Prototype coded aperture miniature mass spectrometer using a cycloidal sector mass analyzer, a carbon nanotube (CNT) field emission electron ionization source, and an array detector

11th Harsh-Environment Mass Spectrometry Workshop
2017-09-21

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• **CAMMS-ES**: Coded Aperture Miniature Mass Spectrometer for Environmental Sensing

• Traditional miniature mass spectrometers suffer from a throughput vs. resolution tradeoff

• CAMMS-ES employs coded apertures to break this throughput vs. resolution tradeoff

• CAMMS-ES will enable the production of portable instruments with high sensitivity and resolution
ARPA-E MONITOR

- Methane Observation Networks with Innovative Technology to Obtain Reductions (MONITOR) program is developing innovative technologies to cost-effectively and accurately locate and measure methane emissions associated with natural gas production.

CAMMS-ES

- Portable mass spectrometer with high resolution and high sensitivity for VOC leak detection
  - Detection of not only methane, but other compounds of interest including
    - Butane, propane, ethane, benzene, ethylbenzene, toluene, xylene
    - Thermogenic/biogenic differentiation using higher order alkyl chains

- Applications
  - Ad hoc leak detection at refineries
  - Fence line monitoring at refineries
People have been trying for 60 years!

Mass spectrometry

Out of the laboratory...into the plant

Cycloidal mass analyzer advertisement in 1956 issue of Analytical Chemistry

CEC's two companion instruments...Types 21-610 and 21-620...have taken mass spectrometry out of the purely laboratory-instrument class and made the inherent speed and accuracy of this analytical method practical for industrial use. As a process-stream analyzer, the mass spectrometer is exceptionally versatile, provides stream-composition information on the spot for regulating plant start-up procedures, optimizing operations and products, and minimizing process interruptions.

SEVERAL MODES OF OPERATION

Both 21-610 and 21-620, together with available accessory systems, work on either a batch or continuous basis: permit...

- continuous determination of a single component
- alternate determination of several components
- automatic scanning of a complete spectrum
- programming up to six mass numbers for automatic, repetitive monitoring
- alternate monitoring of more than one process stream through automatic manifolding, valving, and timing systems.

APPLICATION...INSTALLATION

CEC's Application Engineers offer without charge experienced help in fitting the mass spectrometer to your specific application. In addition, all mass spectrometers are installed and put into initial operation by a skilled CEC Field Service Engineer. Send today for Bulletin CEC 1825B-X.

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Our 4 technologies will finally make this possible!
Four Enabling Miniaturization Technologies

Aperture Coding: increased throughput, no loss in resolution

Microfabricated CNT field emission ion source
Cycloidal mass analyzer
Focal plane array detector
What is Aperture Coding?

- Conventional instruments act as sorters
- Input is sorted via a system architecture and relevant physics
- In the absence of sorting the system throughput is large, however no information can be inferred
- In a conventional system, the architecture is designed using the relevant physics to achieve near perfect sorting
  - Spectra can be obtained via a simple calibration of the sorting parameter
  - Architecture choices limit performance and

Aperture coding breaks the throughput vs. resolution tradeoff
Coded Aperture Sector

**No Sorting**
- Input Ions
- B
- Detector
- No Inference
- No information

**Perfect Sorting**
- Input Ions
- B
- Acceleration Grid
- Detector
- Direct Inference
- Spectrum (wavelength, mass/charge, etc.)

**Coded Sorting**
- Input Ions
- B
- Acceleration Grid
- Detector
- Computational Inference
- Spectrum (wavelength, mass/charge, etc.)
Aperture coding works in a simple 90-degree sector

Matrix method shows excellent pattern mapping with demagnification
COMSOL/particle tracing shows good pattern mapping with similar demagnification and distortion of larger aperture patterns due to sector width
Experiment showed transfer of pattern, however modifications are necessary to reduce the effects of fringing fields at the entrance and exit of the sectors.
The distance along this $x$-axis, known as the pitch, is described by the following equation:

$$a_i = \frac{m_i}{q} \frac{2\pi E}{z B^2}$$

- $a_i$ = distance along $x$-axis
- $E$ = electric field strength
- $B$ = magnetic field strength
- $m_i$ = mass of ion
- $q$ = charge on ion
- $d$ = position of the aperture

*Compatible with aperture coding!*
Thermionic electron emission vs Field emission: Why CNTs?

### Thermionic Emission

- **Stability**: Good
- **Pulsing**: No
- **Lifetime**: Short (1 month, no pulsing possible)
- **Power**: High (10 W)

### Planar Field Emission

- **Stability**: Fluctuating
- **Pulsing**: Yes
- **Lifetime**: Long (1 year of pulsed operation at operating pressure)
- **Power**: Low (<2 mW)

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**Diagram:**
- **Thermionic Emission**
  - Work function
  - Vacuum Level
  - E_Fermi
  - Distance

- **Planar Field Emission**
  - Work function
  - Vacuum Level
  - Effective Barrier
  - Distance

- **Micro-tip field Emission**
  - Work function
  - Vacuum Level
  - Effective Barrier
  - Distance
High pressure ($1 \times 10^{-4}$ Torr room air) lifetime

Pulse Parameters:
- 2 sec ramp
- 10 sec ON
- 8 sec OFF
- Total: $>11,000$ pulses

Continuous operation: $>300$ hours


CNT field emission electron source and ionization volume
1. Vacuum manifold
2. NiFeB permanent magnet
3. Electric sector
4. Electric sector guide
5. Detector
6. Heat rejection block and thermoelectric device
7. Heat pipe
8. Ion source
9. PC Board vacuum feedthrough

10. Inlet feedthrough
11. Cross flow fan
12. Thermoelectric device and electric sector control
The mass range and resolving power of CAMMS-ES depends on the electric and magnetic field magnitudes and the width, pixel size, and position of the detector relative to the ion source.

\[ a_i = \frac{m_i}{z} \frac{2\pi E}{B^2} \]

\[ L = \frac{B^2 d z}{2\pi E} \]

\[ R = \frac{s L}{d} = \frac{s z B^2}{2\pi E} \]

\[ a = \frac{m s}{R} \]

\( a = \) pitch
\( L = \) mass range
\( R = \) resolving power
\( d = \) detector length
\( s = \) detector pixel size
\( B = \) magnetic field
\( E = \) Electric field
\( m = \) mass
\( z = \) charge
Capacitive transimpedance amplifier detector array

Each detector finger has a separate preamplifier, logic, and sample and hold on the custom IC

4 gain levels
Each pixel gain can be set individually

Custom CMOS integrated circuit
3.3 V, 0.35 µm process

Detection limit ~5 ions, dynamic range $10^{11}$: Sensitivity approaching Multichannel plate and dynamic range of a Faraday cup.

Results

(a) Mass spectrum of a mix of 50% argon and 50% dry air using a 50 µm slit

(b) Coded mass spectrum of a mix of 50% pure argon and 50% dry air using a 50 µm element size

Imaging not ideal due to alignment, field uniformity
Simple calibration/reconstruction

• Previously, a sophisticated calibration process was required as field nonuniformity and other system imperfections limited the ‘perfect focusing’ performance of the instrument.

• With the current generation, performance is sufficiently good that we can use a very simple calibration process to validate operation (we ultimately will want an advanced approach to maximize performance; but will do that for next prototype).

• Remember that with perfect focusing, the measurement can be written as the convolution of the system response with the input spectrum:

\[ m = r \ast s \]

• We can estimate the system response (calibrate the system) by deconvolving the true spectrum from the acquired measurements:

\[ r = \mathcal{F}^{-1} \left[ \mathcal{F} [m] / \mathcal{F} [s_{\text{NIST}}] \right] \]
• Extract central region (other are artifacts resulting from system imperfections) as estimated system response. Results have expected structure

• Spectral reconstruction then performed by deconvolving acquired measurements by estimate of system response 
  \[ \text{system} \left( \mathcal{F}^{-1} \left[ \mathcal{F}[\text{meas}] / \mathcal{F} \left[ \hat{r} \right] \right] \right) \]
Spectral reconstruction

>10x increase in signal and improved resolution
## Performance Summary

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Resolving power (FWHM)</th>
<th>Throughput gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal cycloid with 50 µm slit</td>
<td>0.05 amu</td>
<td>n/a</td>
</tr>
<tr>
<td>Lab prototype with 50 µm slit</td>
<td>0.31 amu</td>
<td>1</td>
</tr>
<tr>
<td>Lab prototype with Reconstructed 50 µm slit</td>
<td>0.18 amu</td>
<td>1.67</td>
</tr>
<tr>
<td>Lab prototype with Reconstructed S-11 coded aperture</td>
<td>0.11 amu</td>
<td>10.4</td>
</tr>
</tbody>
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Mass spectrometer miniaturization at Duke, U of A, and RTI

Current Prototype
Future Prototype

Funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0000546. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Support from DARPA INVEST Award -1-340-021530652548L
Traditional H-shaped magnet assembly

Field not of sufficient uniformity for coded aperture imaging
Our new magnet assembly

Field varies by <1% along the ion trajectories = good aperture imaging
Traditional Electric sector geometry

Relatively poor imaging quality due to field non uniformity around the ion source
Improved electric sector configuration

Placing the ion source between adjacent electrodes and making the top and bottom half different potentials improves field uniformity and aperture imaging.