Solid-State/MOS Gas & Vapor Sensors — A 35-Year Retrospective of Successful Atmospheric Monitoring for Health & Safety Purposes

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An Opening Comedy Monologue for the "Geriatrics"* in the Audience:

*That means over the age of 65 but not diagnosed with Alzheimer's.

I. How did you or could you test a hole in the ground for a new sewer manhole made of precast concrete in 1955, if you didn't own a gas detector?

Materials: 3 oily rags from the bulldozer, backhoe, or steam shovel.
A Zippo lighter because BIC butane hasn't been invented yet.

Scenario #1

1. Light the oily rag and throw it high above the open hole.
2. Result:________ "Whoosh"
3. Conclusion:________________

Scenario #2

1. Light the oily rag and throw it high above the open hole.
2. Result:_________ "Squoosh"
3. Conclusion:________________

Scenario #3

1. Light the oily rag and throw it high above the open hole.
2. Result:__________ "Ash"
3. Conclusion:_________________

II. How did you calibrate, field check, field test your combustible gas indicator in 1955 (if you did indeed own a working gas detector)?

Typical devices in the USA: JW Model G "Sniffer" / MSA 2A; "Explosimeter"/ Scott "Alert"
Tools required: Plastic bottle / Metal shot / Glass ampule

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B. What is <u>not</u> a Solid-State MOS / BRH gas sensor?

Thermal conductivity

Electrochemical toxic

Electrochemical oxygen

Catalytic combustion, hot wire, Wheatstone Bridge, Pellistor, CGI

Photo Ionization Detection (PID)

Color change chemistry

Ion mobility spectrometry

Infrared absorption spectros copy (FT/IR)

Differential optical absorption spectrometry

Aerosol mass spectrometry

Paramagnetic oxygen

Raman spectroscopy

Nondispersive infrared spectroscopy (NDIR)

Phosphorous chemiluminescence

Gas chromatography

Surface acoustic wave technology (SAW)

Flame photometry

Photo acoustic infrared spectroscopy

Mass spectrometry

Chemiluminescent ozone detector

II. Historical Quiz for the Gas/Vapor Detection Instrument Makers

Can you make a detection device (portable or continuous) that will detect "xxxx" at the following concentration of Lower Detectable Limit (LDL) to Upper Detectable Limit (UDL) for use in the "yyyy" industry? [Must be interference-free to "zzzz".]

Portable:	• Battery powered (?) • Rechargeable batteries (?) • Approval status (?)
Continuous:	• Controller/main enclosure (Approved) • Sensor/transmitter (Approved) • Sensor element (Approved)
xxxx:	• Sub ppm • 0-1000ppm • 10,000ppm = 1% Vol OR ABOVE
LDL:	Lower Detectable Limit
UDL:	Upper Detectable Limit (sensor damage limit)
yyyy:	Petrochemical / Industrial / Military / Aerospace / Medical / Primary Metals / Agriculture / Automotive / Pharmaceutical / others
zzzz:	Must review sensor cross-sensitivity data

III. A Brief 30-year+ Overview of MOS Sensor Applications

A. Specific Projects

1. In 1970 an exclusive importer in New Jersey brought into the USA several residential (110 Vac) gas alarms using Dr. Taguchi's model #105 metallic oxide semiconductor sensor.* We bought the alarm device (at about $50) and threw away the circuitry alarm, packaging, and power cord. We then conducted some tests, salvaged the solid-state sensor (MOS), designed circuitry, and patented the "AL CO LOK" to preclude starting of an automobile without a 5- to 7-second sample of human exhaled breath that was free of "ethanol" (C_2 H_5OH) to less than .01% to .05% BAC as measured by the law enforcement DUI/DWI instrument of the day: "The Stephenson Breatholyzer".

   *Figaro Engineering, Osaka, Japan

IT WORKED!!

And we sold 3 or 4 @ $5,000.00+ to GM / U.S. DOT / NHTSA. Then came…

Business Lesson #1: "Bushwhacked by the Big Boys"

We were threatened by a $5 billion+/year automotive OEM that they would tie us up in court and bleed us dry financially of working capital, because they had possession of a signed lab notebook that predated our product development by 6 weeks.

- Upon advice of counsel we sold all rights for $10K!
- What lesson here must be learned by every aspiring entrepreneur? Big companies have Big $$ to destroy entrepreneurs if they so wish…and they usually do.

2. In late 1971, we designed the "RSD-14" using the Taguchi #105 sensor. It was packaged to look like a residential wall thermostat (such as Honeywell), powered by 12 to 14 vdc from battery or alternator of a vehicle's electrical system in travel trailer/motor coach/caravan/Winnebago, etc. The design request was by a sales executive of Thetford Engineering Ann Arbor, which had pioneered and succeeded magnificently with "Porta-Potti" (Sealed chemical toilet for boats and recreational vehicles) from1968 to 1970. [Then the EPA mandated on-board human waste control by 1972.] Result: "Safety Sentry"/RSD-14 (Thetford execs felt it would be the next "Porta Potti.")

IT WORKED!!

It detected 10 to 20% LEL of C_3H_8 (propane) or "LPG" as well as 500+ ppm of CO and by 1972 was on-board standard factory equipment for GM Motor Coach, Champion, and others in the USA.

Unexpected Development: 1972 Arab Oil Boycott of USA

Ration books for gasoline were printed in the USA for the first time since 1941, but not issued. A typical recreational vehicle / motor home would get only 8 to 12 miles per gallon, so very few would realistically be on the road fueled by rationed gasoline. Result: By the end of 1972 you could not give away an “RSD-14” Safety Sentry, nonetheless sell one at $59.95 (Factory $20, Rep $5, Jobber $20, Dealer $20).
Is anybody making a profit here?

Business Lessons #2a & 2b:

- World economic factors out of your control can ruin you in weeks when you play with the big boys in consumer markets.
- Entrepreneurs should leave consumer products to the General Electrics and other $50 billion to $100 billion corporate giants of this world.

The ENMET Model CGS-4:

3. An ENMET stockholder, Mr. Ted D. Doan, former president of Dow Chemical in Midland, Michigan, brought a Bacharach Model G Portable Flammable gas detector to us. “We got hundreds of these all over the world at Dow plants—there must be something better than this.”

   Along comes an academic with a penchant for solid-state circuit design who says “I can design a low-power circuit to run that MOS sensor in a hand-held gas detector barely the size of a cigarette package.”

   “Yeah sure, give it a shot. Ha Ha.” But, his name was Professor Joseph Watson (Dr. Watson and I had taught together at the University of California, Davis Campus 1966–1968).

HE DESIGNED IT; IT WORKED; WE SOLD THEM!!!

The CGS-4 was born, and it launched ENMET Corporation as a “Gas & Vapor Detection Instrument Maker” (for industrial health and safety application) as of about fall of 1972.

One-third of a century later (34+ years) we have sold in total over $100M in gas detection instruments—based originally and heavily on a $2 MOS sensor/a clever circuit designer (J. Watson)/and a motivating investor named Ted Doan.

Business Lesson #3

“Hindsight is 20/20”. Every now and then you just get lucky. The harder you work the luckier you will get.

A mini-tale of successful gas detection using solid-state MOS sensors in the 1970’s, but abject failure in the marketplace due to third-party approval labs’ “head in the sand” attitude!

A SMELLY LITTLE TALE ABOUT CARBON DISULFIDE (CS_2)
[CS_2 LEL: 1.3%, FL PT: -22° F, UEL: 50%, AUT IG: 194° F]

4. In 1974, rail car off-loading in Akron, Ohio, involved bulk handling of CS_2. The client (a tire & chemical company) needed an early warning detector alarm for spills of CS_2 during railroad tank car off-loading operations. Hotwire/catalytic combustion sensor makers would not supply detector heads due to fear of "Thermal Runaway" leading to internal "Self-Heat" of the sintered bronze or stainless steel flash arrestor to over 200° F! Because auto ignition point for CS_2 is possibly as low as 194° F, a "hot" catalytic head might ignite a CS_2 gas cloud due to the temperature of the sintered metal housing over the glowing sensor element. ENMET Corporation stepped in to apply solid-state gas sensor technologies ("Fire in the Hole").

   In a covered 55-gallon drum, a concentration of CS_2 was achieved somewhere between LEL = 1.3% by volume/UEL = 50% by volume (in the middle of the explosive range) and the drum was placed in the far portion of our parking lot. An MOS sensor (#308 at 1.5V) was connected to a monitor/alarm circuit inside our building. A heater filament (nichrome wire) had been inserted and run back to an adjustable transformer (0-135Vac) also inside our building. After 30+ minutes of continuous gas alarm from the MOS element inside its double-capped stainless steel cover, no thermal runaway to self-ignition was observed. Then the Variac was run up to achieve yellow to white hot nichrome wire—the explosion was heard and felt inside our building!

In Summary

The Problem:	Achieve CS_2 LEL detection but without thermal runaway of the sensor head
The Solution:	Double S.S. cupped Figaro #308 MOS sensor

Business Lesson #4:

The tire/chemical maker wanted the monitor alarm at any price! However, their insurance company said the device could be purchased and installed only if it had been third-party approved and labeled for hazardous duty location by a laboratory such as UL/FM/CSA. But no North American lab had any testing protocol for a CS_2 gas cloud testing head, and none would create such a new testing protocol—no one had asked for it before!

Result: NO Approval!
NO Sales!
NO Protection at rail tank car off-loading site!

A synopsis of Business Lesson #4:

Bureaucracy and medieval protocol interference often prevails over innovation and creative problem solving.

5. Thin film indium oxide sensors from T.A.C. (Texas Analytical Control Corporation) for H_2S.

   The answer to oil or gas drillers' prayer: Solid-state H_2S detection—fast, rugged, linear, low cost, specific, etc. As stationary points of detection using this sensor for H_2S moved into the Texas oil and gas fields in the mid 1970's, strange reports began to surface about this solid-state H_2S sensor. It had diminished to non-existent response after days of operation (24/7) in clean air free of any H_2S concentration. This was referred to as: "The Sensor Goes to Sleep". The Answer: Wake it up with a shot of H_2S each morning. Re-enter the plastic bottle, metal shot, and glass ampule (of H_2S). Threatened lawsuits, returns, recalls, image damaging and ultimately near company destruction, but it survives today in the oil patch of North America with different H_2S sensor technology.

Business Lesson #5:

Suggestion for the aspiring sensor makers in the audience: burn in for months at your site and conduct field trials with a good customer for feedback before bringing to market a gas sensor or new instrument. You might avoid strong positive (or negative) sensor interference effects, premature failure of sensor performance, and so forth.

B. An MOS "Lightning Round" Application Story Book

1970 USA: ENMET, OSHA & EPA are created

Early 1970's Figaro MOS sensors #105, #109, #202, #308 start to appear.

1972 CGS-4/CGS-8: Portable gas detector MOS #109. Hot for "LEL", cool for "TOXIC"

1973 Carbon monoxide in compressed air used for breathing purposes: ENMET model ISA33-RAL

1974 CGS-10 Tritector, The first portable for three gases (LEL, CO/H_2S toxic/oxygen). MOS sensor (hot or cool) and oxygen sensor

1975 Shell Oil in Plaqermine, Louisiana, needed to detect 0-300ppm ethylene in a pure nitrogen gas stream (0% oxygen). Solution:

1. Pass 100% N_2 over MOS sensor at ½ lpm for 30 minutes. Set to "0" the alarm circuitry.
2. Pass 99.999% N_2 with 300ppm ethylene C_2H_4 over sensor for 30 minutes, and set alarm "trigger" threshold for the monitor.
3. The device can now stay online 24/7 in pure N_2 and will cause alarm and relay trip only when 300ppm C_2H_4 appears in the sample stream of pure nitrogen.

<u>Mini quiz with regard to above</u>:

4. What happens to this device in ambient air (i.e., 20.9% O_2/78% N_2)?
5. Change of O_2 causes change of baseline resistance in which direction? [or: as O_2 ↓, sensor conductivity goes where?]

1980 Wet Well Sewage/Pump Station Monitor alarms using Figaro sensors:
Methane gas via a "hot" MOS sensor
H_2S gas via a "cool" MOS sensor
Plus an electrochemical oxygen sensor

Gradually, markets emerge for sewage pump stations, wet wells, and other sewage treatment plant areas for flammable gases, hydrogen sulfide and oxygen deficiency. ENMET introduces ISA-44-2-OD:

1. LEL with 813 MOS sensor @ 5.5Vdc (Locate "High" because vd = .6)
2. H_2S with 812 sensor @ 4.5Vdc (Locate "Low" because vd = 1.18)
3. Oxygen with electrochemical sensor in a fiberglass corrosion-resistant enclosure (locate in "breathing zone")

[As of summer, 2006 we are still building ISA-44-2-OD's. Production will cease in December 2006.]

Late 1980's "Waste Hauler" Calibration Emerges:

TGS-813	LEL
TGS-812	Solvent/Fuels/Toxic Levels of Freons/Misc.

A tank truck firm in Memphis, Tennessee, provides ENMET with four pages of (possible) chemicals they might truck away from industrial plants to disposal sites, incinerators, etc. ENMET was asked to put a general calibration on a 3-sensor portable for confined space (entry to these tank trucks). Weeks of study shows: "LEL" best done as 5.5V 813 on propane, Toxic best done as 5.0V 812 on methyl chloride (CH_3Cl), plus an electrochemical oxygen sensor. Result: 10 years + of "waste hauler" portable gas detector sales.

January 1993 US Department of Labor:
USA regulatory agency for health and safety in the workplace recognizes the merit of MOS (solid-state) sensors for VOC's in sewers!
["VOC" a common term in the USA today for Volatile Organic Compounds]
See Appendix C and D

Late 1990's Medtronic in Minneapolis, Minnesota, expressed a need for solvent vapor "break through" from activated charcoal beds at about 25 to 50ppm of miscellaneous VOC's.

In a final assembly area for cardiac pacemakers, exhaust air contains VOC's to be adsorbed on the activated charcoal filter beds. ENMET's ISA-M in a flow-fitting housing alarms for " breakthrough" of VOC (i.e., greater than 50ppm). This allows customers to divert from depleted bed #1 to fresh charcoal absorbed bed #2 while replacing or recharging bed #1.

2002 CSI Denver, Colorado: The USA EPA wants to conduct "sewer line forensics" [i.e., who is dumping VOC's into sanitary sewer lines—and when?]
Product selection: ENMET T-5 Target with MOS sensors for solvent. A special version has data logging at 5 to 10 minute intervals and will run for seven days off a deep cycle marine battery.

2004 In the USA the NFPA sets diesel fuel (__?__% Vol = 100% LEL/FP ≈130° F/55° C) to a surprising low occupational exposure limit of 13ppm or 100mg/m3!

USA Coast Guard, marine chemists, industrial hygienists, and shipyard safety officers, among others, need a portable to detect < 50ppm of diesel vapor …only MOS solid-state or PID will work for diesel vapor at these levels.

2005 "Methlab"/"Clandestine labs" North American Law Enforcement:
A need emerges for LEL, and VOC solvents @ 200ppm for use by law enforcement in their investigations of illegal laboratories. A 5-gas sensor portable known as ENMET "Target" can sense, accommodate, NH_3, HCl, PH_3, LEL sensors, and detect solvents with MOS sensors at 0-200ppm equivalent to toluene.

2005/2006 A fertilizer production process [German License to USA Company] is to be constructed in Pennsylvania/USA. A US company has licensed a German fertilizer production process and must show insurance and regulatory agencies the ability to detect (IPA iso propylamine) as low as 5ppm…and as high as 10,000ppm (1%Vol). Low-level IPA (0-200ppm) is well detected by an electrochemical sensor for ammonia (NH_3), but that sensor would be ruined by exposure to 1,000's of ppm of IPA. The MOS sensor is verified by laboratory tests to detect/alarm/and recover from IPA concentration as high as 20,000ppm (2%Vol).

1974 to Present: "Special Calibrations" over the years
Here are our lab records for:

- Acetone to Xylene "A" to "X"
- Refrigerant gases
- Military and commercial jet fuels
- Conventional fuels: gasoline, diesel, kerosene
- Chlorinated solvents: TCE, I-I-I TCE, MC, etc.
- Customer proprietary vapor such as NORPAR, LEKSOL

C. Application Notes—Problem Solving

Application Note: 1995 OMNI-4000

ENMET has maintained for over 15 years a technology partnership with a company based in Arras, France. The company, Oldham, France, has historically been a division of BTR, Hawker Sidley, Invensys, and now Industrial Scientific (2006). Their model MX-21 portable gas detector introduced about 1992 had sensor plug-in options that included up to 20 electrochemical toxic sensors, electrochemical oxygen sensor, catalytic combustion sensor, thermal conductivity flammable gas sensor and non-dispersive infrared plug-in module for CO_2. None of these sensor options was acceptable to the RAF (yes, the RAF) for checking fuel cells in the C-130 transport aircraft (known as the "Hercules" in the UK). Military jet fuels such as JP 4, 5, 8, & 9 have notoriously poor response on catalytic combustion sensors and concern levels were at the 200 to 300 ppm level, not lower explosive limit (LEL) levels. Oldham had never installed an on-board MOS sensor in any portable, but introduced SP-31 (a low-power MOS sensor from F.I.S. in Japan) to meet the RAF requirement for toxic response levels of jet fuel vapor.

Application Note: November 2000 Target

The largest aluminum foil plant in North America (ALCOA—Louisville, KY) has numerous machines where aluminum foil is rolled, wrapped, packaged, and so forth using a proprietary hydrocarbon liquid called “Norpar 13”. This is a heavy, oily product not unlike xylene or diesel fuel in that it has a flash point above 100° F. However, the maker of Norpar 13 recommends human exposure be kept below several hundred parts per million for workers who maintain spaces under rolling mills and inside storage tanks containing this product. NDIR sensing would be impossible (MISTS), catalytic elements don’t give responses below a few thousand ppm’s, and a so-called Figaro 812 at 5.0Vdc heater voltage became the perfect solution to this detection problem using a 5-gas sensor platform from ENMET known as the Target portable gas detector.

Application Note: November 2004
“Red Hill” Fuel Storage Depot (Up hill from U.S. Naval Base/Pacific Fleet)
Pearl Harbor, Hawaii

This site has a huge underground storage tank for fuel that is used by US Navy jets assigned to aircraft carriers of the Pacific Fleet. A variety of non-xp rated electrical equipment is installed (lighting, motors, compressors). Request from the Navy for local alarm monitoring of JP-5 to alert maintenance personnel to fuel storage tank leaks that could accumulate vapors to some fraction of the LEL of JP-5. Low cost/low maintenance/long life is required, and a catalytic element detector does not meet these specifications. The solution: ENMET ISA-M’s on JP-5 with sensor heads 15” to 18” above the floor.

The MOS problem-solving list goes on:

- THF
- R134a
- LEKSOL
- Kerosene/Jet A, JP-4, JP-5, JP-8
- Formcel
- TCE
- I, I, I, TCE
- And others, including
    - “Logistical specificity”
    - “Cost effectiveness”

IV. ENMET MOS Sensor-based Commercial Instruments from 1972 to 2006

[No text is included in this handout, but selected instruments will be discussed by the presenter.]

V. Summary & Conclusions

There is no perfect gas/vapor sensor principle for all industrial/commercial applications!

The instrument selection process may be driven by such application specifications as background oxygen level, humidity, temperature, cost, size, power drain, lifetime, specificity (selectivity) among others. [The speaker's personal opinion with regard to MOS market: State of Massachusetts/April 2006/Mandatory home CO unit alarm! The best on the market is MOS.]

That said, it is clear to me and my corporation after 35 years in business with more than $100M in total sales of MOS sensor-based instrumentation, that solid-state gas sensing certainly has its place in the industrial market—and constitutes more than just a "niche" in that field. Of course, there are sometimes issues such as warm-up time, humidity effects, cross sensitivity, sample flow rates, lower limit of detectability, and so on that may limit, restrict, or preclude selection of solid-state sensors. But in general, it's been a good business for over one-third of a century for a small focused company, paid for several homes, a (nearly) new car, and put three sons through higher education.

Yet today in a world economy of diverse applications and intense competition, ENMET Corporation (founded on MOS sensor technology) puts in our current production models sensors, as necessary, from the list: MOS/electrochemical toxic/electrochemical O_2/PID/catalytic combustion/NDIR and even dew point (for medical compressed air monitors). A sensor technology that practically founded the company 35 years ago, MOS remains a solid contributor to our annual revenue. But no company can remain in today's global competitive markets for gas detection if it does not embrace the wide spectrum of sensing technology that has emerged in the past several decades.

Epilogue:

"Nano Sensors" for gases and vapors--for example, hydrogen specific at 1ppm!
Are they merely laboratory curiosities or are they ready for the oil / gas / petrochem / iron / steel / medical / agricultural / military aero-space / commercial / consumer markets? A possible topic for a symposium in 2007?