Spectroscopic Terahertz Sensors

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Outline

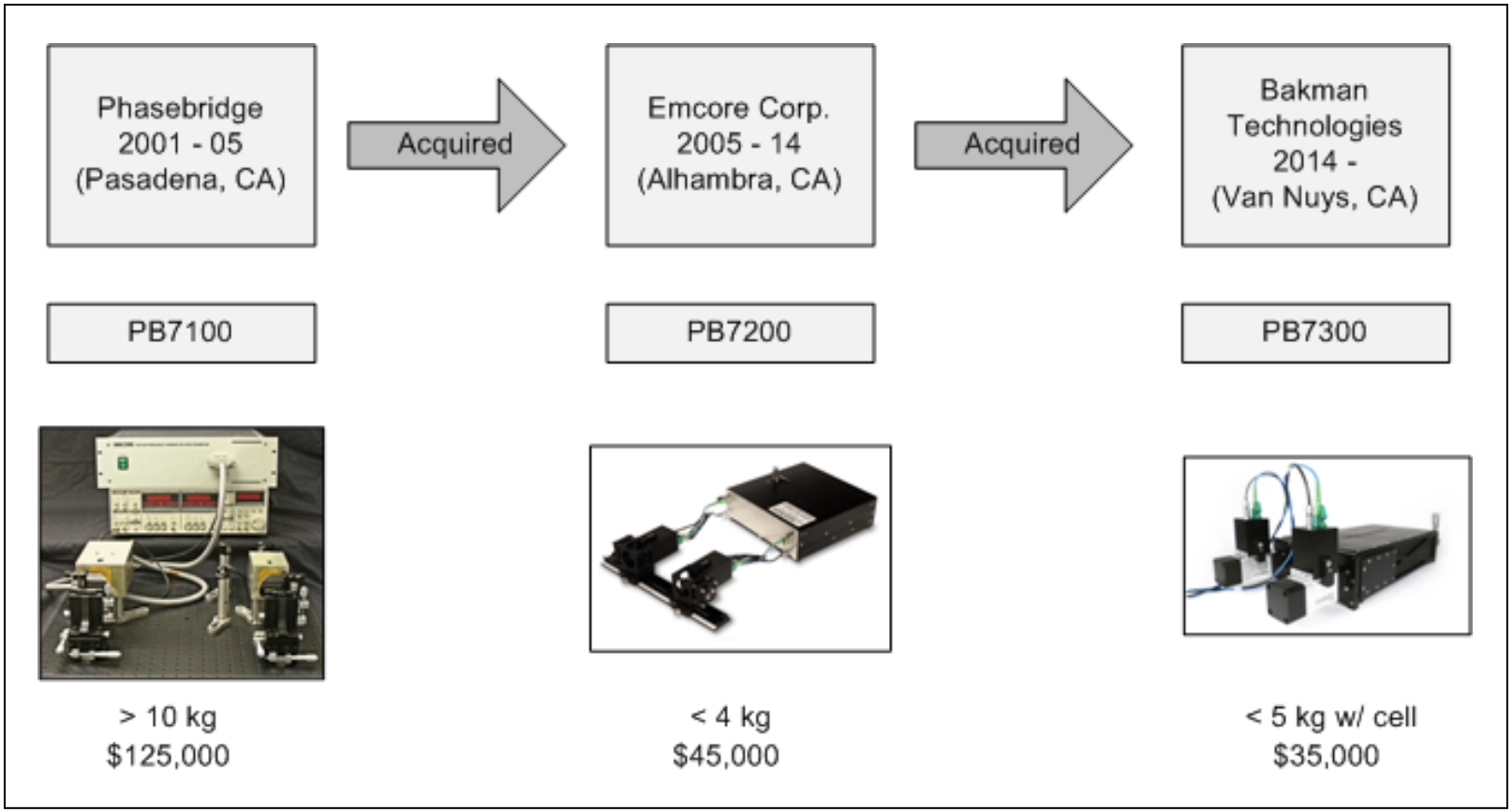
- Who is Joseph R. Demers and Bakman Technologies?
- What is our primary focus with THz technology?
- Where do we think that there is a market and why?
- What has limited the use of THz technology in this market?
  - Market Pull vs. Market Push
- Why does THz spectroscopy have a chance in this market?
- An Example: The Lancom 4 for Portable Emissions Testing
- Summary and Conclusions

Who is Joseph R. Demers

- **Attended University of Dayton in the ’80s and worked at W.P.A.F.B.**
  - **I became an honorary member of the Old Crows Association and I thought “I will never work in mm-wave systems why are they giving me a scholarship?”**
  - **A year or two later I took a laser course that I didn’t like and I decided that I would never ever work with lasers. Seriously.**
- **Attended Ohio State University for graduate school in the ‘90s**
  - **My dissertation involved using a home-built short pulse laser system to generate mm and sub-mm radiation from a photomixer.**
- **Graduated from OSU in 1999 and fled to industry – no more THz!**
- **I was the first hire at Phasebridge, a Cal-tech spin-off in Pasadena, CA that was developing hybrid photonics for telecomm applications**
  - **When the Dot.com bubble burst in 2001, we were scrambling to find work and I came across an SBIR for a THz photomixing system – became the PB7100**
- **Emcore Corp. acquired Phasebridge in 2005 and for the next 9 years I continued to develop, improve, market and sell THz components and instruments**
- **Purchased the Advanced Photonics Division from Emcore in 2014**
- **More than 20 years later I am still using lasers to produce sub-mm radiation**

and loving it!

Who is Bakman Technologies?



- **Look how far we have come! And it only took <u>15 years!</u>**
- **We need to speed things up!**

Focus on THz Spectroscopy

- My Ph.D. is in Chemical Physics, therefore I have always focused on employing THz radiation for molecular spectroscopy
- Bakman Technologies develops, manufactures and sells frequency domain THz spectrometers and components. We have always focused on economical, portable turn-key instruments
- We recently won NSF Phase I & II grants for developing spectroscopic THz sensors for emissions testing
- The primary reason I am giving this talk is to share the market analysis that was performed by Dawnbreaker for our NSF program
- The analysis was <u>not</u> centered on THz technology but on the general spectroscopy market and gas sensors market.

The Spectroscopy Market

- **Global spectroscopy market [1]:**
  - **$13.5 billion (2015) to $15.6 billion (2020) and CAGR* of 2.9%**
  - **Growth primarily "…attributed to the increased demand of instruments in the food, chemical and pharmaceutical industries."**
  - **"Rising interest in eco-friendly technologies and increased environmental concerns has led to increasing need for spectroscopic instruments, analytical products in industrial and academic markets.**

GLOBAL SPECTROSCOPIES MARKET BY TYPE, THROUGH 2020
($ MILLIONS)

Type	2013	2014	2015	2020	CAGR% 2015-2020
Mass and hyphenated spectroscopy	5,360.0	5,612.6	5,567.9	6,165.1	2.1
Molecular spectroscopy	4,201.5	4,413.0	4,192.3	4,663.7	2.2
Atomic spectroscopy	3,258.6	3,522.7	3,588.0	4,580.7	5.0
Other spectroscopies	192.3	196.7	193.9	227.4	3.2
Total	13,012.4	13,745.0	13,542.1	15,636.9	2.9

[1] "Global Markets for Spectroscopy Equipment," BCC Research, June 2016

* Compound Annual Growth Rate (CAGR)

Challenges for this Market

- **Four challenges to increased growth in this market [1]:**
  1. **Spectrometer size and cost**
  2. **Sensitivity and performance**
  3. **High costs in research and development**
  4. **Intense competition in the market**
- **In regards to size and cost "The modern industry needs spectrophotometers, which are portable and sophisticated."**
- **This is the main point in regards to sensitivity and performance as well – smaller, lighter instruments that are more accurate.**
- **Competition is driving these changes**

[1] "Global Markets for Spectroscopy Equipment," BCC Research, June 2016

The Gas Sensors Market

- **Global gas sensors market [2]:**
  - **$708.2 million (2017) to $1.3 billion (2023) and CAGR of 6.83%**
  - **Largest growth in VOC detection market**

Gas Type	2014	2015	2016	2017	2019	2021	2023	CAGR (2017–2023)
Oxygen	137.4	147.6	160.5	176.1	210.1	249.6	294.4	8.95%
Methane	98.2	103.0	108.7	113.9	124.6	135.8	147.4	4.39%
Carbon Monoxide	80.6	85.7	92.2	98.1	110.8	124.5	138.9	5.96%
Carbon Dioxide	75.7	81.7	88.8	96.8	114.8	135.8	159.6	8.69%
Hydrocarbons	58.7	65.3	69.7	74.1	82.8	91.0	98.1	4.78%
Volatile Organic Compounds	52.1	57.0	63.1	71.3	88.9	108.1	129.5	10.46%
Hydrogen Sulfide	57.7	59.5	61.7	63.7	67.9	72.2	76.7	3.13%
Chlorine	52.1	55.3	58.8	62.3	69.4	77.0	84.5	5.21%
Nitrogen Oxides	45.9	49.2	52.6	56.5	64.8	74.0	83.6	6.74%
Ammonia	44.7	47.3	50.4	53.7	60.8	68.5	75.3	5.79%
Hydrogen	5.1	5.4	5.9	6.4	7.4	8.5	9.7	7.08%
Total	708.2	757.1	812.3	872.9	1,002.2	1,145.1	1,297.6	6.83%

[2] “Gas Sensors Market,” MarketsandMarkets, July 2017

Benefits of THz Spectroscopy

- THz spectroscopy is a useful tool for gas analysis because transitions are specific to each molecule
- Non-contact measurements are possible for many industrial applications
- Detection doesn't rely on a chemical reactions and so there are no consumables or poisoned sensors
- Maintaining high quality optics is not required and alignment isn't as sensitive as with laser systems
- Non-polar molecules are transparent (drawback?)
- In volumes COGS should be low (1000 per year)

Market Push versus Pull

The greatest challenge for implementing THz technology in a large scale application isn't technical, it is economical: there isn't an application for which the ROI* makes it the best choice.

There is no *Market Pull*

This means that the only way into an industry is with

Market Push

The THz solution must be *significantly* better, faster *and* cost less to make it attractive.

* Return on Investment

THz Push Challenges (some)

Price-point has been the greatest challenge, but as prices of THz instruments come down, there are still hurdles

1. **Interrupted production = lost $$$ (most important)**
2. **Reliable, reliable, reliable - any new technology must have a proven track record of reliability – this is tough for NEW technology**
3. **You must educate and convince potential adopters because established manufacturing, testing or processing industries are generally extremely conservative**
4. **In their shoes "Why should I take a risk on this?"**
5. **Your new competitors aren't going to sit by**

Portable Emissions Testing

BAKMAN TECHNOLOGIES™

LANCOM4

AMETEK LAND HAS BEEN MANUFACTURING PRECISION MEASURING EQUIPMENT SINCE 1947.

THE LANCOM 4 IS THE MOST ACCURATE, ROBUST AND FLEXIBLE PORTABLE FLUE GAS ANALYSER CURRENTLY AVAILABLE.

In excess of two thousand Lancom analysers are in use today, in a wide range of applications - all subjected to very different measurement conditions.

THE WORLD'S MOST VERSATILE PORTABLE FLUE GAS ANALYSER

FEATURES	BENEFITS
Monitoring of up 17 measurement parameters	One instrument to meet all requirements
Up to 9 gas measurements in a single instrument	User selectable
High quality color display	Visualise your data with new widescreen display
Multiple Language support	Navigate the menu in 6 major languages (others available upon request)
USB Communications Support	Simple interface to PC and data transfer - supports USB memory sticks
Weighs only 6 kg (13 lbs)	Easily carried around plant with shoulder strap
Robust, industrial design	For daily use in the harshest plant environments
Wake and Sleep, semi-continuous operation mode	For periodic unattended operation
Range of user selectable options	Ideally matched to application requirements
Data acquisition & analysis software	Capture, calculate, and report data on your PC
Simple field upgrade	Add features and options as and when required
Meets ASTM D-6522 with Dry Sampler probe	Report generation to recognised standards
Convenient Catchpot - Visible and Accessible	Side mounted, highly visible for fast and easy removal and emptying
Clip-In Filters - Quick to change	Recessed into the side; replacement is straightforward

In business over 70 years

In excess of 2000 units in use today (low??)

Up to 9 different gases

Weighs 6 kg but considered portable

Filters needed

Lancom 4 continued

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Sensor	Detection Limit	Full Scale Range
O_2	0.2 %	0 to 30 % v/v
CO (low)	2 ppm	0 to 6000 ppm
CO (H_2 compensated)	2 ppm	0 to 4000 ppm
CO (high)	20 ppm	0 to 10 %
SO_2	2 ppm	0 to 4000 ppm
NO	2 ppm	0 to 5000 ppm
NO_2	2 ppm	0 to 1000 ppm
H_2S	4 ppm	0 to 1000 ppm
CO_2 **	0.2 %	0 to 20 % v/v
Hydrocarbons (CxHy)	(Application dependent)	0 to 5 % v/v
Flue Gas/Ambient Temperature	Measured	
Draft	± 50 hPa / 20" Water Gauge ***	
Flow (velocity)	1 to 50 m/s	

2 ppm is best detection limit

SENSOR TYPES

Electrochemical	CO Low, CO High, CO Low H_2 compensated, O_2, NO, NO_2, SO_2 and H_2S
Infrared	CO_2
Pellistor/Catalytic	CxHy

3 Different Sensors mostly electrochemical

Base Unit Price Point?

Lancom 4 continued

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Base Unit Price Point?

$7400 USD*

*Probably higher with options and consumables. This is a low volume price.

The Fine Print

Every sensor has an issue – with the electrochemical it is poisoning, saturation, lifetime and cross sensitivities

Nitrogen Dioxide (NO_2)

Sensor Type:	Electrochemical
Range:	0 to 20 ppm
Max Overload:	150 ppm
Resolution:	0.1 ppm
Bias/Equilibration:	Bias on; 6 hours after installation
Temperature Range:	-4° F to 122° F (-20° C to 50° C)
Pressure Range:	Atmospheric ±10%
Operating Humidity:	15 to 90% RH non-condensing
Drift:	< 2% signal/month
Storage Life:	6 months in sealed container
Storage Temperature:	32° F to 68° F (0° C to 20° C)
Operating Life:	2 years in air
Warranty:	1 year from date of shipment
Calibration Gas:	5 ppm NO_2, balance air

Cross-Sensitivity Data, NO_2 Sensor

Gas	Concentration	Response
Cl_2	1 ppm	-1 ppm[1]
CO	300 ppm	0 ppm
H_2S	15 ppm	-1.2 ppm[1]
NO	35 ppm	0 ppm
SO_2	5 ppm	-5 ppm[1]

1 - CAUTION! Negative cross-sensitivities may cause the sensor to produce lower readings than the true concentration of gas in ambient air.

Cross Sensitivities

Cross-Sensitivity %	Gas							
Sensor	CO	H_2S	SO_2	NO	NO_2	HCN	NH_3	PH_3
CO	100%	0%	0%	0%	0%			
CO-Extended Range	100%	0%	0%	-29%	0%			
CO-H_2 Compensated	100%		3%	6%	5%		1%	
H_2S	1%	100%	0%	9%	-20%			
H_2S-Extended Range	0%	100%	0%	9%	0%			
SO_2	1%	0%	100%	0%	-100%			
NO	0%	-10%	0%	100%	30%			
NO_2	0%	-8%	-100%	0%	100%			
HCN	5%	600%	375%	-80%	-400%	100%		
NH_3	0%	10%					100%	
PH_3 (032-0108-000)	0%	80%	20%				0%	100%
PH_3	0%	80%	20%				0%	100%
PH_3-Extended Range	0%	27%	100%				0%	100%
ETO-A	40%							
ETO-B	40%							
ETO-C	40%							
CL_2	0%	-30%	0%	0%	120%		0%	
ClO_2	0%	-25%						
H_2	20%	20%	0%	29%	0%	30%		
CH_3SH	0%	220%	50%	1%	-60%			
HCHO	70%							

CAUTION! Negative cross-sensitivities may cause sensors to produce lower readings than the true concentration of gas in the air.

- **Standard techniques is to use filters to deal with cross sensitivities**
- **The limitations of the sensors are understood in the industry**
- **Even with limitations from what I can tell the are still widely used**

Summary

- The Lancom 4 is a single example from many
- There is a long list of other sensing technologies:
  - Laser Spectroscopy, Raman Spectroscopy, FT-IR, On-chip optical sensors, UV absorption…
- Each technique has benefits and drawbacks and discussing them would take days
- There are niches where a spectroscopic THz sensor employing molecular spectroscopy has definite benefits
- Need to educate potential customers while growing volumes to decrease costs
- Certification testing can be very time consuming and expensive, so need to start that as soon as possible.

Conclusion

There is a market for spectroscopic THz sensors!

But the community needs to think Ford *not* Ferrari

- **Economical (under $10k)**
- **Reliable for everyday use (20 year lifetime)**
- **High performance levels (ppb sensitivities)**
- **Volume manufactured (not hand crafted)**

The car analogy is appropriate since there is a long road ahead!

Thank You!!!

Stop by **Booth 243** to see our demonstration system flown over Paramount Ranch July 5th 2016.

Come see my talk 11010-35 Tuesday at 5:45 in room 341

"Detecting atmospheric DHO with a spectroscopic THz sensor"

That's right, its during happy hour, so bring your drink along!

This project is partially funded by the National Science Foundation under award 1831168 – Many thanks!