A Statistics Problem from Spectroscopy that Hints of Compressive Sensing

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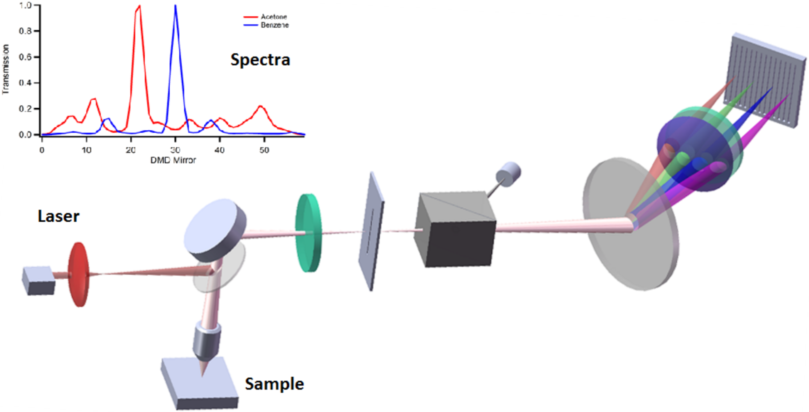
Raman Spectroscopy

- Illuminate chemical sample with laser (**single frequency**).
- Photon absorbed by molecular bonds. Molecule gives off photon.
- Very rarely, molecule gives off a photon of a **different** frequency ($\Rightarrow$ Nobel prize for Raman).
- Photons given off from that sample have a characteristic distribution of energies, the **spectrum**.
- A spectrum can be interpreted as a **probability distribution**.
- The photons with different energies can be **separated physically**, like a prism separates colors in the rainbow.

Experimental Setup



Mathematical Model—Poisson Process

Quantum mechanics $\Longrightarrow$ **photon emission** is modeled extremely accurately by a **Poisson process**, which is a **counting process** $N(t)$, where $N(t)$ is the number of discrete **events** that happen in the interval $[0, t]$, with $N(0) = 0$.

$N(t)$ satisfies the following:

- Distribution of $N(t+h) - N(t)$, $h > 0$, is **independent of** t**.**
- The random variables $N(t_j') - N(t_j)$ are **mutually independent** if $\bigcap_j [t_j, t_j'] = \emptyset$.
- $P[N(t+h) - N(t) > 1] = P[N(h) > 1] = o(h)$ as $h \to 0$.
- Some technical assumptions.

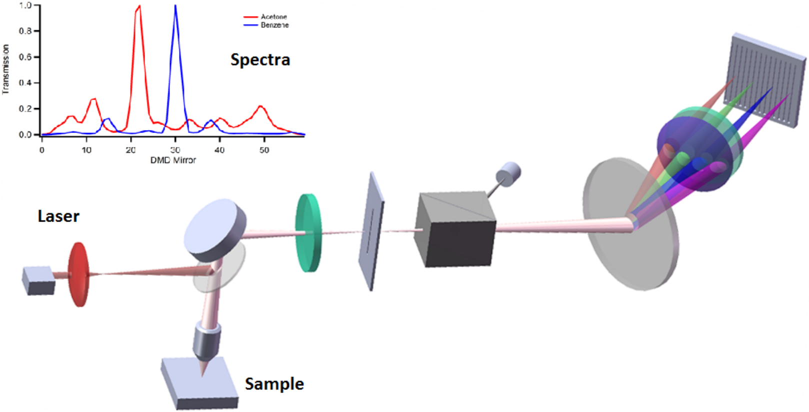
Mathematical Model—Poisson Distribution

Properties of Poisson process $\Longrightarrow$

- There is a $\lambda \geq 0$, known as the **rate constant** such that the distribution of $N(t+s) - N(s)$ has a **Poisson distribution** with parameter λt:

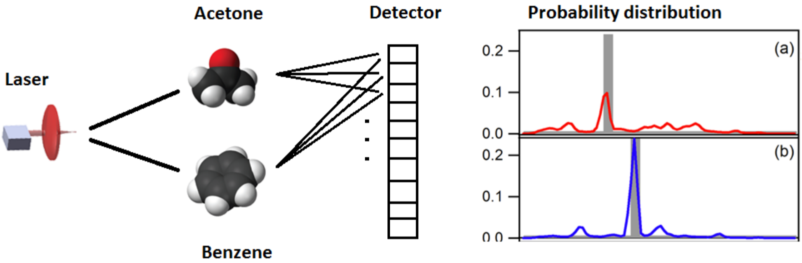
$$E[N(s+t) - N(s)] = \mathrm{Var}[N(s+t) - N(s)] = \lambda t.$$

Experimental Setup (again)



The Game

- We have a list (< 30) $S_1, S_2, \ldots, S_n$, of n **known possible chemicals**.
- The **energies of the photons** in the spectrum of each of these chemicals can be divided into N **bins**.
- We want to estimate **the rate** Λ_j **at which photons are emitted from each chemical** S_j in the sample.
- Estimating the **rates** Λ_j can help us estimate the **concentrations**.



Measurements

Three kinds of measurements:

- Put **CCD array** under spread of photons, count how many hit each subarray (like **digital camera**).
- Put **micro-mirror array** under spread of photons, direct some energies **to a photon counter**, other energies **to a photon sink**.
- Put **spatial light modulator (SLM)** under spread of photons, direct a **fraction** of photons with each energy to a photon counter, other photons are **absorbed**.

CCD array has many small detectors, acting in **parallel**.
Micro-mirror array and **SLM** send photons to a **single detectpr**.
The **pattern** of which photon energies are sent to detector can be considered a **filter**.

Other Properties of Poisson Processes

- If you **randomly assign colors** to electrons according to a **fixed probability distribution**, then each stream of colored photons is a **Poisson process**.
- If, from a Poisson process with rate λ, you **randomly remove counts** with **fixed probability** p, the result is a **new Poisson process** with **rate** $\lambda(1-p)$.
- If you **add two independent Poisson processes** with rates λ_1 and λ_2, then the result is a **new Poisson process** with rate $\lambda_1 + \lambda_2$.

Noise Characteristics

CCD array:

- **Many** small detectors, read noise with **standard deviation about 8 photon counts** for **each energy bin**.

Micro-mirror array/SLM and photon counter:

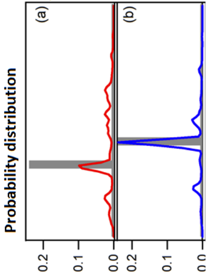
- **One** high quality detector, **no** read noise.

In **low signal** environment **micro-mirror array wins**.

In particular, for **short time** measurements, **micro-mirror array wins**.

Matrix:

$$P = \left(\begin{pmatrix} P_{11} \\ \vdots \\ P_{i1} \\ \vdots \\ P_{N1} \end{pmatrix} \quad \cdots \quad \begin{pmatrix} P_{1n} \\ \vdots \\ P_{in} \\ \vdots \\ P_{Nn} \end{pmatrix} \right) =$$



Column j is the **normalized spectrum** of chemical S_j.

P_{ij} is the **probability** that the energy of a photon **emitted by chemical S_j will land in energy bin** i.

P is **known** from long-term measurements.

Measurement Model

- $\Lambda = (\Lambda_1, \ldots, \Lambda_n)^T$ is the **vector of rates** of photon emission by the chemicals $S_1, \ldots, S_n$ in the sample.
- **Rate** that photons hit the *i***th energy bin** is $(P\Lambda)_i$.
- We'll take M **measurements**.
- We take **measurement** k for **time** T_{kk}.

What is a Filter?

A filter basically **programs** or **determines** which photons to choose in a measurement.

- In measurement k, we pick a **filter** $F_k = (F_{1k}, F_{2k}, \ldots, F_{Nk})^T$ such that the **probability that a photon with energy** i **is sent to the photon counter in measurement** k is F_{ik}.
- For **spatial light modulators**, $0 \leq F_{ik} \leq 1$.
- For **micro-mirror arrays**, $F_{ik} = 0$ or 1.

Full Experimental Model

- Let the columns of the **matrix** F be the **vectors** F_k.
- **Normalize:** $\sum_k T_{kk} = 1$.
- Our **vector of measurements** $\hat{x}$ is independent **Poisson** with means **and variances**

$$T(F^T P)\Lambda,$$

  where $T = \mathrm{diag}(T_{kk})$.
- Let

$$\hat{\Lambda} = BT^{-1}\hat{x}$$

  be the **Best Linear Unbiased Estimator** of Λ given a vector of measurements $\hat{x}$.
- **"Unbiased"** means $E(\hat{\Lambda}) = \Lambda$ so $B(F^T P) = I$.
- **"Best"** has a particular statistical meaning that I won't explain.

Big Questions

How to design filters to best estimate Λ?

What does "best" mean?

Experimental Design Objectives

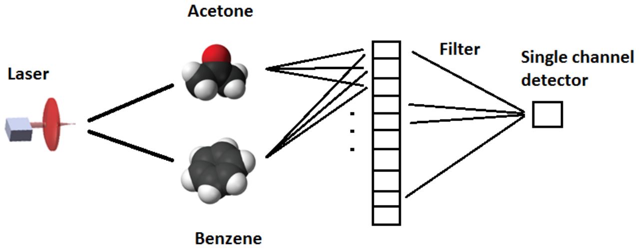
Choose:

- M, the **number of measurements**,
- the matrix $F = (F_{ik})$ of **transmittance filters**,
- the (Gauss–Markov) matrix B, and
- the matrix $T = \mathrm{diag}(T_{kk})$ of **measurement times**,

to **minimize**

$$\sum_j E(\hat{\Lambda}_j - \Lambda_j)^2.$$

Called **A-optimality** in **Optimal Design of Experiments**.



Computational Considerations

- **Non-convex** optimization problem on a **convex domain** D: Given a **design** $\bar{\Lambda}$ and P, find M, F, and B to minimize

$$\sum_{i=1}^{M} \|B\mathbf{e}_i\| \sqrt{(F^T P \bar{\Lambda})_i}$$

  subject to $B(F^T P) = I$, $0 \leq F_{ik} \leq 1$. Calculate T from F, P, and B. Optimal for this $\bar{\Lambda}$, good for other Λs.
- The **variance** of each measurement **depends on the filter**—the more photons you expect to collect in a measurement, the larger the variance. The standard analysis assumes that the variances of the measurements don't depend on the design.
- Still don't know how to solve problem efficiently in all cases.
- MATLAB does pretty well.

Partial Theoretical Results

Modified formulation:

- Can transform to **convex** optimization problem on a **non-convex domain** $\tilde{D}$.
- The **optimum** solution on the **convex hull of** $\tilde{D}$ is the **same as the solution to the original problem**.
- Still don't know how to solve it efficiently.

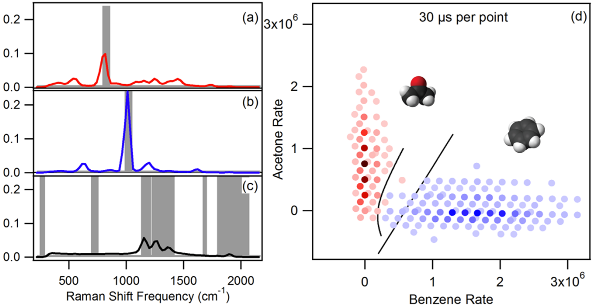
Standard:

- The **optimal** M satisfies $n \leq M \leq n(n+1)/2$.
- If you have the **optimal** M, then **the optimal** F_{ik} satisfy $F_{ik} = 0$ or 1; i.e., **micro-mirror arrays are optimal**.

New:

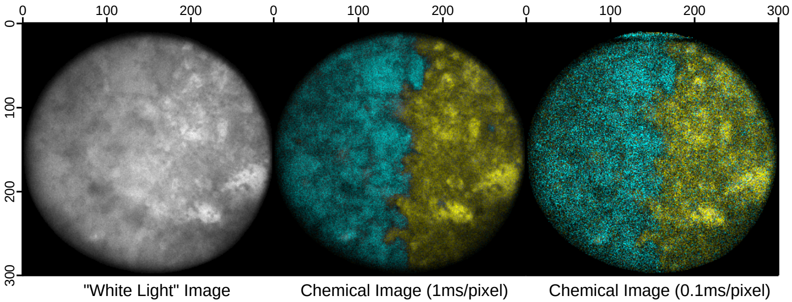
- If you **don't have** the optimal M, then **the optimal** F_k **for that** M can be chosen with **at most** $n-1$ components not equal 0 or 1 (so **micro-mirror arrays are near optimal**).

Example: Distinguish Benzene from Acetone in 30μs



- **Left:** Spectra. **Right:** Estimated Λ for pure solutions.
- **Grey bars:** Where mirrors are **on**, i.e., $F_{ik} = 1$.
- **Mean Photons emitted:** < 50. **Experiments:** 2,000.
- **Measurement times:** 15.867μs, 12.585μs, and 1.548μs.

Example: True Chemical Imaging



- **Cyan:** Glucose. **Yellow:** Fructose.
- **Left:** "White light" image.
- **Middle:** 1ms/pixel, 90s/image.
- **Right:** 0.1ms/pixel, 9s/image; ~30 photons measured/pixel.

Moral

Applied mathematicians and chemists need more statistics.

References

- *Photon Level Chemical Classification using Digital Compressive Detection*, by David S. Wilcox, Gregery T. Buzzard, Bradley J. Lucier, Ping Wang, and Dor Ben-Amotz, Analytica Chimica Acta, **755** (2012), 17–27.
- *Digital Compressive Quantitation and Hyperspectral Imaging*, by David S. Wilcox, Gregery T. Buzzard, Bradley J. Lucier, Owen G. Rehrauer, Ping Wang, and Dor Ben-Amotz, Analyst, **138** (2013), 4982–4990