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Microfabricated BTU Monitoring Device for System-Wide Natural Gas Monitoring

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Abstract

The natural gas industry seeks inexpensive sensors and instrumentation to rapidly measure gas heating value in widely distributed locations. For gas pipelines, this will improve gas quality during transfer and blending, and will expedite accurate financial accounting. Industrial end-users will benefit through continuous feedback of physical gas properties to improve combustion efficiency during use. To meet this need, Sandia has developed a natural gas heating value monitoring instrument using existing and modified microfabricated components. The instrument consists of a silicon micro-fabricated gas chromatography column in conjunction with a catalytic micro-calorimeter sensor. A reference thermal conductivity sensor provides diagnostics and surety. This combination allows for continuous calorimetric determination with a 1 minute analysis time and 1.5 minute cycle time using air as a carrier gas. This system will find application at remote natural gas mining stations, pipeline switching and metering stations, turbine generators, and other industrial user sites. Microfabrication techniques will allow the analytical components to be manufactured in production quantities at a low per-unit cost.

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List of Acronyms and Abbreviations

BTU – British thermal unit
°C – degrees Celsius
C1 – methane
C2 – ethane
C3 – propane
C4 – n-butane and isobutene
C5 – n-pentane and isopentane
C6+ – hydrocarbons containing 6 or more carbon atoms
CA – California
cm – centimeter
D – depth
DAQ – data acquisition
deg. – degrees
FID – flame ionization detector
GC – gas chromatograph (analytical instrument) *or* gas chromatography (analytical method)
Hz – Hertz, cycles per second
I.D. – inner diameter
Inc. – Incorporated
L - length
LDRD – Laboratory Directed Research and Development
mL – milliliter, 1×10^{-3} liter
min – minute
mm – millimeter, 1×10^{-3} meter
mW – milliWatts, 1×10^{-3} Watts
NETL – National Energy Technology Laboratory
NG – natural gas
nm – nanometer, 1×10^{-9} meter
PA – Pennsylvania
PECVD – plasma enhanced chemical vapor deposition
PID – proportional-integral-derivative
P.O. – post office
PDMS – polydimethylsiloxane
p.s.i. – pounds per square inch (pressure)
RT – retention time
sec – seconds
TCR – temperature coefficient of resistance
TX – Texas
U.S. – United States
USB – universal serial bus
VAC – volts alternating current
VICI – Valco Instruments Company Incorporated
W – width
 μ L – microliter, 1×10^{-6} liter
 μ m – micron *or* micrometer, 1×10^{-6} meter

Introduction

The Natural Gas Industries

The natural gas industry and large volume consumers are seeking inexpensive methods for real-time monitoring of natural gas (NG) constituents. For pipelines, it is important to have information on the composition of NG in the main pipeline and of that blending in at every mixing location. When the fraction of heavier components is too high, it becomes unsuitable for certain end users. Heavier components may also condense where temperature and pressure drop, such as at meters, valves, and various locations in end-user facilities. It is also desirable by natural gas sellers and buyers to have immediate knowledge of the BTU value for equitable trade. Because instrumentation for accurate natural gas analysis is expensive to purchase, operate and maintain, ubiquitous metering devices provide only volumetric measures of the quantity of natural gas consumed. However, final billing is determined a month or more later when information from lab analysis is used to convert the volumes to heating values. This difference, known as unaccounted for gas content, can be reduced, producing more timely and accurate billing. A 10% improvement will benefit the industry by about \$45 million annually.¹

Certain industrial users have a strong interest in knowing the composition of incoming natural gas. For NG fueled turbines efficiency of power generation is dependent on fuel properties and the temperature of the combustion cycle. Turbine controls are based on models that indirectly calculate peak combustor temperatures based on estimates of the fuel heating value. Inaccuracies as high as 40°C limit the ability to operate at the optimum firing temperature. Controllers error on the side of safety to prevent part-life degradation from overfiring the turbines. General Electric Company estimates that a 1% increase in operational efficiency of natural gas-fueled power has the potential to save 0.155 quads of natural gas per year with a financial impact of \$4.85 billion in fuel savings. The related annual reduction in nitrogen oxide emissions would be in excess of 19,000 metric tons.²

The standard method for natural gas BTU analysis is gas chromatography (GC). This method is extremely accurate, but expensive in terms of equipment, maintenance, operation, and personnel. Samples are often collected into bottles for once-a-month lab analysis, resulting in billing accuracy delays of a month or longer. On-line GCs are only used at large custody transfer stations where accounting delays would become more costly. In addition, standard GCs and detectors require pressurized specialty gases, some of which are flammable. While slightly less expensive field-portable devices are becoming available, detector requirements have not changed. Automated on-line GCs are currently too expensive to widely distribute over the pipeline infrastructure for real-time analysis. A number of research organizations are attempting to perfect inferential techniques using thermal conductivity or speed of sound measurements. Inorganic compounds such as carbon dioxide, carbon monoxide, and nitrogen confound these measurements, so their concentrations must be independently determined. So far, these techniques cannot determine nitrogen concentration without resorting to gas chromatography.

Sandia has been at the forefront of fabricating microGC columns in silicon in a revolution commonly referred to as “fast-GC.” In fast-GC, analysis duration is reduced with little or no loss of performance by scaling down analytical component size, volume, and dead space. As a unique

invention, a packable microGC column has been developed that takes advantage of countless research successes in commercial packing materials for analytical separations. By combining commercial technologies with fast-GC, chromatographic separations have been performed that rival or exceed the performance of commercial GC systems. Most fast-GC research at Sandia has been directed towards homeland security applications. The program developed here applies existing and new technologies to industrial applications.

Sandia's Microfabricated BTU Monitoring Instrument

For market acceptance, a monitoring system must be of low cost. Widespread implementation at high-impact locations will only occur below a threshold cost of approximately \$5000 per instrument. It is anticipated that this per-unit cost can be achieved in part by using microfabricated analytical components. To achieve this goal, a Microfabricated BTU Monitoring Instrument has been developed at Sandia National Laboratories using existing and modified microfabricated components. The instrument consists of a silicon gas chromatography micro-column in conjunction with a catalytic micro-calorimeter. A reference thermal conductivity sensing element provides sensor diagnostics and surety. Microfabrication techniques allow these components to be manufactured in production quantities at a low per unit cost.

Sandia's patented micro-hotplate platform was previously developed into a micro-calorimeter for determining BTU heating values of natural gas and other fuel gas streams. The system provides stand-alone gas monitoring where low precision analysis ($\pm 5\%$ BTU) is acceptable. While simple and inexpensive, it does not provide direct information on constituents of the NG stream. The sensing device consists of a thin catalyst layer deposited on a 1-micron thick resistively heated surface. The fuel, premixed with air, catalytically combusts on this surface. The heat of combustion is measured directly from a feedback circuit powering the sensor. This rapid and sensitive sensor provides a direct measurement of the BTU content of the fuel. When combined with a density measurement, the Wobbe Index³ can be determined, which is an important fuel property used to aid combustion control in systems such as gas turbines. To date, the sensor has been field tested at natural gas and syn-gas facilities in conjunction with General Electric Corporate Research and Development Center.

For applications requiring speciation and/or accuracy of $\pm 0.1\%$ BTU, the full BTU Monitoring Instrument can be used. Higher accuracy is achieved through separation of the compounds using Sandia's novel microGC columns before sensing. The micro-calorimeter serves as the sensor, measuring only combustible constituents, which contribute to the BTU value. This combination allows for continuous calorimetric determination with a 1 minute analysis time and 1.5 minute cycle time using air as a carrier gas and oxygen source for the catalytic sensor.

Characterization of the individual constituents of natural gas samples enables precise determination of the BTU content of the samples. Our expectations are that this simple instrument will fill niches in the natural gas industry where more information about gas content is needed and where the cost of full GC instrumentation is currently prohibitively high. Potential monitoring sites include smaller pipeline switching stations, large industrial consumer locations, and remote natural gas production wells where sample tanks are filled in a time-integrated manner and typically analyzed on a monthly schedule. The use of air as the carrier gas for truly

field-portable gas chromatography is a feature that distinguishes Sandia's research from other research institutions.

Market Analysis

A market analysis was performed to assess the interest of natural gas end users in a portable gas chromatography-based instrument for determining natural gas composition. As natural gas is sold by the BTU, improved analysis will produce more equitable trade between buyers and sellers by reducing unaccounted for gas content. A 10% improvement in gas accounting through improved sampling and analysis will benefit the gas transport industry by approximately \$45 million annually. Industrial users will benefit through continuous feedback of physical gas properties during consumption, in particular with gas turbine engines used for power and electricity generation. A further complication arises during gas transfers between wholesale or commercial entities along the gas supply chain when both gas volume and heating value indices can be used in the transaction. Discrepancies between the two can result in billing errors or lost revenues. A gas transfer system based solely on heating value and made possible by a low-cost microtechnology approach would be beneficial to the natural gas industry.

For market acceptance of an advanced monitoring system, there is a trade-off between cost, performance (accuracy), and sensor lifetime. Utilities currently charge residential and small industrial customers based on a volumetric meter reading. This type of metering device has a typical maintenance schedule of 11 to 17 years. A new technology would not only need to meet this lifetime, but could not cost more than \$20. From a cost stand-point, a microGC in every home is not practical. However, the stand-alone micro-calorimeter system may fall into this performance and cost range, though more frequent maintenance would be required. The accuracy of the micro-calorimeter is +/-5% BTU when heating values vary over a wide range, though little speciation information is obtained. This may be sufficient for many users. When variations in the composition of the natural gas fall within a narrow range, accuracy with this sensor has been shown to increase to +/-1.2% BTU. A potential customer base for this system is medium- to large-volume natural gas consumers who desire continuous knowledge of gas characteristics as it is delivered, and/or confirmation data of their consumption independent from the utility metering and billing systems. Small-turbine companies have also expressed an interest in this level of precision and cost.

For many users, including gas transfer/mixing stations and electricity generating turbines, accuracy of 0.1% BTU is required.⁴ For pipelines and turbines, speciation is necessary to obtain the hydrocarbon dew point.⁵ The dew point is defined by a combination of gas temperature and gas pressure where unwanted condensation of natural gas components begins to take place.⁶ For medium-sized utilities just seeking to improve energy utilization, the cost trade-off for a sensor system is lower, with a threshold cost of \$2000 per instrument. Where large quantities of natural gas are consumed (medium-size or larger switching stations, gas-turbine electricity generators), and all fuel properties need to be known, widespread implementation of advanced monitoring techniques would occur at a threshold cost of approximately \$5000.¹ Currently available instruments of a similar nature cost \$25K or more. It is anticipated that a competitive manufacturer could build the instrument developed at Sandia and meet this cost threshold (cost plus profit) in production runs of 1000+ units per year by using microfabricated analytical components. Through economies of scale, this unit cost could be further reduced by as much as 50%. No data exists for annual maintenance costs, which will depend on many external factors. Long-term field testing of the sensor system will provide much of this needed information.

Technical Accomplishments

Technical research for the Microfabricated BTU Monitoring Instrument was largely divided into three major task areas. The first task tailored a microfabricated gas chromatography (GC) column to separate injections of natural gas. The second task experimented with micro-hotplate calorimeters to respond to natural gas compounds, with emphasis placed on rapid responses to chromatographic exposures. The third task took place entirely in the second year: a complete field-portable gas chromatographic instrument was fabricated using the above components and other commercially available parts.

Chromatography Development

Development of the natural gas separation task began with hardware assembly and testing of a number of microfabricated GC columns that are known to separate two or more natural gas components. The goal was to determine if a single column could separate all of the combustible components from one another. As the noncombustible components (mainly carbon monoxide, carbon dioxide, and nitrogen) do not contribute to the BTU value, their presence is only important from a volumetric standpoint. Volumetric analysis comes from a fixed volume loop injection into the GC column at a known temperature (80-140°C) and pressure (625 Torr). The micro-columns tested fit into two distinct categories – wall-coated open tubular (rectangular cross-section) and packed (with coated solid beads or polymer beads). Each of these columns presents relative advantages and disadvantages. In general, which type of column to use ultimately depends upon the nature of the compounds being separated and the operating conditions of pressure and temperature that constrain the analysis or equipment. While literature exists to guide most traditional separation applications, fast-GC on micro-columns has been explored almost exclusively with low volatility samples in open tubular columns.

Testing began with combining test hardware with an existing commercial GC instrument (Agilent Technologies; Palo Alto, CA; model 6890), hereafter referred to as “Agilent.” A bottle of natural gas standard (Scott Specialty Gases, Inc.; Plumsteadville, PA; manufacturer number 01027113) was connected through the side of the Agilent’s oven to a 6-way diaphragm valve (VICI; Houston, TX; model DV22-2116) inside. In the valve’s static position the gas sample passed through a 5 microliter sample loop and exited the Agilent to exhaust. The inlet apparatus of the Agilent provided pressurized carrier gas (nitrogen or air) to one port of the valve via deactivated capillary column, and another port led to the Agilent flame ionization detector (FID). The final two ports were connected through deactivated capillary to the micro-column, which was contained in a test fixture. When the valve was actuated the fluidic train changed to direct the sample loop contents into the micro-column. Carrier gas flowed through the micro-column to the FID in both valve positions. **Figure 1** shows a schematic of the two valve positions.

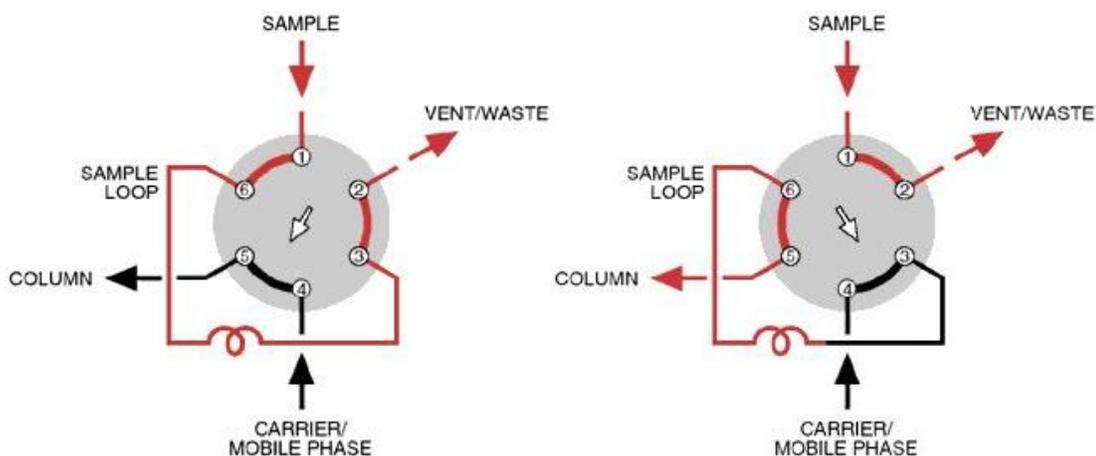


Figure 1. Sample loop in loading position(left). Sample injected towards GC column (right).⁷

The first tests were conducted using a 20 cm long micro-column packed with Carboxen 1000, shown in **Figure 2**, right (note: all packed column channels here have cross-sectional dimensions of 300 μ m W x 300 μ m D). This column had previously shown very good separation of methane, ethane, ethylene, and acetylene. Using a moderate temperature (120°C) and pressure (30 p.s.i.) C1-3 (methane through propane) eluted from the column with excellent separation in less than one minute. However, isomers of butane and pentane took up to 2 ½ hours to elute. Conditions of 150°C and 40 p.s.i. improved the elution time to ~90 minutes. However, separation of C1-3 degraded beyond use. Experiments with a 5 cm long micro-column also showed excellent separation of C1-3, but retention times of C4-5 were still unacceptable. The Carboxen 1000 packing was clearly not acceptable by itself, but could prove very useful in two-column configurations, which are under consideration for applications beyond the scope of the LDRD work presented here.



Figure 2. Left, micro-GC column filled with HayeSep D chromatography beads. Right, close up with Carboxen 1000 beads. Approximate column dimensions: 0.5" x 0.5" x 0.040" thick.

Microfabricated open-tubular columns were tested next. Commercial capillary columns coated with PDMS (polydimethylsiloxane), which are commonly 15-30 meters in length, are

adequate for simple separations of C1-5 and their conformational isomers. Sandia's microfabricated open-tubular columns are designed for faster separations, though with less efficiency. Two such columns coated with PDMS were selected in lengths of 117 cm (75 μ m W x 250 μ m D) and 229 cm (25 μ m W x 100 μ m D). Under no experimental condition did either prove adequate. At best, the C5 compounds eluted on the tail of one large C1-4 peak.

The next packed micro-column showed much better general performance. A 20 cm long column packed with HayeSep B polymer beads separated C1-C3 in under 15 seconds at 100°C and 10 p.s.i. Complete elution of all compounds occurred in just over 2 minutes. As Figure 3 shows, the C4 and C5 groups are well separated from each other, but there is overlap of the isomers. Various combinations of temperature and pressure were attempted to improve the resolution of these pairs. The BTU values of conformational isomers are similar to within 0.2%. For many industrial applications elucidation of isomers is not necessary, with much higher emphasis on faster analysis times. Assuming 12% total concentration of C4 and C5 isomers, and using the average of their BTU values, less than 0.01% of systematic error is created in the total BTU calculation. With this caveat, analysis of C1-5 with partial separation of isomers can be performed in less than 70 seconds before degradation of the C1/C2 peaks occurs with this column. A 25 cm long column would baseline separate the isomers, but at a cost of 25% longer analysis time and the need for a higher driving pressure.

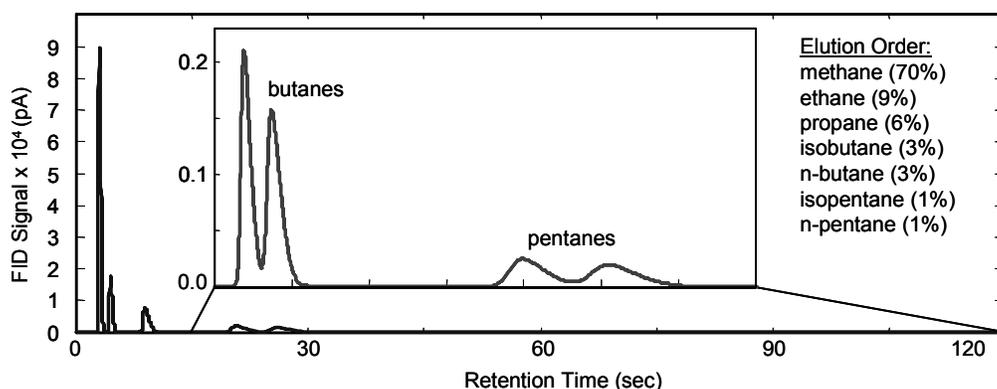


Figure 3. Separation of 5 μ L natural gas using 20 cm long microGC column packed with HayeSep B, 100°C, 10 p.s.i.

A 15-cm column packed with HayeSep D was found to separate all of the constituents in the calibration tank by carbon number, but with little isomer separation, in less than one minute (**Figure 4**). Thermal ramping of the low-mass silicon column speeds the run time considerably while maintaining excellent resolution of the first eluting compounds. Partial separation of the isomers produces a maximum 0.009% error in the BTU (heating) value for each one percent of C4+ hydrocarbon in the mixtures – well within industry requirements, and sufficient for most combustion applications. This column was selected for further evaluation. Any column material chosen for use with the micro-calorimeter sensor must be compatible with air as a carrier gas up to the maximum separation temperature. Thermo-gravimetric analyses were performed on samples of the HayeSep D. **Figure 5** shows that this material does not decompose until above 300°C. This is consistent with Supelco specification sheets when used with inert gases. To further test for other detrimental effects with high temperature air exposure, the column's

chromatography performance was tested over the course of 400 chromatography runs. The packing showed no degradation in this experiment, with thermal cycling from 80 to 120°C. This is evidenced by excellent reproducibility of all peak positions over the course of the runs (**Figure 6**). This column was chosen for insertion into the BTU Monitoring Instrument.

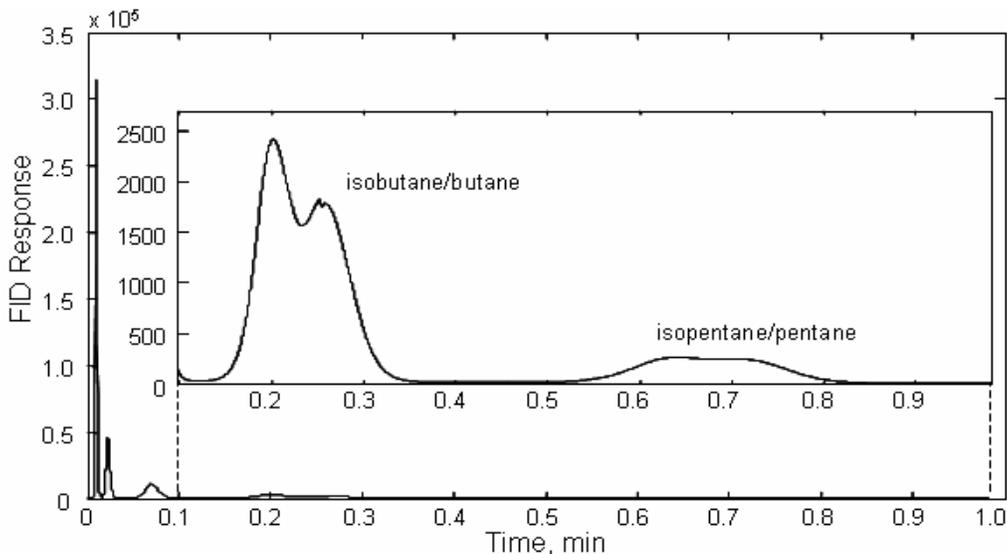


Figure 4. Separation of 5 μ L natural gas injection using 15 cm micro-column packed with HayeSep D, 20 p.s.i. air carrier, temperature ramp from 80 to 120°C at 40°C/min. Inset is magnified 100X.

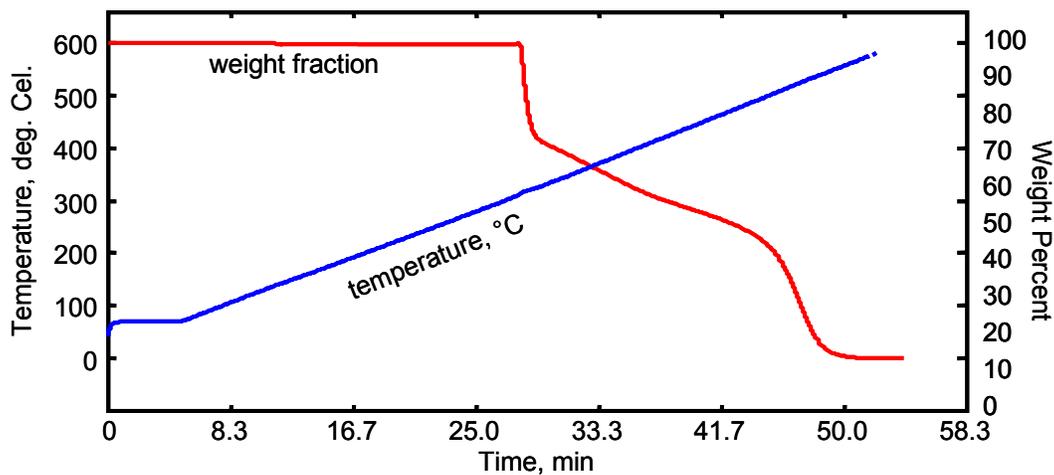


Figure 5. Thermo-gravimetric analysis of HayeSep D sample. Degradation begins at 312°C

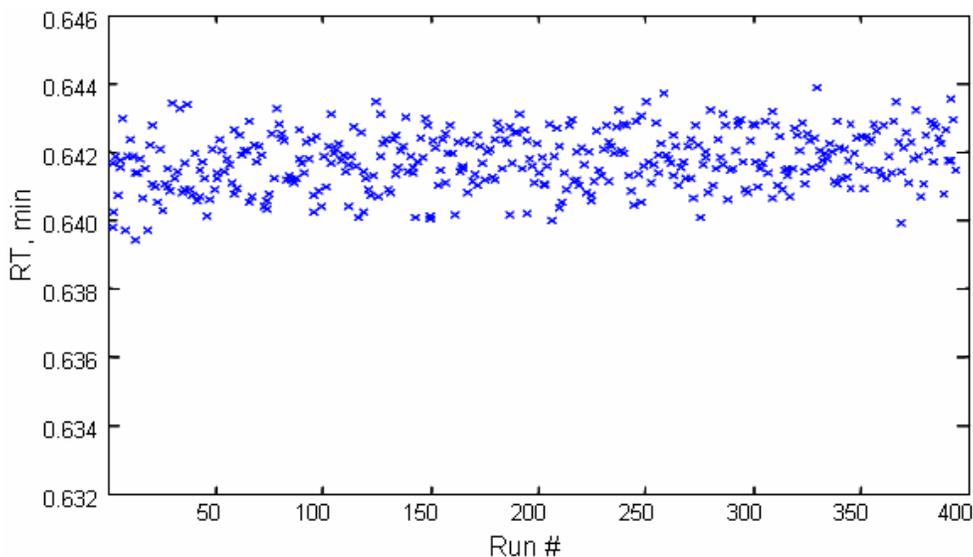


Figure 6. Retention time stability of pentane is 0.05 seconds absolute standard deviation, or 0.1% drift on 39 second retention time.

Other separation columns and materials indicated in the literature for C1-5 separations were tried with inadequate success. These include alumina F100 with various surface deactivations, and SP1700, both from Supelco, Inc. (Bellefonte, PA). According to literature⁸, these materials can separate hydrocarbons C1-6. Using our packed micro-columns in 15 to 25 cm lengths, moderate success was only achieved with C3-5. In future work we hope to achieve separations of C1-12 using microfabricated porous-layer open-tubular columns, which are a cross between packed and wall-coated open-tubular⁹.

Sensor Development

Prior to the start of and during the BTU Monitoring project, a significant amount of work was performed on developing the micro-calorimeter, also known as the Lower Heating Value sensor.¹⁰ The ultimate goal was to develop an array of catalytic sensors, each with a different protective coating. The different responses of the different sensor elements in various combustible gas mixtures would speciation and quantification of multiple natural gas constituents. It was found that an unprotected surface was the best candidate to use as a rapid response gas chromatography sensor. The sensor platform is based on Sandia's micro-hotplates design.¹¹

Fabrication

The micro-hotplate device consists of a one-micron thick silicon nitride membrane suspended from a frame of silicon. The fabrication process starts with a silicon wafer with a thin layer of low-stress silicon nitride. A thin-film pattern of electrically resistive metal is deposited on the membrane over the future etch pit. This later serves as a heater to elevate the membrane temperature during catalytic operation. The heater is typically composed of a 10 nm tantalum adhesion layer under ~170 nm platinum layer. The temperature coefficient of resistance (TCR) of the platinum is used to dynamically monitor membrane temperature during operation.

Alternating layers of plasma enhanced chemical vapor deposition (PECVD) silicon nitride and silicon dioxide are then deposited over the wiring to provide a diffusive barrier to oxygen and moisture. These layers are approximately 50-100 nm thick, with the total stack thickness measuring ~300 nm. This dielectric stack also improves adhesion of the catalyst layer (see **Catalyst Coating** below). Photolithographic patterning coupled with deep reactive ion etching or potassium hydroxide etching are then used to selectively remove silicon in a pit underneath the heater wires, releasing the silicon nitride membrane. The membrane then serves as support for a high surface area platinum catalyst layer. The front and back sides these devices are shown in **Figure 7**.

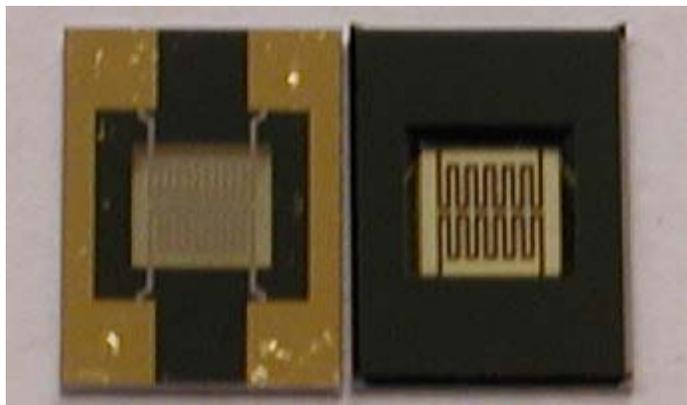


Figure 7. Front and back sides of micro-hotplates.

The use of dielectric layers and choice of tantalum as an adhesion layer are recent improvements to the fabrication process based on the works of Firebaugh¹² and Briand¹³. The last coating of silicon dioxide serves as an adhesion layer to the subsequent catalyst deposition. These device modifications have produced micro-pellistor devices capable of prolonged, multi-month, high-temperature testing without breakage or degradation.

Catalyst Coating

Subsequent to fabrication, a catalyst layer is deposited directly on the micro-hotplate membrane. The catalyst is 10% platinum particles (w/w), with gamma alumina particles forming the balance. A slurry consisting of these particles and pH balanced water is created to facilitate deposition. A similar slurry of alumina is also prepared to deposit on a second set of reference devices. Initially, micro-pen contact writing was used to deposit the slurries. However, this failed to produce robust and repeatable catalyst coatings. Catalyst films cracked and spalled from the substrate during the drying process due to poor adhesion. Better results have since been obtained depositing with a nebulizer. The nebulizer sprays the catalyst slurries through a shadow mask onto devices heated to 160°C via an external heater. This quickly evaporates the liquid, resulting in well-defined and robust catalyst spots. After deposition, the devices are placed in a vacuum oven for 12 hours at 60°C to make certain all liquid is removed before device operation. **Figure 8** (left) shows the surface of a device with a catalyst spot deposited by this method. **Figure 8** (right) shows the surface of a device made by the micro-pen method after several hours of use. The dielectric stack, developed during this project, was in place on the device on the left, but not on the right.

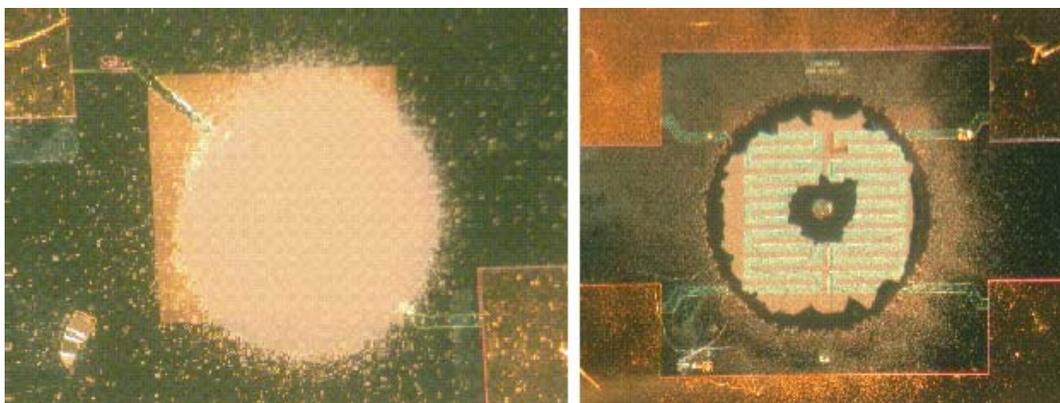


Figure 8. Left, micro-calorimeter device with good catalyst layer deposited by nebulizer over adhesion layers. Right, poor adhesion of micro-penned catalyst film without adhesion layer.

Test Setup and Operation

Most of the operational development of the sensor was performed by exposing micro-calorimeters and reference devices to steady hydrocarbon streams pre-mixed with air. A schematic of the aluminum sensor fixture with fluidic and electrical interconnects and a small heater cartridge is shown in **Figure 9**. The fixture has an internal chamber approximately 9 mm x 2 mm (L x W), which allows for two hotplates to be placed side-by-side. The height above an inserted device is 0.5 mm. The first hotplate in the fluidic stream is a reference sensor with an alumina coating. The reference device corrects the active sensor signal for flow variations and thermal conductivity variations caused by the gas and air flowing over the heated devices. The second device possesses the catalyst spot, and hence records the hydrocarbon combustion. Fixture heating, usually to 40°C, was used to minimize signal drift caused by environmental fluctuations. Water condensation from combustion was carried away by the gas streams before condensation could occur.

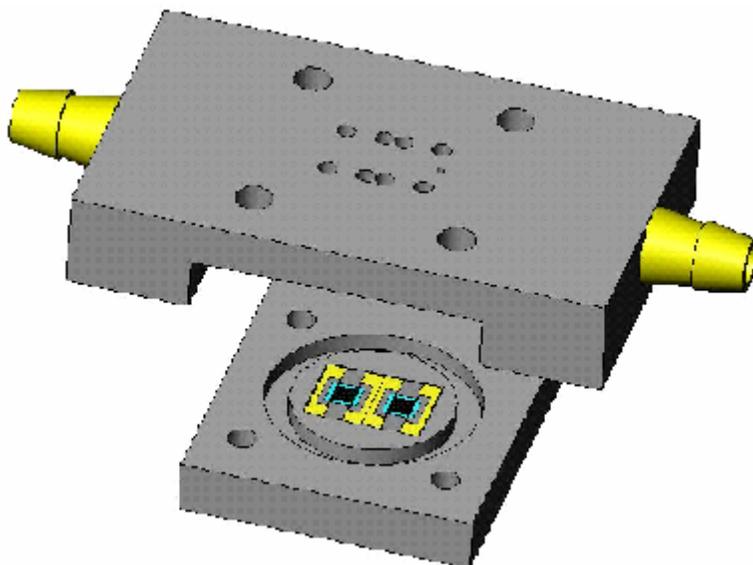


Figure 9. Low dead-volume fixture for micro-calorimeter and reference sensors, shown inside. Pogo-pins make electrical connections through small holes in the lid.

During operation, both devices are connected to a temperature-control circuit. The circuit maintains the microhotplates at a user-defined temperature, usually 400-500°C, by monitoring the resistance of the membrane heater and controlling the input power in an active feedback loop. External heating from hydrocarbon combustion, or cooling from gas flow, tries to drive the temperature up or down, thus modifying the effective resistance of the membrane heater. This causes the circuit power to change to maintain the desired resistance. This feedback mechanism maintains constant micro-hotplate resistance, and hence constant temperature. Excursions in applied power from the zero-hydrocarbon baseline power constitute the signal of the sensor. Power is recorded as the product of applied voltage and current. Given the unattended intent of the BTU Monitoring sensor system, the micro-calorimeter devices have been built for robustness, high temperature resilience, thermal shock, catalyst adhesion, and overall device survivability. A single device may survive months of laboratory testing, but more progress is needed in this area.

Experiments were conducted to understand the mechanisms of catalytic combustion for the micro-calorimeter sensor, and to optimize combustion behavior during chromatography. This involved optimizing combustion efficiency by optimizing flow rate, dead volume over the sensor, and sensor temperature during static hydrocarbon exposures. These experiments were performed while using a commercial gas chromatograph (Agilent Technologies; model 3000A) to monitor percent combustion of each individual natural gas constituent at the outlet of the sensor fixture. It was found that sensor temperature is inversely related to lifetime of the supporting membrane. An average surface temperature of 480°C was determined to maximize combustion while providing lifetimes of weeks or longer. Dead volume over the sensor did not seem to affect the combustion percent, though it does cause spreading of chromatography peaks. After flow rate optimization in the range of 30 to 40 mL/min, it was determined that combustion efficiency does not exceed 35% at this time, though the combustion percent for each compound

is highly reproducible under a given set of experimental conditions. Future work will address the issue of incomplete combustion, which will increase the sensitivity and lifetime of the sensor. Limited experiments were also performed to determine the effects of sulfur poisoning of the catalyst material. While carbon disulfide is found to poison the catalyst, the effect can be reversed through continuous exposure to hydrogen at combustion-level temperatures. No other sulfur-based catalyst poisons were tested, but these compounds are known to affect the long-term use of platinum catalysts. As exposures during gas chromatography will be limited to 5 microliters per injection, one part per million sulfur content in test samples will poison 5% of the catalyst after 2 million injections, or approximately 6 years. This is longer than the anticipated service life.

To test the suitability of the micro-pellistor sensors for gas chromatography, whole natural gas injections were made upstream of the fixture inlet. Rapid combustion responses were measured on the catalyst sensor, along with negative responses on the reference sensor. As the thermal conductivity of methane is quite high relative to air, its cooling affect on the hot reference line was strong. Next, the sensors were connected to a commercial chromatography column (Agilent Technologies; 15 m, 0.53 mm I.D., DB-1, 1.25 μm phase) at room temperature. The 6-way valve provided 5 μL injections, and a lecture bottle delivered 20 p.s.i. air. A separation using this setup is shown in **Figure 10**. Electronic noise and an inadequate data acquisition board produced a rather messy chromatogram (data rate, 20 Hz). This noise was removed for this image using digital signal processing with a low pass filter. Natural gas compounds C1-4 can be clearly seen, and the pentane isomers are still visible.

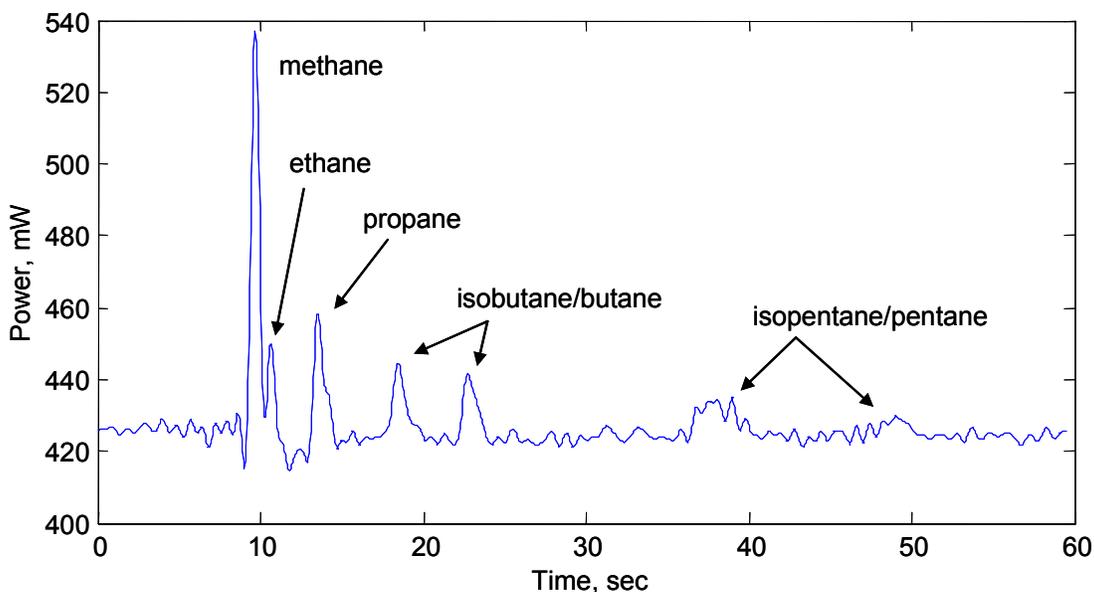


Figure 10. Detection of natural gas compounds separated using commercial column. Digital signal processing with a low-pass filter removed extraneous noise.

Instrument Development

As a critical step to bridging laboratory research to field application, hardware and circuits from the stand-alone BTU analyzer and micro-chromatography system were assembled into a field-portable GC instrument (**Figure 11**). The commercial 6-way pneumatic injection valve is included to inject microliter sample volumes into the microGC column chosen above. A solenoid valve operated by a relay controls the injection valve. A custom electronics board provides independent PID (proportional-integral-derivative) temperature control of the microGC column and micro-calorimeter fixture. A second custom board provides feedback control of the micro-calorimeter and reference sensor. This board has voltage outputs that are proportional to the input powers to the sensors. These two boards are controlled and read through a commercially available data acquisition (DAQ) board (National Instruments Inc.; model NI USB-6009). The USB (universal serial bus) DAQ board and all instrument functions are controlled through custom LabVIEW™ (National Instruments Inc.) programs. These components are fixed inside a travel-size suitcase, which also holds a small laptop. The only external component is a small tank containing 2 cubic feet of zero-air, enough for 100 hours of continuous operation. Facility air supplies can be plumbed through the same port, provided virtually limitless run-time. The entire system is designed to run from 120 VAC wall current. As this instrument has only recently reached final assembly, it has yet to be tested in its entirety at this writing.



Figure 11. Field-portable natural gas analysis instrument. Chromatography hardware is visible to the right of the computer. Electronics boards are located under laptop.

Next Steps

The next steps in this program involve further testing, expanding our capabilities, and commercialization. We are actively negotiating a proposal with a consortium of natural gas utilities. The goal is to expand the analysis capability of the current BTU Monitoring prototype instrument to analyze natural gas samples for constituents up to C10. This will involve further characterization of the micro-calorimeter for heavier compounds, and development of hardware and protocols for simultaneously analyzing light and heavy compounds. For improved durability, the micro-calorimeter sensor will be further ruggedized. In addition, a foundry has been identified to produce the sensor in bulk. Our collaboration with General Electric Company has strong potential to develop into a commercialization partnership. During this process, field-testing of the prototype instrument will yield data on maintenance requirements, long-term accuracy and precision, and other important marketing information.

While the primary impetus for this project is increased efficiency for the gas pipeline industry, there are application overlaps in the area of pipeline security. With low-cost instruments, distributed sensing of the natural gas infrastructure can occur. Improved real-time information on the composition of gas throughout the system will allow early detection of deleterious events such as pipeline leakage or fouling.

Conclusions

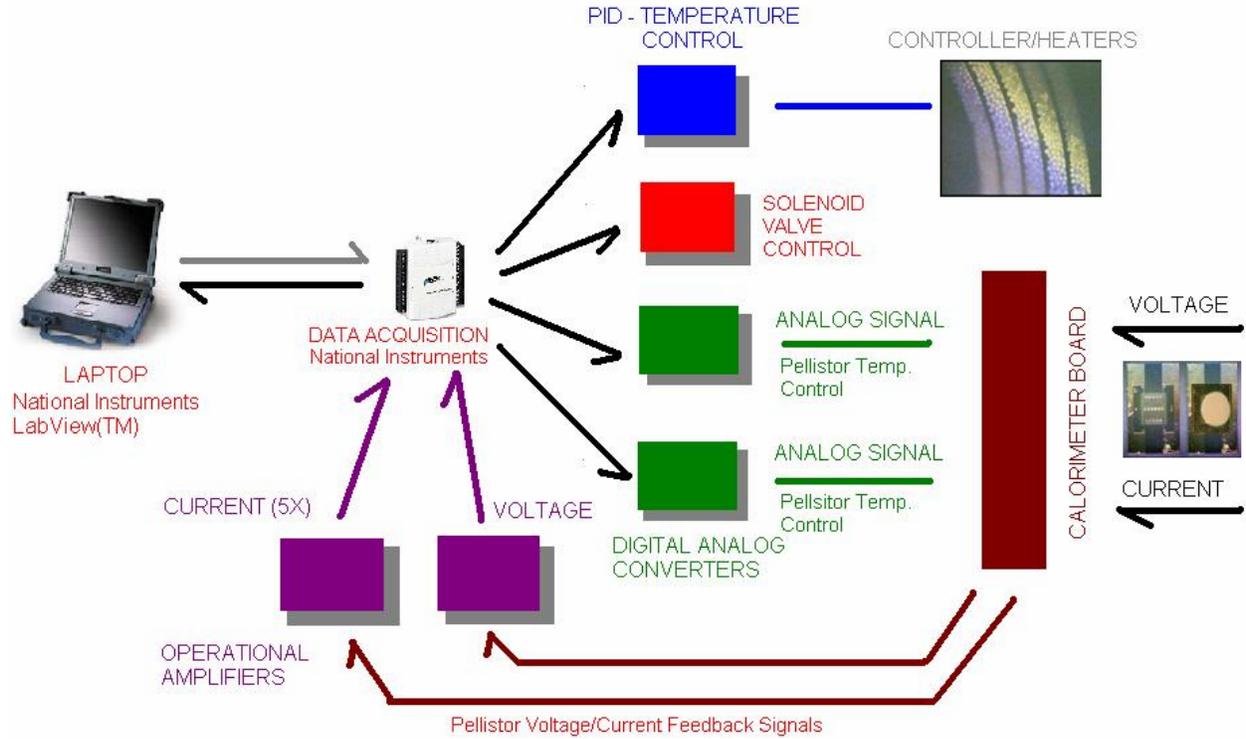
A prototype BTU Monitoring Instrument has been assembled using existing and modified microfabricated components. This instrument addresses market needs for natural gas characterization at key points in the national natural gas distribution network and at end-user facilities. In conjunction with a commercial injection valve, the instrument uses a silicon microfabricated, packed, gas chromatography (GC) column. A microfabricated calorimeter with a reference element serves as the detector. Batch microfabrication techniques will allow these components to be manufactured in production quantities at a low cost in order to meet industry requirements for cost, lifetime, and performance. A market analysis reveals that the current system may be suitable for large commercial users, as well as niche applications. Proposals to improve the existing components and move closer to commercialization have been submitted to NETL and the Northeast Gas Association.

This project addresses important needs identified by the gas transfer industry and natural gas end users. Instrumentation currently supporting custody transfer is limited to relatively expensive field GCs with significant installation infrastructure requirements and ongoing maintenance costs. Under present conditions, the limited number of instrumentation locations within the gas pipeline network results in significant errors in mass balance and cost recovery that directly influence custody transfer operations. Development of low-cost systems, like the BTU Monitoring Instrument, within the pipeline network will translate to increased revenues for the gas industry by virtue of more detailed information on the heating value of gas within the system at any given time. Gas heating value and flow measurement errors on the order of a percent or less can have significant impacts to the industry in the areas of lost revenues and cash flow since many pipeline networks possess gas transfer capacities that range from 0.5 to 1 billion cubic feet per day. Industrial end users will benefit running natural gas fueled turbines closer to design limits, safely maximizing power while maintaining pollution control.

Successful deployment of this technology in the natural gas industry will create a sensor market that does not presently exist within the pipeline network. The availability of low-cost BTU measurement systems will cause pipeline network managers to re-think their present-day strategy of limited sensor placement. With a low-cost micro-analytical sensor system, the advent of a much higher density sensor network is likely, particularly if the sensors can be linked via real-time communication networks.

Appendix

Diagram of Natural Gas Analysis System



References

1. Market study by Thermo-ONIX, Houston, TX, 2002.
2. General Electric Research & Development Center, "Smart Power Turbine Volume II— Technical Application" Public Abstract submitted to U.S. Department of Energy, National Energy Technology Laboratory in response to DE-PS26-00FT40759, Area 7-Advanced Turbines and Engines, June 1, 2000.
3. The Wobbe Index is the ratio of the heating value of a gas to its density, commonly given in units of megaJoules per cubic meter of gas.
4. ASTM D 3588 "Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels" requires precision of 1 part in 1000 at a single lab, but only +/-5% for analyses between labs.
5. NYSEARCH, 1/2005.
6. "Gas Processing Effects on Gas Quality," AGA Engineering Technical Note, draft 04/04/04, provided by NYSEARCH (Northeast Gas Association's research branch).
7. Images from VICI website, <http://www.vici.com/support/app/app11j.php#top>.
8. Supelco, "Bulletin 743L," pp. 5-6, 1995.
9. Z. Ji, R.E. Majors, E.J. Guthrie, "Porous layer open-tubular capillary columns: preparations, applications and future directions," *Journal of Chromatography*, v. 842, pp. 115-142, 1999.
10. M. Moorman, R.P. Manginell, T.W. Hamilton, W. Antel Jr., N. Nirmalan, R. Orenstein, "Lower Heating Value Sensor for Fuel Monitoring," submitted to *IEEE Sensors*, 2005.
11. G.C. Frye-Mason, R.P. Manginell, E.J. Heller, C.M. Matzke, S.A. Casalnuovo, V.M. Hietala, R.J. Kottenstette, P.R. Lewis, C.C. Wong, "Microfabricated Gas Phase Chemical Analysis Systems" Sandia National Laboratories, Department Literature, Micro-Total-Analytical Systems, 2005.
12. S.L. Firebaugh, K.F. Jensen, M.A. Schmidt, "Investigation of high-temperature degradation of platinum films with an in situ resistance measurement apparatus," *Journal Of Microelectromechanical Systems*, v. 7, pp. 128-135, 1998.
13. D. Briand, S. Heimgartner, M. Leboeuf, M. Dadras and N.F. de Rooij, "Processing influence on the reliability of platinum thin films for MEMS applications," *MRS Symposium Proceedings*, v. 729, pp. 63-68, 2002.

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