# Investigation of Biological Fingerprints Using Atmospheric Solid Analysis Probe Mass Spectrometry (ASAP-MS)

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**Sandia National Laboratories, Albuquerque, New Mexico, Unlimited, Unclassified Release.**

## Overview

**Purpose:**

- **Develop a rapid mass spectrometric method to identify complex systems of solid materials.**
- **As examples, pollens represent diversity and complexity.**

**Methods:**

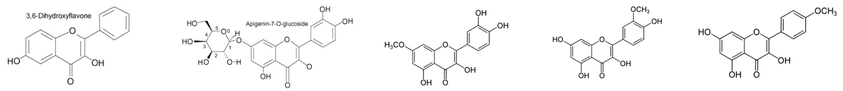
- **Atmospheric Solid Analysis Probe Mass Spectrometry (ASAP-MS):**
  - **direct analysis without time-consuming sample preparation**
  - **results in two dimensional temperature-spectra profiles**
  - **soft ionization for easy mass interpretation**

**Results:**

- **Specific two dimensional temperature-mass spectra profiles**
- **Specific flavonoid fingerprints**

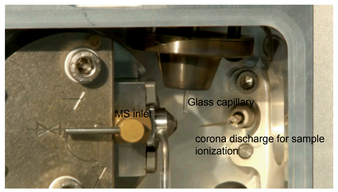
## Introduction

- Pollens contain a wide variety of chemicals, including carbohydrates, organic acids, carotenoids, flavonoids, phosphate lipids, and proteins. Identification of pollen via chemical fingerprint has been an area of research interest for many years.
- From allergies to reproduction, pollens have important impacts, on the health of human and plant populations, respectively, yet identification of pollen grains remains difficult and time-consuming.
- pyrolysis-gas chromatography/MS (Py-GC/MS) is only able to identify volatile and semi-volatile compounds.
- Plants, including pollens, possess a wide variety of flavonoids.
- Flavonoids may be distributed in a variety of isomers.




## Methods

1. Collection of pollens or pollen grains.
2. Mortars and pestles were used to break apart pollen pellets before analysis.
3. Attach the powders to the glass capillaries,
4. Hot nitrogen gas was used to thermally degrade pollens.
5. Temperature dependent mass spectrometry was obtained with the gradually increased temperature.
6. Low energy collision fragmentation was used to identify the mixture and their structures.




**ASAP-MS setup**

## Advantages

- Spectral pattern recognition methodologies assure only **positive** identifications
- Rapid and straightforward analysis with **reproducibility** and **accuracy**
- **Sensitive, Selective, and ease of mass interpretation**

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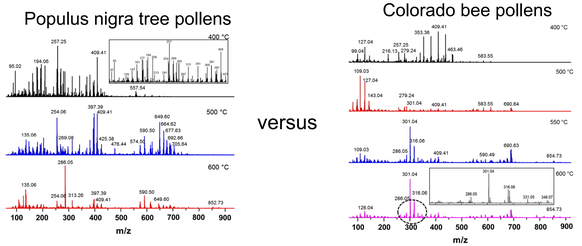
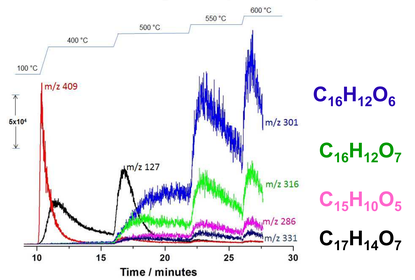
## Results and discussion

### 1. Specific two dimensional temperature-mass spectra profiles



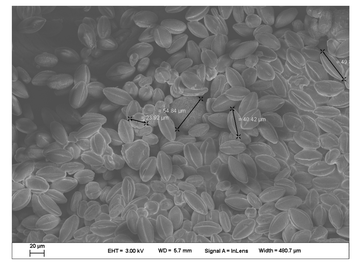

Temperature dependent mass spectra from thermal desorption of *Populus nigra* tree pollens (left) and Colorado bee pollens (right).

### 2. Low and high temperature products

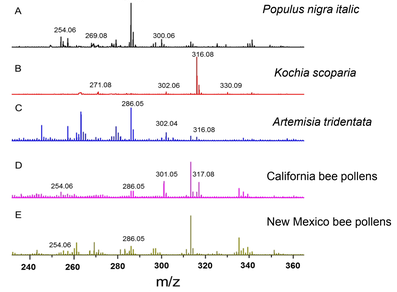



The production rates and the ratio of flavonoids

### 3. SEM image of Colorado bee pollens

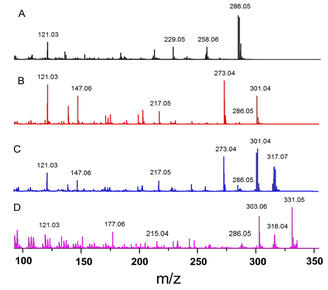


### 4. Specific flavonoid fingerprints



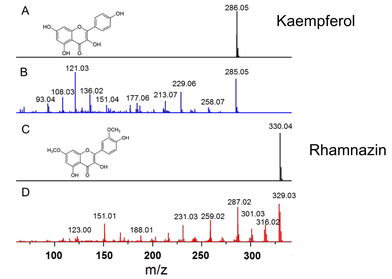

A mixture of flavonoids is obtained for each individual different pollens

### 5. Flavonoids are structurally related




Low energy collision fragmentation reveals structural relationships and backbone similarity

### 6. Low energy collision fragmentation




Standard flavonoids fragmentation is used for structural identification

## Conclusions

- ✓ ASAP-MS is demonstrated to be a powerful tool for rapid fingerprinting of pollen samples. With ambient pressure ionization, we were able to identify distinct flavonoid signatures for pollens, yet pollen samples were analyzed directly, eliminating sample extraction steps requisite for other MS platforms such as gas or liquid chromatography MS. Upon thermal desorption, pollens produce a wide variety of chemicals, which are temperature dependent and specific to the type of pollens. The mass charge ratio (m/z) region ranging from 250 and 400 is complex due to the production of flavonoids, including their isomers. The masses, along with their relative mass intensities, generate specific fingerprints allowing for identification of pollens.
- ✓ Pollen flavonoids are shown as molecular radicals in our ASAP-MS, confirming soft ionization and ease for molecular interpretation. Low-energy collision induced fragmentation experiments were simultaneously performed for the flavonoid mixtures to identify their structural relationship.
- ✓ Increasing the throughput of pollen identification has implications for many fields including public health, agriculture, and ecology, and will allow for monitoring of changes in pollen densities and assessment of regional changes in plant populations via windborne and bee-borne pollens.
- ✓ We expect that ASAP-MS can also be developed as a simple, direct, and cost-effective technique for obtaining fingerprints for other biological entities such as bacteria and viruses.

## Manuscript to be submitted

## Acknowledgements

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