PROCESS ENGINEERING IS CHANGING
YOU CAN $ENSE IT

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Abstract: The role and responsibilities of the Process Engineer are rapidly evolving. This is in part because economic drivers to automate control of batch and continuous operations for consistent molecular compositions also apply to maintaining consistent process performance to meet more demanding product specifications. Both of these criteria are showing a greater return on investment (ROI) initiated by traditional process control strategies, but enhanced with specific (on-line) composition analysis. Incorporation of state-of-the-art point-of-use physical property measurements (temperature/pressure/flow) combined with chemical specific (molecular species) sensors provides unique feedback enabling the process engineer to better apply "model predictive control (MPC) " techniques. Such sensor technologies may allow the engineer to know the process composition at each tray in a distillation tower, or at purification tower positions in temperature or pressure swing absorbers (TSP or PSA) in "real-time" to alert for break-thru. Chinese Taoist philosopher Lao Tzu circa 600 BCE said, "To Know and not to do is not to know". It is our role as chemists and engineers to know and to do to gain true process control. Knowing the capabilities and limitations of the new sensor technology and how such sensors are evolving, can provide unique insights for the process engineer, who in turn will challenge the process analytical chemist to improve sensor specificity and performance. *Copyright © 2004 Air Products*

Keywords: Chemical microsensors; monitoring; chemical sensor; analytical approximations; active control

1. INTRODUCTION

 The role and responsibilities of the Process Engineer are rapidly evolving. The process-manufacturing paradigm has changed from analytical testing, solely to document product quality and rejecting/recalling products of unacceptable quality, to a new paradigm of "make it right the first time"-using continuous quality assurance. This is in part because economic drivers to automate control of batch and continuous operations for consistent molecular compositions also apply to maintaining consistent process performance to meet more demanding product specifications. Both of these drivers give a greater return on investment (ROI) initiated by traditional process control strategies, but enhanced by specific composition analysis. Incorporation of state-of-the-art point-of-use physical property measurements (temperature /pressure /flow) combined with chemical (molecular species) sensors are providing unique feedback enabling the process engineer to better apply "model predictive control (MPC)" techniques (Smilde, et al 2002). Such sensor technologies may allow the engineer to know the process composition at each tray in a distillation tower, or at purification positions in temperature or pressure swing absorbers (TSP or PSA) in "real-time" to define break-thru. Knowing the capabilities and limitations of the new sensor technology and how such sensors are evolving, can provide unique insights for the process engineer, who in turn will challenge the process analytical chemist to improve sensor specificity and performance (Chauvel, et al 2002; Gunnell and van Vuuren, 2003).

This review will provide a brief historical perspective of process analysis, a view of current analytical technologies, a summary of the major sensor technologies being applied today, and an example of sensor technology applied to hydrogen production.

1.1 Historical Perspective.

Some one hundred years ago our sense of touch (temperature), taste (acid/sweet), smell (H_2S/NH_3), sight (color of smoke or product) and feeling/hearing (compressor sounds/motor torque-vibration) were our process analytical tools, usually associated with a few well-experienced operators/engineers. These skills were hard to find, difficult to train in others, and hard to quantify /document.

 Figure I . Chemical Plant –1800's

Potyrail (Potyrail, 2001) reports "process chemicals analysis originates from the development of IR absorption (K.F. Luft at I.G. Farbenindustries-1938) and magnetic oxygen recorders in the late 1930s". Twenty-five years ago Exxon (ExxonMobil) led the way with Dow (Henslee, 1996), DuPont, Air Products, and others, with process engineering farsightedness to tie process control to the output of on-line/at-line analytical systems that sensed the molecular composition changes in chemical processing, refinery operations, bulk gas production, pharmaceutical and specialty chemical manufacturing. In some cases this has led to fully automated "lights out" manufacturing, and unattended delivery of liquefied gas products via the "auto-load" process at Air Products.

The development of the new electronic chip-based technologies over the past 20+ years has had major impact on the process analytical chemist's ability to provide the process engineer with "molecular thermocouples". The well-developed review by Harris *(Harris, 2002)* expanded upon by Workman, et al. (Workman, et al., 2001; Workman et al, 2003) provides insight to how such new analytical technologies have added to the tool kit of the process engineer and process analytical chemist. A good measure of such technology grew out of federally sponsored programs to detect biological species as weapons, chemical warfare agents, and new medical diagnostic systems. Workman, et al. (Workman et al, 2003) have stated "Measurement science has benefited recently from advances in technology in the computing and communication industries as well as from sensor-related research conducted in the US Government laboratories and agencies. Of particular mention are those developments in miniaturization, electrooptics, new materials (interfaces) and information/data handling."

The term applied to this advancing disciple that links the engineer and the chemist is Process Analytical Technology (PAT). Most recently, the US Food and Drug Agency (FDA) under Deputy Director Dr. Ajaz S Hussain (CDER Branch) put forth an initiative to foster the pharmaceutical application of PAT in the US (Mendricks, 2004).

PAT is defined by Hussain (Hussain, 2003) as a "system for analysis and control of manufacturing processes based on timely measurement during processing of critical quality parameters and performance attributes of raw and in-process materials and processes to assure acceptable product quality at the completion of the process".

1.2 Current Process Analytical Tools

Within the past thirty years (Creasy, 2003; Smilde et al., 2002) we have seen the movement of laboratory based (off-line) analytical systems into the plant environment (at-line or on-line) (Trevathan, 2003). For example, the HP/Agilent gas chromatograph (GC) became an ABB or Siemens or Daniels Process GC. For more complex feed/process streams requiring fast response time the ABB or Thermo Process Mass Spectrometer (MS) has moved from the lab (off-line) to an analyser shelter (at-line). These MS systems can have 1-10 sample streams being fed to them and carry out analyses every 30 sec or less from 500 feet away in the plant using continuous by-pass flow sampling technology. Such systems require 2-10 calibration/validation gases for routine operation. All actions feed back to a DCS computer to control the plant and manage the instrument remotely.

Fig II Agilent Lab Gas Chromatograph (GC)

Fig. III ABB Process Gas Chromatograph

Fig. IV ABB Questor IV Process Mass Spectrometer

The most recent advance in GC design is by both Sandia National Labs (Martin, 2003) and Honeywell Corporation (Bonne, 2003). Sandia made a GC on a chip "The Micro GC". The unit was most recently used by the Department of Defence in Iraq. The unit can detect, at the trace level, chemical warfare agents—or be used in a chemical plant to monitor specific off gases, for which it has been programmed, and do the analysis in < 60 seconds!

Fig. V Sandia National Labs –Micro GC

2 Sensors

New chemical specific sensors have benefited from micro machining to provide cost-effective processing (Goode, 2001; Bonne, et al 2004). Silicon-based metal-oxide chemical sensors were the first step. They were fabricated using standard semiconductor manufacturing and micromachining techniques (80-s/90-s). Such products deliver the key sensor benefits currently demanded by process analytical/engineers: low cost; lower power drain; robustness; small size; and ease of use.

2.1 Metal Oxide Sensor

Trautweiler, et al. (Trautweiler, et al, 1999) have summarized the metal oxide sensor technology. The figure below shows a MicroChemical Systems silicon-based metal-oxide chemical sensor. The sensor chip contains a thin-film sensing element fabricated from tin oxide and includes a buried polysilicon micro heater. The gas-sensitive layer measures concentration by electrical conductivity changes when exposed to air. The thin-film heater controls the operating temperature of the sensor to optimize selectivity and sensitivity.
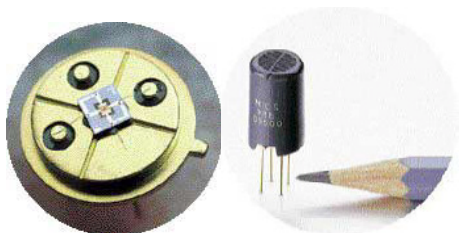

Fig VI   Metal Oxide Chemical sensors

Trautweiler et al. have summarized: "The heater and sensing element are built on a micro machined diaphragm precision formed from a silicon oxy-nitride ceramic with thermal properties that minimize sensor power consumption and response time. Heater power consumption levels are <40 mW with drive currents <40 mA, meaning that the chemical sensor is fully compatible with standard digital electronics components. This compatibility allows product engineers to design simpler, lower cost gas-detection products for consumer, industrial, and automotive applications. The underlying silicon micro-machined substrate is a standard sensor platform containing electrical interconnects to the sensor and device heater, as well as electrostatic discharge (ESD) protection diodes".

Trautweiler et al. go on to explain "The sensing film is constructed from an n-type tin oxide and ionic semiconducting material. During sensor operation, ambient O_2 molecules chemisorb onto the sensing film surface and dissociate into oxygen ions. Heating the tin-oxide film to ~450°C using the buried heating element facilitates this process. Formation of the oxygen ions removes free electrons from the tin-oxide grain surfaces, producing an increase in the sensing film's resistance. The presence of a reducing target gas such as CO reacts with the O_2 to produce CO_2 and releases electrons back into the sensing film with a corresponding increase in conductance or a decrease in film resistance. As CO concentration increases, the sensing film resistance decreases further. If the target gas were an oxidizing agent, such as NO_2, the opposite effect on sensing film resistance would occur."

2.2 Electrochemical Sensors

Electrochemical sensors are prevalent in the detection of oxygen and toxic environmental gases. "Each sensor is designed to be specific to the gas it is intended to detect. Electrochemical sensors are essentially fuel cells composed of noble metal electrodes in an electrolyte. The electrolyte can be an aqueous solution of strong inorganic acids or base. When a gas is detected, the cell generates a small current proportional to the concentration of the gas" (Anderson & Hadden 1999).

The RKI Instruments (R Pellissier, 2004) carbon monoxide (CO) and H_2S SAFETY Sensor Watches are examples of commercial electrochemical sensors; the O_2 sensor is of a Galvanic type. The Galvanic sensor is a special type of electrochemical cell. The galvanic oxygen sensor is essentially a battery that produces energy when exposed to oxygen and, is therefore consumed with exposure to oxygen. It is rugged and insensitive to shock and vibration.


Fig VII   RKI Instruments GasWatch 2

"In its simplest form, an electrochemical sensor consists of a diffusion barrier, a sensing-electrode (sometimes called the working-electrode, measuring-electrode, or anode), a counter-electrode (sometimes called the cathode) and an electrolyte. In an environment free of chemically reactive gases, oxygen diffuses into the cell and adsorbs on both electrodes. The result is a stable potential between the two in which little, theoretically zero, current flows. The cell's chemical process at this point is" (Anderson & Hadden 1999).

$$O2 + 4H+ + 4e - \rightarrow 2H2O \qquad (1)$$
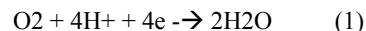
"When a chemically reactive gas passes through the diffusion barrier it is either oxidized (accepts oxygen and/or gives up electrons) or reduced (gives up oxygen and/or accepts electrons), depending upon the gas. The resulting potential difference between the two electrodes causes a current to flow" (Anderson & Hadden 1999).

For instance, when carbon monoxide, a reducing gas, diffuses to the sensing electrode, it is oxidized causing the potential of the sensing electrode to shift in a negative (cathodic) direction. The cell's chemical process is:
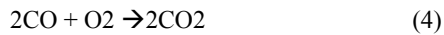
Sensing-electrode
$$2CO + 2H_2O \rightarrow 2CO_2 + 4H^+ + 4e^- \qquad (2)$$

Counter-electrode
$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad (3)$$
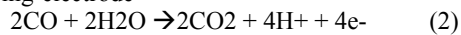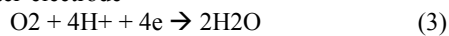
Cell reaction
$$2CO + O_2 \rightarrow 2CO_2 \qquad (4)$$

The newest form of toxic gas cell utilizes a third electrode called a reference electrode. This electrode has a stable potential from which no current is drawn. It is used to eliminate interference from side reactions with the counter-electrode. "In addition it allows the sensing-electrode potential to be biased with respect to its rest potential. Biasing is one method of controlling sensitivity to a particular gas. To provide for extended storage, a shorting clip is connected across the sensing and reference terminals. This short maintains the electrodes at the same potential and keeps current from flowing through the cell" (Anderson & Hadden 1999).

Electrochemical reactions are temperature dependent; therefore, electrochemical sensors incorporate a sensitive temperature sensor to compensate for temperature variations.

Electrochemical sensors are widely used and have the following advantages and disadvantages (Anderson & Hadden 1999).

- Advantages
  a) very linear
  b) good selectivity
  c) excellent repeatability and accuracy

- Disadvantages
  a) limited temperature range and sensitive to changes in temperature
  c) destabilized by humidity extremes
  d) sensitive to EMF/RFI
  e) limited storage life
  f) slow start-up if depolarized
  g) safety concerns-electrolyte has a strong acid.

2.3 Interfering Gases

Interfering gases, producing cross-sensitivities, are gases other than the target gas, which will cause the cell to respond. Like virtually any sensor, electrochemical cells are not completely specific. Despite the use of: carefully selected and engineered electrodes and electrolytes, changes in the operating potential of the sensing electrode, and selected chemical filters, it is difficult to develop a cell chemistry that will not respond to a more active gas than the target gas. Attempts to increase selectivity are not without side effects; for example, filters often slow the response of the cell.

2. 4 Blocking Mechanisms

Blocking is a condition that causes the cell to function poorly, or not at all until the condition is removed. Normally the block does not damage the sensor permanently as a poison would. The most common blocking mechanism for electrochemical cells is oxygen deprivation (Anderson & Hadden 1999).

2. 5 Oxygen Deprivation

Oxygen is an essential ingredient in the cell reaction with the target gas. If the oxygen supplied to the counter-electrode is cut off, the current cannot be sustained. Under normal conditions, when detecting small concentrations of a target gas in ambient air, an adequate supply of oxygen can easily be achieved (Anderson & Hadden 1999).

2. 6 Catalytic Bead

The catalytic bead sensor is made with two separate beads. One bead (active) is made of a small coil of wire, sealed in a ceramic substance, and coated with a catalyst. The second bead (reference) is identical to the active bead except a passivating substance is used in place of the catalyst. The reference bead compensates for changes in ambient temperature, humidity, and pressure variations.

Catalytic bead sensors operate above a threshold or "turn-on" voltage corresponding to the bead temperature that can, in the presence of the catalyst and oxygen, ignite the gas. Consequently, a flame arrestor is required around the sensors. (Anderson & Hadden 1999).

When a combustible gas diffuses through the flame arrestor, it oxidizes on the catalytically treated active bead. This oxidation reaction is exothermic, causes an increase in temperature relative to the temperature of the reference bead, and increases the electrical resistance of the small platinum coil embedded in the active bead. The change in resistance is proportional to the amount of chemical energy released by the oxidation reaction. Electronic circuitry immediately detects this increase in resistance and reduces electrical power to the bead until the active bead resistance is restored. The decrease in electrical power is linearly proportional to the combustible gas concentration present.

As the sensor ages, the catalyst slowly deactivates on the bead. The threshold voltage gradually increases, and the sensor sensitivity decreases. These changes cause increased zero

drift and noise. The result is the sensor must be replaced.

2.7 *Field Effect Transistor (FET)*

The FET as summarized by Wroblewski, (Wroblewski, et al, 1996; Hughes 2003) measures the conductance of a semiconductor as a function of an electrical field perpendicular to the gate oxide surface. In a simple version, (i.e. a metal oxide semiconductor field effect transistor, n-channel MOSFET), a silicon substrate (bulk (B)) contains two n-type diffusion regions (source (S) and drain (D)). The structure is covered with a gate oxide layer (2) on top of which a metal gate electrode (1) is deposited.
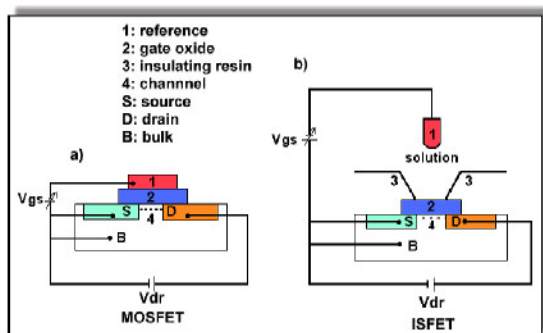

Fig VII MOSFET & ISFET Diagram

When a positive voltage (with respect to the silicon) is applied to the gate electrode, electrons (which are the minority carriers in the substrate) are attracted to the surface of the semiconductor. Consequently, a conducting channel is created between the source and the drain, near the silicon dioxide interface. The conductivity of this channel can be modulated by adjusting the strength of electrical field between the gate electrode and the silicon, perpendicular to the substrate surface. At the same time a voltage can be applied between the drain and the source (Vds), which results in a drain current (Id) between the n-regions.

In the case of the ISFET, the gate metal electrode of the MOSFET is replaced by an electrolyte solution, which is contacted by a reference electrode. The metal part of the reference electrode can be considered as the gate electrode of the MOSFET.

When SiO2 is used as the insulator, the chemical nature of the interface oxide is reflected in the measured source-drain current. The surface of the gate oxide contains OH-functionalities, which are in electrochemical equilibrium with ions in the sample solutions (H+ and OH-). The hydroxyl groups at the gate oxide surface can be protonated and deprotonated and thus, when the gate oxide contacts an aqueous solution, a change of pH will change the SiO2 surface potential. A site-dissociation model describes the signal transduction as a function of the state of ionization of the amphoteric surface SiOH

groups. Typical pH sensitivities measured with SiO2 ISFETs are 37-40 mV/ pH unit.

The selectivity and chemical sensitivity of the ISFET are completely controlled by the properties of the electrolyte/gate-oxide interface. Other inorganic gate materials for pH sensors like Al2O3, Si3N4 and Ta2O5 have better properties than SiO2 with respect to pH response, hysteresis and drift.

2.8 *Microcantilver Sensors*

Microcantilevers, as described by Thundat (Thundat et al., 2003; Dravid, 2003) appear to be a universal platform for real-time, in-situ measurement of physical and chemical properties. Based upon micro-electro-mechanical (MEMS) fabrication of silicon, combined with the sensitivity utilized in atomic force microscopy, the technique promises to revolutionize applications where multiple properties need to be economically monitored. A robust multielement sensor array can be constructed for pressure, temperature, viscosity and other physical measurements as well as the speciation of organic and inorganic constituents in harsh environments. By monitoring the deflection or resonance vibration of the cantilever, mass and stress changes induced by environmental conditions can be precisely and accurately recorded. For example, temperature changes can be measured to microdegrees by coating the cantilever with two dissimilar materials (bimetallic effect), and the viscosity of liquids and gases has been measured over four orders of magnitude using a single cantilever.

Microcantilever chemical sensors have also been made by coating the cantilevers with selectively absorbent films. For example, vapor detection of mercury, natural gas, and water vapor has been demonstrated with picogram sensitivity. Additional chemical coatings are being developed for inorganic, organic, and biological species (Hardy, 2004).

3. *PAT Application – Hydrogen Sensor*

A recent addition to process analytical technology is the H2scan hydrogen sensor system. This solid-state sensor detects concentrations of hydrogen gas, with or without oxygen present, in concentrations (actually partial pressures) from 10 parts per million to 100%.

H2Scan uses the Robust Hydrogen Sensor™, a thin film palladium-nickel (Pd/Ni) resistor deposited on a silicon substrate that changes resistance in the presence of hydrogen. The resistance of the Pd/Ni increases in direct correlation to the absorption of hydrogen molecules into the Pd/Ni lattice. No other gasses or environmental controls are necessary for these measurements; no oxygen is required for a reading; essentially the sensor counts hydrogen molecules.

In another configuration the Pd/Ni resistor becomes a Palladium Field Effect Transistor (FET) sensor that enables the unit to detect concentrations as low as 10 parts per million.

The sensor-module features a temperature sensing diode and on-board heaters. Using these, the system can maintain the sensor substrate at a constant temperature. This controlled elevated temperature assures that sensor operation is unaffected by ambient temperature.

FIG IX H2Scan Hydrogen Sensors

The H2Scan sensor system can be provided in a Class I/Div II Group B housing with "Z" purge to permit its operation in a flammable gas plant environment.

Fig X Process Configuration H2 Sensor

The H2scan system, with modifications by Air Products, was tested at an APCI plant for on-line monitoring of the H2 content (70-90 vol. %) in a mixed gas (Ar, N2, CO, CH4, H2O & CO2) process stream. The data were compared to an off-line GC over a 30 day period.
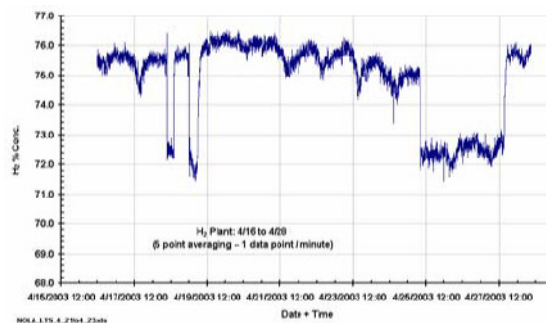

Fig XI On-Line Hydrogen Measurement

The H2 sensor system provided a partial pressure hydrogen content analytical result every 2 seconds, compared to the GC operation, which was routinely taken every four hours. During the trial, we observed periodic oscillations (dips) in the H2 content (+/- 3% H2). The dips correlated to maintenance times when modifications were being done to the Shift Reactor. The dips had not been quantified before in terms of H2 content. The concentration of H2 quantified correlated to the GC data (matched by time) +/- 0.5% H2.

4.   Sensor Technologies
Tables (I, II, III) provide a summary for reference of the current sensor technologies on the market (Table I) or being developed, along with a means to contact the vendor. Because hydrogen is the current centerpiece to our Nation's economy for energy, fuel cells, and automotive application (Table III), as well as industrial applications (refinery/hydrogenation-edible oil-Table II) we have provided more details in this market segment.

5.   Summary

The evolution of micro-sensor technology to replace our "five senses", and to replace sophisticated analytical instrumentation for on-line process control and final product certification is well under way. We are seeing the changes take place, slowly for sure, but taking place because we need to quantify the process variable (composition or   T/P/F) to initiate closed loop process control in the time required to "Deliver the Difference" for safety, consistent process control and final product properties & performance at the lowest cost.

Table I Current Sensor Technology Vendors

Firm	Contact	Analyte	Technology
Alphasense	www.alphasense.com	O2, CO, H2S, SO2,Cl, NO2	Fuel cell, Electrochemical
Analytical Indust	www.aii1.com	O2	Galvanic cell
Applied sensors	www.appliedsensor.com	Various	MOS, (metal oxide) FE (field effect) QCM (quartz crystal microbalance)
Avalon Photonics	www.avap.ch	O2 and various	Vertical cavity surface emitting laser
Axsun	www.axsun.com	In development	NIR- Mems
ConductTech	www.conductivetech.com		Electrochemical-thin film
City Tech	www.citytech.com	O2, CO, H2S, SO2, Cl, NOX combustible	Electrochmical, Pellistor, IR, MOS
Cyranose Science	www.cyranosciences.com	Organic vapors	Sorption on carbon film
Detcon	www.detcon.com	H2S, CO2, O2,	MOS, catalytic bead, IR,electrochemical
Figaro	www.figaro.com	Combustible, toxic, CFCs , indoor, O2 auto	MOS
Hohner	www.surfacesensor.com	color, refraction, reflection	Optical encoder for Visable, UV
IR Micro	www.ir-microsystems.com	various	Pyroelectric array detector
IT		O2, CO, H2S, SO2, Cl, NOx	Electrochemical, galvanic
e2V	www.e2vtechnologies.com	Combustibles, CO2,methane	Cataytic, TCD,NIR
Ion Optics	www.ion-optics.com	aroius, CO2	NDIR
	www.sixth-sense.com	O2, CO, H2S, SO2, Cl, NOx	Electrochemical, galvanic
Microsensor	www.microsensorsystems.com	Toxic, EO, hydrocarbon	SAW
Sensicore	www.sensicore.com	Waste water analysis	Micro-electrochemical
TAOS	www.taosinc.com	Light, reflection	Micro-IR
Vaisala	www.iprocessmart.com/vaisala	CO2	Micro-R
Sensors, Inc	www.sensors-inc.com/	Emissions-auto	Portable IR,UV

Table II H2 Sensor Technologies Process

Type	Property	Vendor	Range
Pd alloys (Thin film)	Resistance	H2SCAN	0.1 – 100%
Nanotube	Resistance	Nanomaterials Research	1000 ppm – 2%
Arrays (Thin film + FET)		H2SCAN	50 ppb – 100%
Electrochemical	Voltage	Unisense	0.02% to 25% H2 in H2O

Table III H2 Sensor- Leak Detection

Type	Property	Vendor	Range
Pt/Ni alloys (Thin film)	Resistance	Applied Sensors	50 – 5000 ppm
PdO/Si	Resistance	Thermodyne Systems	10-1000 ppm
Pd/AlN/Si	MIS-capacitor	Wayne State Univ	1 ppm
Pd alloy	Resistance	Microchemical Systems	
FET	Resistance (iV)	H2SCAN	50-1000 ppm
Catalytic bead	Resistance	RKI Instruments	0-5%
Catalytic bead	Resistance	Fuel Cell Safety Inc	1-5%
Catalytic bead	Resistance	Analytical Technology Inc	0-100%LEL
Semicond oxides	Resistance	Dupont	0-1000 ppm
Semicond. oxide	Resistance	RKI Instruments	0-2000 ppm 0-10,000 ppm
Semicond. Oxide (SnO)	Resistance	Figaro Engineering, Inc	50-1000 ppm
Mixed metal oxide	Resistance	City Technologies	0-1000 ppm
Microheater and thin film	Heat of reaction	NGK Spark Plug, Ltd.	0-80%
Electro-chemical	Current	Control Instruments	100-1000 ppm
Electro-chemical	Current	Draeger Safety Inc	100-1000 ppm
Electro-chemical	Current	Bionics Instrument Co., Ltd	0-4%
Electro-chemical	Current	Toxalert, Inc	0-1000 ppm
Fiber optics	Optical absorption/relection	Optisense	
Fiber Optics	Optical absorption/relection	H2SCAN	
Fiber optics	Optical absorption	Davidson Instruments	
Nanotube	Resistance	Nanomix	
Nanotube	Resistance	Univ of Calif	1-10%
Nanotube	Resistance	NanoMaterials Research	10-1000 ppm
Nanotube	Resistance	Applied Nanotech Inc	

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