.

Manual Injection vs. Automated Injection Performance. The GC-TCD settings are largely unchanged from the manual injection method. However, the switch from a manual syringe injection to automated valve injection demonstrated significantly more precision compared to manual injection. The efficiency of injection by the automated sample gives much greater peak shape and less sample loss during injection. The peak tailing effects seen during manual injections is significantly less, giving more Gaussian peaks on the chromatogram. That precision, along with retaining more of the sample, is also apparent from the peak height. When testing a 50µL sample injected both

manually and by the sampling valve, that of the sampling valve actually caps-out the detector. For this reason, the TCD sensitivity setting had to be changed to 'low' for the automated method.

MDL, Accuracy and Precision of the Single Point Standard GC-TCD Analyzer. Eleven consecutive sample runs were performed on a completely purged system for the 5% hydrogen in 95% argon single point standardization gas. These had an average peak area of 12.281 and a standard deviation of 2.048×10^{-1}. Having performed previous MDL, accuracy and precision studies during the proof of concept phase, the TCD has been proven to exhibit a linear response. Assuming this linear response through the origin, a theoretical signal for 1% hydrogen was calculated to have a peak area of 2.456. Using these values a theoretical slope was obtained using the point-slope formula,

$$m = \frac{y_2 - y_1}{x_2 - x_1}.$$

Detection limit is the smallest quantity of analyte distinguishable from baseline noise. It is defined as 3 times the standard deviation of the signal divided by the slope. A signal that is 10 times as great as the noise is defined as the lower limit of quantification (LOQ), or the smallest amount that can be measured with reasonable accuracy and is calculated as 10 times the standard deviation of the signal divided by the slope (Harris, 2007). Calculating with these values the detection limit for this analyzer is 0.25% and the LOQ is 0.83% using single point standardization. The precision of the analyzer by calculation of %RSD for the peak area of the check standard is 1.7% (compared to 3.7% from the proof of concept calibration).

Optimization of Hydrogen Gas Monitoring Studies. On the sample part of the system, there was a sample-loss problem when continuous sample runs were performed, shown in figure 5. An optimization study was done to correct this problem. Upon consecutive runs, the amount of analyte reaching the sample loop exhibited a drop off. When the valve would rotate to inject the sample, the carrier gas would flow through the sample loop. As the valve rotated back to the load position, a plug of argon from the carrier gas remained in the loop. This plug of argon did not equilibrate throughout the headspace of the vial; in fact, it would not even equilibrate when the needles were left open to ambient air. Needle gauge, tubing length, and ID were adjusted. Large gauge needles, bigger ID tubing, and shorter lengths improved equilibration ability. By incorporating a peristaltic pump to the sample line though, circulation of the headspace gas can be controlled, thus solving for the sample loss problem.

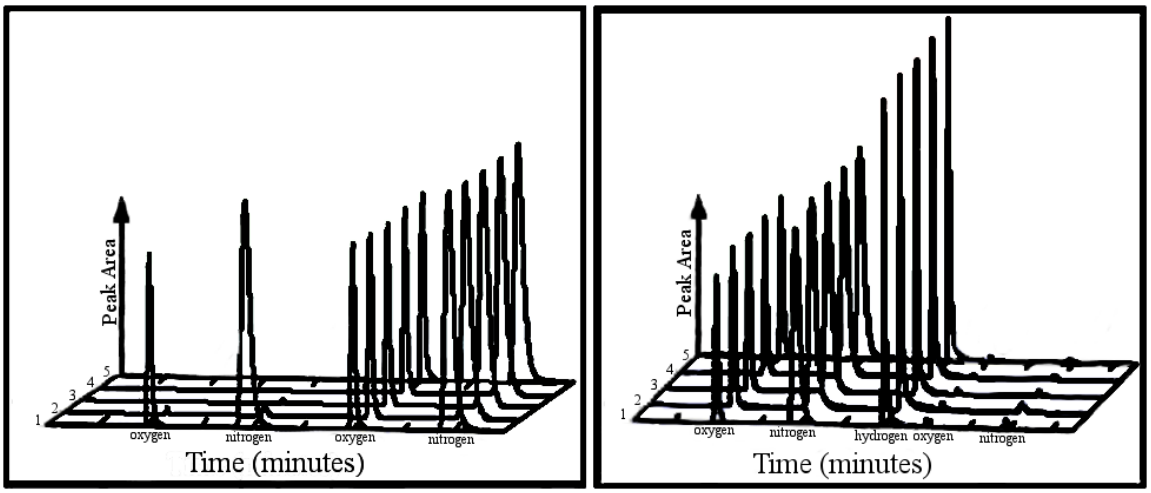

Figure 5. The left chromatogram shows the loss of sample using the injection valve (sample side is open to ambient air and standard side has zero grade air for comparison). The right chromatogram shows the correction after implementation of the peristaltic pump (sample side open to ambient air and standard side with non-purged 5% hydrogen single point standard gas).

The stirring conditions inside the sample vial must also be considered when performing monitoring studies. Once the electrocatalyst solution is injected into the vial the stir plate is turned on. The placement of the vial on the stir plate and the level of applied magnetism must be checked. If either of these is not right, the stir bar has been shown to splash up the electrocatalyst solution which could then be pulled into the sample tubing. In the event that enough makes its way into the sample tubing, it could be circulated through to the sample loop and hence onto the column. This results in extreme baseline disturbance commonly known as 'wander' and makes column replacement or refurbishing a necessity.

Reproducibility. Comparing the chromatogram on the right of figure 5 to the proof of concept chromatogram in figure 4, simply by observation it is clear that a much higher degree of reproducibility is achieved using an automated system. To get a better idea quantitatively on the level of reproducibility gained using this automated system 11 continuous runs were made for the check standard and integrated for comparison. It is worth mentioning that the integration function was set to auto-integrate, once again saving the analyst time. The peak heights for these eleven runs were averaged and the standard deviation was taken. It had an average peak height of 3.110 mV and a standard deviation of 8.779×10^{-3} mV. Comparing the standard deviation value to the numerical value for the baseline noise (~0.040 mV) we show that the variance between runs is significantly lower than the approximate noise of the detector. Also, taking the peak height standard deviation and average, the %RSD is determined to be 0.28%.

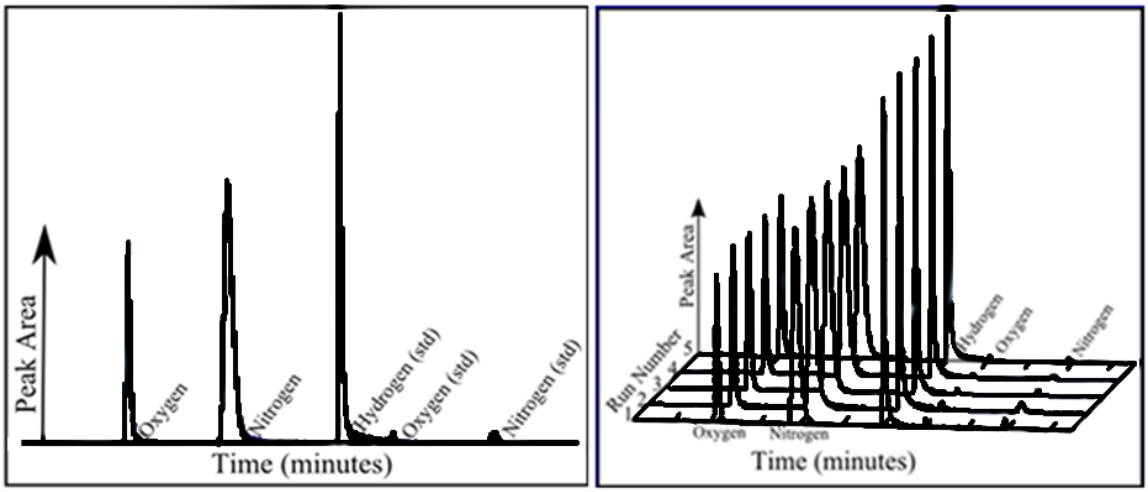

Figure 6. Five automated chromatograms overlaid showing reproducibility and precision.

SPS-GC-TCD vs manual GC-TCD w/ IS: Which is more appropriate? A comparison study was performed using the SPS-GC-TCD method compared to one of the group's other manual injection methods utilizing internal standardization. When making a sample for AP reaction, the vial would be purged with a gas mixture of 95% argon and 5% methane. After being purged the electrocatalyst solution would be injected then irradiated as previously described. Upon examining the internal standardization method that was being used by the AP researchers for some of their reactions, certain problems were found in their established method when compared to the SPS method (in addition to the previously explained shortcomings of manual injection methods and experience level of GC analyst).

The pressure in the flask from the purge was not taken into consideration. There is a sample loss problem both as the reaction is proceeding and during sampling. More importantly than these problems, internal standardization requires a response factor, *F*, to accurately calculate ratio proportions of samples and a standard. This response factor had not been calculated or included in data manipulation. One of the great benefits to internal

standardization is the first two problems significant effect on the reliability of data is greatly diminished if not totally negated. As the standard is in environment with the sample, any effect on the sample will also be done to the standard in the manner. This is of great benefit to manual injection methods of gas analysis as the primary error of sample injection equally affects the standard and sample. Internal standardization is especially useful for analyses in which the quantity of sample analyzed or the instrument response varies slightly from run to run. (Skoog, Holler, & Nieman, 1998) Trying to automate analysis in this manner for comparison to SPS is problematic.

To get reliable data using internal standardization the response factor must first be calculated. If the detector responds equally to the standard and the analyte, then $F = 1$. To calculate the response factor a known concentration of the analyte, [X], is tested against a known concentration of standard, [S], and the peak areas of the two, A_X and A_S, are used with the concentration values to solve for *F*.

$$\text{Response Factor: } \frac{A_X}{[X]} = F\left(\frac{A_S}{[S]}\right)$$

The response factor of methane to hydrogen for this analyzer is 0.522, meaning the TCD responds approximately half as well to methane as it does to hydrogen. Not knowing the dilution factor of IS added to unknown hydrogen being produced (because the IS gas is the background gas for the reaction, not spiked into an unknown amount of hydrogen already generated) it was omitted in calculating [S] for internal standardization and concentration is approximated at 5%.

Summary of Automated, On-line, Single Point Standard GC-TCD Analyzer. The flow controlled system works very well with automated, on-line analysis for monitoring AP reactions over time. The automation of sample injection gives much

greater precision when introducing the sample as compared to manual injection, resulting in sharper peaks with less tailing and much larger peaks. By changing the TCD sensitivity to low, the larger peaks can be made to not cap out the detector. Sample loop size was examined from around 1µL up to 250µL and found to have a linear response in terms of sample injection capacity. In the event that a future sample was found to be outside the analyzer's dynamic range, the sample loop and sensitivity settings could be adjusted to alter the dynamic range to avoid implementation of a dilution or standard addition step to the method. The sample vial during the purge was found to have a signal slightly above that of the standard, when the same gas was being tested on both systems. To adjust for this the fine tuning flow controller was adjusted to increase the flow rate of the standard through the standard loop. The flows were optimized and analyzed numerous times in a row. These values were averaged together to see any further discrepancy between the two systems conditions. The difference in peak area at this optimized setting is believed to be negligible as the corresponding peak area difference is near that of the common baseline noise.

The system will work fine for extended monitoring studies provided caution is taken at the parts of the procedure warning of possible air interferences that could be introduced. If these steps are not meticulously performed and air does make its way into the sample, the reaction has been shown to not succeed in producing hydrogen.

Internal standardization is subject to the same conditions of the sample, as it is included in the sample as the reaction is proceeding. Because of this, there will be a little sample loss that will equally affect the sample and the IS together, that would not be represented in the SPS signal. SPS offers the benefits of being inexpensive, easier to use

in the method, and it has the same response factor as it is the same species that is being tested. The significance here is that as more gas is generated by the reaction and carrier argon is being introduced into the flask from the rotation of the valve, the percent volume composition of the internal standard will become increasingly smaller. This percentage is then also subject to a response factor of about half that of hydrogen, so as it is ever slightly decreasing that effect is being compounded by the detectors inability to respond as well to it. It has been found that after approximately nine consecutive same runs that there will be a significant decrease to methane IS peak area. By using SPS, over longer monitoring studies the accuracy of this form of calibration will be more and more reliable than the use of internal standardization.

Deuterium analysis. The AP research must also be able to properly determine the source of H_2 production. The AP reaction is validated if the hydrogen production can be correctly attributed to the electrocatalyst being tested and not from a hydrocarbon present in solution. The reaction run in H_2O should produce H_2 and in deuterated water (D_2O) should produce D_2. If a hydrocarbon was present in D_2O and H_2 is produced, then it came from the hydrocarbon rather than D_2O. To perform these tests with this analyzer the carrier gas must be switched back to helium, as it has a thermal conductivity between deuterium and hydrogen. When H_2O was used, a negative peak at a retention time of ~0.8 min is consistent with hydrogen formation. In contrast, a positive peak at that time suggests the formation of D_2 (Zhao, 2011). This positive versus negative orientation is

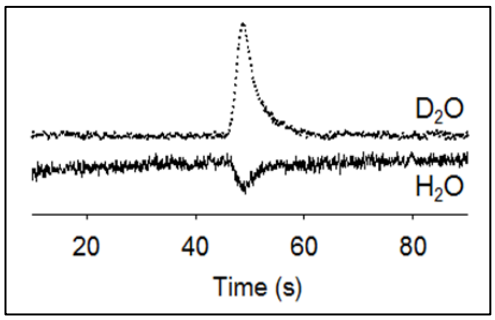

Figure 7: Deuterium versus hydrogen

obviously dependent upon the polarity settings of the method both within the GCs functionality setting and that of the data processor.

Conclusions

The GC-TCD with on-line, single point standardization can separate all analyte gases from a headspace sample and a manufactured check standard on the same chromatographic run at a total analysis time of approximately 10 minutes. It has acceptable MDL, accuracy, and precision values for AP research applications. The single point standardization allows for much simpler calibration procedure with very similar results. Added on-line capabilities greatly increase the reproducibility over traditional manual methods, significantly increase the precision of injection, and eliminate numerous potential sources of error.

Automated injections exhibited much greater response from the detector, which can be attributed to error associated with injection technique and sample loss. This method is a great overall improvement to traditional gas sampling methods because it can be recalibrated within each sample run and is capable of continuous sampling at any desired interval using the on-line capabilities. This allows for extended monitoring studies to be easily carried out without need for analyst supervision.

Future work

Five industrially made standards of varying concentrations will be purchased to perform a comparison study of method validation between external calibration with manufactured standards and the manufactured SPS calibration protocol. These standards will be free of all the associated sample preparation interferences and will be subject only to the percent accuracy of the manufacturer. This will provide the truest form of method

validation for the use of single point standardization, as both forms of calibration will be almost completely free of the numerous sources of error that they were subject to during the proof of concept study. As concluded before, it is expected that the five point calibration curve and check standard analysis will give excellent results for MDL, accuracy, and precision; and that the single point standardization method will give comparable data to that method with much less effort, time, and cost.

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