The impact of CMOS technology on mass market applications in the submillimeter/terahertz spectral region: chemical sensors and imaging through obstruction

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The submillimeter/terahertz (smm/thz) spectral region has played a major role in the development of important scientific disciplines, including interstellar astrophysics, upper atmosphere remote sensing, and physical chemistry. However, none of these are mass market, public applications. There are two public applications that have long been recognized and demonstrated by use of the specialized technology that has been developed for the aforementioned scientific applications: chemical sensors and imaging through obstructions. With the rapid growth of the wireless community and its desire for ever more bandwidth, a public technology for smm/thz is beginning to emerge to support these public applications. The development of a CMOS technology will greatly accelerate the movement of the smm/ thz into the mainstream. The fundamental advantages of an electronic approach for these applications and examples of both the applications and the technology required to support them will be presented.

TxACE e-seminar Dallas September 24, 2010

Overview

The Gas Sensor (Imaging) Application

Background: Why has it taken so long? Why is now the time? The underlying physics Consequences of the physics: strengths, weaknesses, impact on design strategy

A Current Implementation

DARPA one cubic foot box

Technical considerations for submillimeter sensors

The submillimeter technology A small absorption is a large amount of power New noise sources / Townes noise Dynamic range issues

Moving Forward with CMOS

The high frequency requirements Frequency control and relation to cell phones



AT THIS POINT IN TIME -- GAS ANALYSIS EMERGES FROM A CONFLUENCE OF SCIENCE AND

Physics Always Favorable (1955)

TECHNOLOGY

HP 40 GHz MW Spectrometer(1974)

MICROWAVE SPECTROSCOPY

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CHAPTER 18

THE USE OF MICROWAVE SPECTROSCOPY FOR CHEMICAL ANALYSIS

The well-known varieties of spectroscopy have been so widely and successfully used for chemical analysis that the reader has undoubtedly already wondered whether or not microwave spectroscopy can also be successfully applied in this way. Although microwave spectroscopy appears to be well suited for certain varieties of analytical work, actual applications of this type have so far been very limited.

McGRAW-HILL BOOK COMPANY, INC.

New York Toronto London

1955

Microfabrication => small, inexpensive in quantity (2001)





Growth in computing power to handle information

Broadband wireless market

CMOS?



Enablers



Spectroscopic and Analytical Background

A Fast Scan Submillimeter Spectroscopic Technique, **Rev. Scient.** Instrum. 68, 1675-1683 (1997).

FASSST: A new Gas-Phase Analytical Tool, Anal. Chem. 70, 719A-727A (1998).

Fast analysis of gases in the submillimeter/terahertz with "absolute" specificity, **Appl. Phys. Lett. 86, 154105 (2005).**

Chemical analysis in the submillimeter spectral region with a compact solid state system, **Analyst 131, 1299-1307 (2006).**

A new approach to astrophysical spectra: The complete experimental spectrum of ethyl cyanide (CH_3CH_2CN) between 570 and 645 GHz, **Astrophysical Journal 714, 476 - 486 (2010)**

Submillimeter spectroscopy for chemical analysis with absolute specificity, I. R. Medvdev, C. F. Neese, G. M. Plummer, and F. C. De Lucia, **Opt. Lett. 35, 1533 - 1535 (2010).**



Sub-Millimeter Spectroscopy Introduction

High resolution SMM spectroscopy exploits rotational transitions of molecules
100 000 resolution elements and complex thermally excited signature provides
'absolute' specificity

Technique ideal for gas phase detection

- High specificity
- High sensitivity
- Low false alarm rate
- Fast measurement and analysis
- Broad range of analytes
- Small, low power technology

GHz

Rapid technology commercialization in the MM/SMM makes this long held promise a practical foundation for a entirely new sensor approach

Spectrum of a Mixture of 20 Gases



Consequences of the Physics

Optimum pressure is ~ 10⁻⁵ atmospheres (Doppler) and sample is static

- => very small sample requirements
- => sampling volumes for large preconcentration gains are small (1 liter STP gives 10⁵ gain)
- => vacuum requirement greater than in IR/Op
- => atmospheric clutter limit ~1 ppt (aided by spectroscopic specifics as well)

Electronic sources are essentially delta functions, even in Doppler limit

Small Power provides very high brightness (1 mW in 1 MHz corresponds to 10¹⁴ K) => path to very small an inexpensive technology

Spectral density strong function of molecular size => large molecule limit



Current System







			Power (W)	Cost(parts)	Size (cm ³)
X-band drive/synthesis	COT Synthesis	/YIG/SB gen		\$25,000	2925
mm-wave system	2-VDI			\$50,000	3250
Pumping	Diaphram + tu	irbo 150 W	150	\$10,000	8580
Sorbant	tube				5
Computing	PC cage			\$1,000	5200
Interface	USB device in	n cage		\$500	
LockIn/Signal Processing	Card in cage			\$2,800	
Absorption Cells					
Non-Resonant	1 m, folded		0	\$1,000	2600
Cavities	10 cm, 1.5 GH	z FSR	0		
Stark					
Power Supply			0	\$2,000	2340
· · ·					
Total			150	\$92,300	24900

Some power is missing from this roll-up



An implementation as a point in trade space



'absolute' specificity on mixture of 32



2 ppt sensitivity demonstrated on one gas



1 Cubic Foot Package

Demonstrated that atmospheric clutter insignificant



Results of Numerical Analysis

	Name	Partial Pressure	Uncertainty	σ
1	Hydrogen Cyanide (HCN)	0.00005887	0.00001177	5.0
2	Cyanogen Chloride (CICN)	0.00000373	0.0000863	0.4
3	Cyanogen Bromide (BrCN)	0.00001529	0.00001190	1.3
4	Acetonitrile (CH₃CN)	0.06179212	0.00010329	598.2
5	Carbonyl Sulfide (OCS)	-0.00002180	0.00004785	0.5
6	Methyl Fluoride (CH₃F)	0.02696802	0.00008850	304.7
7	Methyl Chloride (CH ₃ Cl)	0.00000402	0.00006642	0.1
8	Acrylonitrile (C ₂ H ₃ CN)	0.06608506	0.00015278	432.5
9	Sulfur Dioxide (SO ₂)	0.05412899	0.00016715	323.8
10	Dichloromethane (CH ₂ Cl ₂)	0.00011741	0.00009868	1.2
11	Methyl Iodide (CH ₃ I)	0.13009995	0.00032185	404.2
12	Methyl Bromide (CH₃Br)	0.08504046	0.00021784	390.4
13	Difluoromethane (CH ₂ F ₂)	0.00015923	0.00015236	1.0
14	Ethylene Oxide (C ₂ H ₄ O)	-0.00002183	0.00016894	0.1
15	Trifluoromethane (CHF ₃)	0.07005161	0.00025661	273.0
16	Acrolein (C ₃ H ₄ O)	0.05893068	0.00020953	281.2
17	Propionitrile (C ₂ H ₅ CN)	0.06061219	0.00018844	321.7
18	Pyridine (C ₅ H ₅ N)	-0.00011725	0.00014392	0.8
19	1,1 Difluoroethene (CH ₂ CF ₂)	0.05567078	0.00028872	192.8
20	Vinyl Fluoride (C ₂ H ₃ F)	0.04030862	0.00024987	161.3
21	Vinyl Chloride (C ₂ H ₃ Cl)	-0.00055029	0.00027035	2.0
22	Oxetane (C_3H_6O)	0.03009420	0.00032445	92.8
23	1,1,1 Trifluoroethane (C ₂ H ₃ F ₃)	-0.00007049	0.00021531	0.3
24	Propyne (C ₃ H ₄)	-0.00016353	0.00034151	0.5
25	Carbonyl Fluoride (COF ₂)	0.00467462	0.00048952	9.5
26	Thietane ((CH₂)₃S)	-0.00089690	0.00049489	1.8
27	Methyl mercaptan (CH ₃ SH)	0.00009574	0.00060512	0.2
28	Methyl isocyanate (CH₃NCO)	0.00080489	0.00052955	1.5
29	Methanol (CH ₃ OH)	0.00026869	0.00046662	0.6
30	Thionyl fluoride (F ₂ SO)	-0.00063312	0.00058645	1.1
31	Vinyl bromide (CH ₂ CHBr)	0.07177855	0.00058255	123.2
32	1,2 dichloroethane ($C_2H_4Cl_2$)	0.07311919	0.00088521	82.6
		∑ = 0.888408		



Broad Coverage of TIC Gases

USACHPPM Toxic Industrial Chemicals [27] Info Card - Updated last: hauschildvd PAGE 1 of 2 11/1/01

	Chaminal	Rate of	Persists in	Toxicity Thresholds (ppm/hour)	BDO/	Oder	Related hazards/ Source/	Field De	etection	Symptoms	Decontamination and	
	citemear	Onset	Environ ment	impairment fatality	Effective	Gaor	Use	Sensidyne tube (#)	205Aseries Miran SapphiRE	(trom inhalation and dermal contact)	Treatment	
-	Allyl alcohol (colorless liquid)	Immediate	Days- weeks, +	22	?	Mustard-like	Rapidly absorbed through skin highly flammmable with caustic fumes; used as contact pesticide, plastic/perfume manufacture	Not available (liquid)	Not available (liquid)	Seneral Mild Health Effects: Nausea, dizziness; headaches; chills; coughing, choking, throat irritation	Decontamination: - Flush (15 min) eyes & skin with water; - Soan optional after	
-	Acrolein (colorless-vellow lig)	Immediate	Immediate Minutes 0.1 Poor 1 ppm -sharp, acrid, sweet Herbicide Herbicide Herbicide Standard Effects:	Specific and More Severe Effects:	initial water rinse							
-	Acrylonitrile (clear/pale yellow lig)	Immediate	Minutes to HOURS	35 75	Poor	17 ppm - unpleasant, sweet (peach)	Flammable gas; used in Plastics, coatings, adhesives industries; dyes; pharmaceuticals;	#191	Standard	Eyes: - Irritation; tearing/watering; pain: intolerance to light (a.g.	Treatment & Diagnostic procedures/ options:	
-	Ammonia (colorless gas)	Immediate	Minutes	110	Poor	17 ppm - sharp,suffocati ng,dry urine	Explosives manufacture; pesticides; detergents industry	#3M	Standard	from Hydrogen Sulfide) Skin (particularly if liquid contact):	 Saline wash Antibiotic ointments 	
-	Arsine (colorless gas)	Immediate to 24 hours	Minutes to hours	0.2	Good	0.5 ppm - garlic-like	Reacts with H20 (don't use H2O in fire); Used in electronics ind	#19L	Not standard	 Irritation; burning; blisters (eg with Hydrogen Fluoride); 	Skin burns/blisters/irritation	
НСІ	Chlorine (greenish-yellow gas)	Immediate to hours	Minutes to hours	3 22	Good	3.5 ppm- pungent (bleach), suffocating	Imitating corr fumes; heavier than air; Cleaner/disinfectant in many industries; water treatment; WWI war gas;	#80	Not standard	 vesiculation (nitric & sultrunc acid); dermatitis; and frostbite (e.g. Acryonitrile) Respiratory Tract/Lungs: 	 topical corticosteroids and/or antihistamines Inject MgSO4 at affected site (Hydrogen 	
	Diborane (colorless gas)	Immediate	Minutes to hours	>1	Good	2.5 ppm -sickly sweet	Very flammable; Intermediate chemical manufacturing;	#22	Not standard	 Breathing difficulty.respiratory distress; 	fluoride)	
-	Ethylene oxide (colorless gas/liq)	Immediate	Minutes to hours	45 200	Poor	425 ppm - sweet, ether- like	Very flammable; Rocket propellant; fumigant; sterilization in health care industry;	#163L	Standard	 Jaryngeal spasm (e.g., from hydrogen chloride or hydrogen bromide); 	Oxygen & ventilation Prophylactic antibiotics Xravs	
-	Formaldehyde (clear- white gas/liq)	Immediate	Hours	10 25	Poor	1 ppm -pungt suffocating	Flammable, Disinfection/ germicide; fungicide; textile; health care (tissue fixing)	#91D (Dosi)	Standard	Chest/Heart: - chest pain; tachardia (rapid	Pulse ox/blood gas NOTE: avoid mouth to	
-	Hydrogen bromide	Immediate	Minutes to hours	3 30	Good	2 ppm -sharp stinging	Chemical manufacturing industry; very corrosive	#15L	Not standard	heartbeat) Systemic; Blood	mouth to protect against cross contamination	
-	Hydrogen chloride (hydrochloric acid) (pale yellow-colorless lig)	Immediate	Minutes to hours	22 104	Good	0.77 ppm - pungent, irritating	Corrosive liquid; Ore, other metal refining/ cleaning; food/pickling; petroleum;	#80	Not standard	 Cyanotic (blue skin from lack Oxy to blood) (e.g. from SO2, SO3, NO2, ethylene oxide): 	Broncospasm/Pulm Edema - Inhale corticosteroids - Beta2 agonist	
-	Hydrogen Cyanide (colorless-white-pale blue gas; liquid <75F)	Immediate	Minutes	7.0	Good	1-5 ppm- bitter/sweet almond-like	Weak acid except in water or mucous membranes – then corrosive/irritating; used as War gas, pesticide, Herbicide; other industries	#12L	Not Standard	Hemolytic anemia; kidney damage (Arsine) Additional Chemical Specific Symptoms:	Endotracheal intubation Hemolysis (e.g. Arsine): IV, transfusion	
-	Hydrogen fluoride (colorless gas/fuming liq)	Immediate & Delayed	Minutes to hours	24 44	Good	0.4 ppm - strong irritating	Corrosive liq; Aluminum and other metal industries; insecticide manufacturing-	#17	Not standard	pink/froth sputum: Ammonia mucoid frothy sputum: SO2,SO3,	Seizures: - Diazepam	
-	Hydrogen selenide (colorless gas)	Immediate	Minutes - Hour	0.2	Poor	0.3 ppm- decayed horseradish	Highly flammable/explosive; can cause burns/frostbite; decomposes rapidly to form elemental selenium Metals &semiconductor prep;	Not available	Not standard	peculiar taste: Ethylene oxide asphyxia: Acrylonitrile metal taste & or garlic breath:Hydrogen Selenide		
-	Hydrogen sulfide (colorless gas)	Immediate & Delayed	MINUTE S to hours	30	Good	0.1 ppm -rotten egg	Disinfectant lubricant/oils; interm for HC manufacture; deadens sense of smell	#44	Not standard	,	See page 2	

Simultaneous Recovery with 'Absolute Specificity' in Mixture

Chemical	Rate of Onset	Persists in Environ ment	Toxicity Thresholds (ppm/hour impairment	BDO/ Mask Effective	Odor	Source/ Use/other hazard	Field D	etection 205Aseries Miran	Symptoms (from inhalation and dermal contact	Decontamination and Treatment
Methyl hydrazine	Immediate & Delayed (LUNGS)	Hours - days	fatality	Poor?	1 –10 ppm- ammonia like	Irritating vapors; Flammable- Once ignited continues to burn; Used as solvent, rocket fuel;	#185	Not standard	General Mild Health Effects: - Nausea, dizziness; headaches; chills; coughing, choking, throat irritation Specific and More Severe Effects: Eyea: - Irritation; tearing/watering; pain; intolerance to light (e.g. from Hydrogen Sulfide) Skin (particularly if liquid contact): - Irritation; burning; blisters (eg with Hydrogen Fluoride);	Decontamination: - Flush (15 min) eyes & skin with water; - Soap optional after initial water rinse Treatment & Diagnostic procedures/ options: Eye injuries: - Saline wash - Antibiotic ointments Skin burns/blicters/irritation - topical corticosteroids and/or antihistamines - Inject MgSO4 at affected site (Hydrogen fluoride) Breathing/respiratory distress: - Oxygen & ventilation - Prophylactic antibiotics - Xrays - Pulse ox/blood gas NOTE: avoid mouth to mouth to mouth to protect against cross contamination Broncoapaam/Pulm Edema - Inhale corticosteroids - Beta2 agonist - Endotracheal intubation Hermolysis (e.g. Arsine): IV, transfusion Seizures: - - Diazepam
Hydrazine Colorless, oil (fuming) liquid/waxy solid or crystals	Immediate & Delayed (LUNGS)	Hours - days	13 35	Poor?	3-4 ppm- Ammonia -like	Flammable- Once ignited continues to burn; irritating vapors; Used as solvent, rocket fuel;	#3D (Dosi)	Standard		
Methyl isocyanate (colorless liquid)	Immediate	Minutes to hours	0.5	Poor	2.1 ppm -sharp pungent	Intermediate in manufacturing; reacts with H20 (don't use in fire)	Not available (liquid)	Not standard (liquid)		
Methyl mercaptan (colorless gas; liquid <43F)	Immediate	Minutes to hours	5.0 23	Poor	0.002 ppm- rotten cabbage (1 ppm odor fatigue)	From decayed organic matter – pulp mills, oil refineries; highly flammable; liquid burns/frostbite	#71	Not standard		
Nitrogen dioxide (colorless gas/pale liq)	Delayed (24-72 hrs)	MINUTES to hours	12 20	Poor	1 ppm - ?	Intermediate for manuf of nitric acid & sulfuric acid; explosives/rocket propellant	#9D (Dosi)	Not standard	acid); dermatitis; and frostbite (e.g. Acryonitrile)	
Nitric Acid (colorless, yellow, or red fuming liquid)	Immediate	Hours- days +	4.0 22+	Poor	~1 ppm- Choking, sweet – acrid	Used in many industries; Very corrosive to skin/mucous membranes as well as metals & other materials;	#80	Not standard	Respiratory Tract/Lungs: - Breathing difficulty.respiratory distress; laryngeal spasm (e.g., from hydrogen bromide); pulmonary edema Cheat/Heart: - - chest pain; tachardia (rapid heartbeat) Systemic; Blood - - Cyanotic (blue skin from lack: Oxy to blood) (e.g., from SO2, SO3, NO2, ethylene oxide): - Convulsions/seizures - Hemolytic anemia; kidney damage (Arsine) (sulfurio acid, hyrdazine) Additional Chemical Specific Symptoms: pink/froth sputum: Ammonia mucoid frothy sputum: SO2,SO3, SO2 peculiar taste: Ethylene oxide aphyxia: Acrylonitrile metal taste & or garlic breath: Hydrogen Selenide Miosis, sweating, U ACHe	
Parathion (pale yellow to brown liquid)	Immediate but often Delayed (weeks)	Days to weeks	0.2 0.8	Good	0.04 ppm	Organophosphate (insecticide); similar symptoms (and thus treatment) as nerve gases; penetrates leather/canvas and plastics/rubber coatings	Not Available (liquid)	Not Available (liquid)		
Phosgene (colorless – light yellow gas)	Immediate & Delayed (LUNGS)	Minutes - HOURS	0.3	Good	0.5ppm- musty hay	Dye, pesticide, and other industries; history as war gas, corrosive/irritating	#16	Standard		
Phosphine (colorless gas)	Immediate & Delayed (LUNGS)	Minutes- hours	0.3	Good?	0.9 ppm- rotten fish, garlic	Insecticide; used in manufacture of flame retardants and incendiaries;	#7LA	Not Standard		
Sulfuric Acid (clear colorless- brown oily liquid)	Immediate	Hours, days	2.5	Good	Odorless (acrid taste)	Toxic fumes when heated Battery/dyes/paper/glue/metals industries; volcanic gas;	Not available (liquid)	Not Available (liquid)		
Sulfur dioxide; sulfur trioxide; -form sulfuric acid (colorless gas)	Immediate & Delayed	MINUTES to hours	>3	Good (SO2); Marginal (SO3)	1 ppm; pungent; metallic taste	Disinfectant and preserving in breweries and food/canning; textile industry; batteries	# 5L	Standard		
Toluene diisocyanate (2,4) (water-white to pale vellow liouid, or crystals)	Immediate	Hours - weeks	0.08	Good	0.4-2 ppm- sharp pungent	Skin irritant Polyurethane (wood coatings, foam), nylon industries;	Not Available (liquid)	Not Available (liquid)		

How are the requirements for an absorption spectrometer different from those of a network analyzer?

Previously discussed: frequency agility software strategy spectral recognition

To follow: noise dynamic range

Small Absorption vs. Small Signals Special Considerations for System Design (How do we differ from a network analyzer?)

1. There are new fundamental noise sources that are typically orders of magnitude greater than the receiver noise (a 10⁵ effect).

2. There are systematic non-white noise sources resulting from standing waves that need to be suppressed and signal processing schemes based on the narrowness of the spectral lines implemented (a 10⁶ effect).

3. Strategies need to be implemented so that excessive digitization are not required to recover 10⁻⁷ fractional absorptions.

4. Fundamental misconceptions about white noise in the submillimeter exist (a 10¹⁰ effect).

Townes Noise in Absorption Spectrometers

Assume that we have a probe power (carrier) of P_{p} . Then in a waveguide of impedance *Z*, the voltage associated with this probe power is

$$V = \sqrt{2ZP_p}$$

Similarly, the noise voltage associated with the thermal radiation is

$$\Delta V = \sqrt{4ZkT\Delta\nu}$$

Townes Noise

The net power flow is then

$$\frac{\left(V \pm \Delta V\right)^2}{2Z} = P_p \pm 2\sqrt{2kT\Delta v} P_p + 2kT\Delta v$$

Because P_p is typically many orders of magnitude greater than the thermal power, the cross term dominates the noise in a system designed to observe a small change in P_p .



System Numbers

For a receiver noise temperature $T_N = 3000$ K and $b = B = 10^6$ Hz, $P_N = 5 \times 10^{-14}$ W.

If we have a carrier power of $P_c = 1$ mW, we must also consider the noise associated with the adding of the blackbody noise *voltage* with the carrier. For this case

 $\frac{P_c}{P_N} \sim 10^{10}$

$$P'_n \approx \sqrt{kT\Delta\nu P_c} = \sqrt{(5\times10^{-14})(10^{-3})} \approx 10^{-8} W$$
 Five

Five Orders of Magnitude

This is about five orders of magnitude above the receiver noise.

The system S/N is then

$$S/N = \frac{P_c}{P_N'} \sim \frac{10^{-3}W}{10^{-8}W} \sim 10^5$$

This is the impact of the so called 'Townes Noise'.

Impact is only large when we are looking to detect a small change in a large P_c

The THz is VERY Quiet even for CW Systems in Harsh Environments



Noise, detectors, and submillimeter-terahertz system performance in nonambient environments

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Received June 23, 2003; revised manuscript received February 10, 2004; accepted March 10, 2004

All noise from 1.6 K detector systemm

Cell Phone Architecture and Gas Sensors

Conceptually Multiply or Up/Down Convert Cell Phone Technology to 200 – 300 GHz

Synthesizer

Spectral Purity Frequency Sweep and Agility FM modulation

IF amplifier Bandwidth 1 – 10 MHz Phase sensitive demodulation at FM modulation frequency Dynamic range

[6] 2008: 130nm 9mm² Bluetooth SoC (Atheros)

- Bluetooth v2 (EDR): GFSK (1Mb/s), QPSK (2Mb/s), 8PSK (3Mb/s)
- Calibration needed for the two-point frequency modulator of the analog polar TX





Current System-relation to cell phone





Rashaunda Henderson



Figure 2, 200-220 GHz frequency generator using a fractional-N synthesizer.

Fig. 5. Two-step heterodyne down conversion architecture for the spectrometer receiver. The first down conversion is performed using an APDP sub-harmonic mixer to an IF of around 100 GHz.



Dynamic Range



The problem: detect a molecular absorption of width 1 MHz that is 1/10⁷ of total power against a baseline that varies by 1/10 over 500 MHz and 1/1.5 over 10 GHz

Strategy 1: Use 'AC' coupling to roll of the more slowly varying baseline.

Strategy 2: Use FM modulation f at ~50 kHz with a deviation of ~1 MHz that modulated the narrow line, but not the broader baseline features.

Specific Implementation: Modest IF gain, followed by detector, followed by narrow band amplifier at f or 2f.







Submillimeter Sensors of Static Samples Summary

• Dominates a significant portion of spectroscopic sensor space

- Absolute specificity
- Extremely small samples with good sensitivity
- Favorable trades of sensitivity for speed (agility of electronic synthesis)

Clear path to small and inexpensive implementations

- Electronic synthesis
- Wireless technology and CMOS
- Small sample requirements allow less elaborate vacuum systems

Challenges and opportunities

- Limits on applicability to larger molecules unclear bounds
- Vacuum strategies
- Not a mature technique
- Significant up side potential fundamental limits very favorable
- Still a steep curve between proven capability and research effort (good? bad?)