Headspace Analysis of Volatile Compounds Using Segmented Chirped-Pulse Fourier Transform mm-wave Spectroscopy

Brent J. Harris, Amanda L. Steber, and Brooks H. Pate
Department of Chemistry
University of Virginia
# Instruments for Spectroscopy

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Molecular Energy Levels</th>
<th>Commercial Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF (&lt;1 GHz)</td>
<td>Nuclear Spin in Magnetic Field</td>
<td>NMR, MRI</td>
</tr>
<tr>
<td>MW (9-90 GHz)</td>
<td>Electron Spin in Magnetic Field</td>
<td>EPR/ESR</td>
</tr>
<tr>
<td>MW-THz (2-2000 GHz)</td>
<td>Overall Molecular Rotation</td>
<td>NONE</td>
</tr>
<tr>
<td>IR (100-4000 cm(^{-1}))</td>
<td>Molecular Vibration</td>
<td>FTIR, NDIR, Diode laser</td>
</tr>
<tr>
<td>UV-VIS (100-800 nm)</td>
<td>Electronic Excitation</td>
<td>Fluorimeters, Imaging, LIBS, Raman microscopy</td>
</tr>
<tr>
<td>X-rays (&lt; 100 nm)</td>
<td>Inner Core Electron Excitation</td>
<td>X-ray emission for chemical analysis</td>
</tr>
</tbody>
</table>
“The Routine Rotational Spectrometer”

1) Competitive performance metrics

2) Benchtop operation, low sample consumption, no consumables or cryogens

3) Multispecies analysis (broadband spectrum)
Chirped-Pulse Fourier Transform for Room-Temperature Gases

Why millimeter-wave?

Effect of temperature

Effect of molecule size/mass

260-295 GHz best window for high power sources and 3-5 heavy atom, room-temperature, volatiles
CP-FTmmW Spectrometer

Block schematic and segmented waveform

1) 12GS/s, 12 bit Arbitrary Waveform Generator for custom excitation, local oscillator waveforms

2) 45 mWatt Peak Power, High Bandwidth Active Multiplier Chain

3) 4GS/s High Speed Digitizer with FPGA Signal Accumulation (16M averages)
Segmented CP-FTmmW

Segmented
(lowers performance requirements for digitizers)

Chirped Pulse
(add instantaneous bandwidth to utilize entire source power)

Fourier Transform
(relieve pressure broadening in digital signal processing)
(enhance analysis with time resolved analytical tools)

Near 100% duty cycle

Noise Level: 0.002 mV
1L Chamber Volume
160 fmol detection
Partial Pressure: 3 nTorr
8 minutes
$^{18}O{C^{36}S} (1 : 3.4$ million)

1) Sampling Directly from Air
Max Cell Pressure: 100 mTorr (collisional broadening)
Detection Limit: 30 ppb (good, similar to CRDS)

2) Gas Processing to Isolate Volatiles
Gas Sample: 1 L-atm
Total Volatiles less than 100 mTorr
Detection Limit: 4 ppq (excellent)

For a large number of volatiles, segmented CP-FT offers sub-ppb detection limits in a 10 minute broadband measurement with gas processing.
4(5)-Methylimidazadazole

Unknown impurity – Prediction does not match

\[ \text{Intensity (mV)} \]

\[ \text{Frequency (MHz)} \]

5 mTorr total pressure

\[ \text{Experiment} \]

\[ \text{4-methylimidazole computation} \]

\[ \text{P}_{\text{vap}} = 0.007 \text{ Torr} \]
4(5)-Methylimidadazole

Identification of unknown

A search for low molecular weight, common synthesis solvents

“Submillimeter wave spectrum of acetic acid”

Glacial acetic acid residual solvent identified with pure reference spectrum

Melt solid to evaporate solvents and analyze purified crystals
Mixture analysis - Solutions

EPA VOC mix 6: 2000 µg/mL each component in methanol Analytical standard

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Mass (amu)</th>
<th>Henry's Law Constant (atm m³/mol)</th>
<th>Net Dipole Moment</th>
<th>S/N 100mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloromethane</td>
<td>ClCH₃</td>
<td>50.49</td>
<td>8.82E-03  b</td>
<td>1.9 e</td>
<td>26,000:1</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>ClCH₃CH₃</td>
<td>64.51</td>
<td>1.11E-02  b</td>
<td>2.1 e</td>
<td>6000:1</td>
</tr>
<tr>
<td>Bromomethane</td>
<td>BrCH₃</td>
<td>94.94</td>
<td>6.24E-03  c</td>
<td>1.8 f</td>
<td>6000:1</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>ClCHCH₂</td>
<td>62.50</td>
<td>2.70E-02  c</td>
<td>1.5 e</td>
<td>5000:1</td>
</tr>
<tr>
<td>Dichlorodifluoromethane</td>
<td>Cl₂F₂C</td>
<td>120.91</td>
<td>2.25E-01  c</td>
<td>0.5 e</td>
<td>25:1</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>Cl₃FC</td>
<td>137.37</td>
<td>9.70E-02  d</td>
<td>0.5 e</td>
<td>35:1</td>
</tr>
<tr>
<td>Methanol a</td>
<td>CH₃OH</td>
<td>32.04</td>
<td>4.55E-06  c</td>
<td>1.7 e</td>
<td>7000:1</td>
</tr>
</tbody>
</table>

a) Diluent  
c) USEPA, Industrial Environmental Research Laboratory, Cincinnati, OH, USA, 1982.  
Mixture analysis - Solutions

Unbiased Search
Components well resolved
Spectral redundancy
Isotopic ratios
2 minutes to acquire
## Linearity and LDL

![Graphs showing linearity and LDL](image)

### Table 3.4: Detection Limits in Water

<table>
<thead>
<tr>
<th></th>
<th>Broadband (5min, µg/L)</th>
<th>Target Mix (10min, µg/L)</th>
<th>EPA 524.2 60 min (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloromethane</td>
<td>5.0</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Bromomethane</td>
<td>22</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>26</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>42</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Dichlorodifluoromethane</td>
<td>100,000</td>
<td>1000</td>
<td>0.1</td>
</tr>
<tr>
<td>Trifluorochloromethane</td>
<td>100,000</td>
<td>1000</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Regulation Limits for Residual Solvents: 10-1000 µg/L
Conclusions

1) Segmented CP-FT mmW provides high sensitivity broadband detection of volatiles.

2) In favorable cases, headspace detection has a sensitivity that rivals GC/MS.

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