

Development of an atmospheric monitoring mass spectrometer for universal real-time applications

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Overview

- Mass spectrometer designed for real-time atmospheric monitoring
- Demonstrated applications:
 - plant metabolism
 - bioenergy production



Fig. 1. Automated prototype real-time atmospheric monitoring mass spectrometer.

Introduction

Successful application of real-time atmospheric mass spectrometry (MS) relies on selection of a sampling rate that provides desired sensitivity and dynamic range while accounting for dilution factors and pressure variations within the system being monitored. Additionally, the ability to measure two or more analytes at dramatically different concentrations may require different sampling rates to cover their analytical ranges.

We report on a prototype real-time atmospheric mass spectrometer outfitted with a variable sampling rate inlet that offers the flexibility necessary to address a wide range of applications. Examples presented here include atmospheric measurements of CO₂ in a plant (or plant leaf) during light cycling and of fungal fermentation products, CO₂ and ethanol.

Methods

Electron impact data were collected using a Shimadzu QP2010 quadrupole mass spectrometer fitted with a novel patented atmospheric inlet technology that allows for adjustable instrument and sampling rates. An independently flow controlled filter or cartridge trap can be used for parallel sampling of particulates and/or non-volatile compounds for alternative instrument analyses, e.g., ICP of particulates or identification of biological agents.

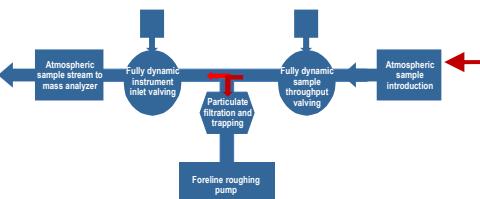


Fig. 2. Basic design of the new atmospheric inlet technology (AIT)

Plant monitoring

A whole plant or a single plant leaf was placed inside of a plastic bag containing a port for sampling air at rates from 2-10 mL/min. Fresh air was available through a second port to replace air sampled by the mass spectrometer. The fresh air was delivered to a tee fitting at ~140 mL/min in such a manner as to insure the enclosed air volume remained constant and circulated. The bagged plant or leaf was then placed inside a homemade enclosure for controlled light and dark cycling.



Fig. 3. Inside of an exposure control chamber (left) a creosote bush prepared for whole plant monitoring and (right) a common household corn plant prepared for single leaf monitoring by real-time high definition MS using accelerated scan ratios and reduced dilution effects to resolve metabolic processes.

Fermentation process monitoring

Fungal fermentation processes were investigated with regard to relative production of ethanol and carbon dioxide. Pre-fermenter supply air and fungal fermentation process exhaust were collected at three time points – 3, 96, and 144 h – for comparison. This preliminary investigation was conducted off-line to demonstrate proof of concept. Implementation of an online capability is now underway.

Results

Instrument calibration

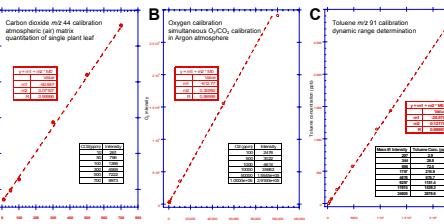


Fig. 4. Demonstrations of linearity and dynamic range: A) CO₂ in air, B) O₂ and CO₂ in Argon, and C) toluene in air from 2.9 ppb to 2.9 ppm.

Plant metabolism

Carbon dioxide was monitored at a rate of 10 mL/min from a whole, common household corn plant during random light cycling. The rapid, real-time monitoring capability provides a detailed profile of the plant moving between respiration and photosynthesis. The data in Fig. 5A indicates short dark cycles adversely effects carbon fixation efficiency. Fig. 5B and 5C show zoomed views of the plant switching between respiration and photosynthesis, providing insight into the time required for an individual plant to change metabolic pathways.

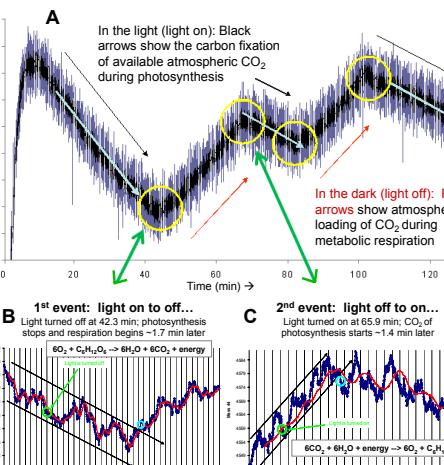


Fig. 5. Whole corn plant monitoring of photosynthesis and respiration: A) initial and subsequent carbon dioxide uptake and loading rates with critical areas, and B) and C) the plant requires on the order of 1-2 min to change between photosynthesis and respiration. Blue circles denote where metabolic pathway switches.

A similar experiment was then repeated, but at a reduced sampling rate of 5 mL/min. The reduction in dilution effects provided an even higher resolution picture of metabolic cycling, revealing what appears to be two separate loading and fixation rates (Fig. 6).

Next, a single leaf was isolated and monitored at a rate of 2 mL/min (Fig. 7 and 8). At the single leaf level, a very clear picture of respiration and photosynthesis rates emerge. A close look at the data band width indicates that plant stomata might do something similar to 'breathing', by opening and closing to regulate CO₂ input during photosynthesis and output during respiration.

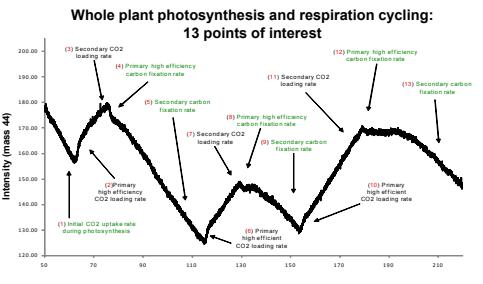


Fig. 6. Graph of whole household corn plant monitoring showing the raw data definition exposed (points of interest) by reducing the sampling rate from 10 mL/min (Fig. 5A) to 5 mL/min.

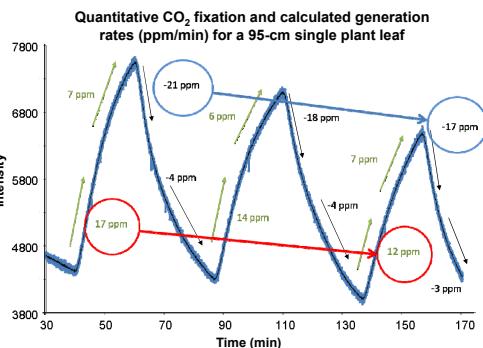


Fig. 7. Demonstration of plant stress resulting from metabolic pathway switching over a short time period. Note the raw data definition exposed by reducing the sampling rate to 2 mL/min.

We see that respiration and photosynthesis initial efficiency decreases by approximately 28% and 21%, respectively. Turning on and off lights in your own home may have a similar effect on common house plants.

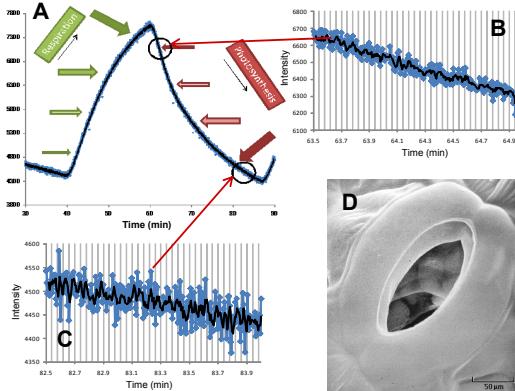


Fig. 8. For a single leaf: A) the correlation between carbon fixation efficiency and data bandwidth. Comparison of B) high efficiency carbon fixation and C) low efficiency data regions that may correspond to an unrealized biphasic primary and secondary carbon fixation activity in D) plant stomata.

Bioenergy production

Excellent results were obtained from monitoring a fungal fermentation process for ethanol and carbon dioxide production. The data demonstrates that real-time mass spectrometry can be used to improve production yields through the optimization of growth media using real-time MS for real-time feed back.

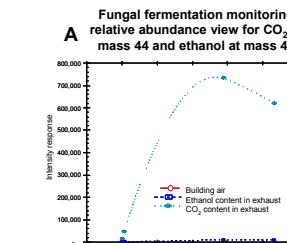
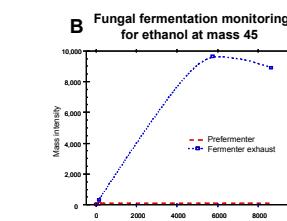


Fig. 9. Bioenergy production. Dramatic increases in A) CO₂ and B) ethanol are clearly observed confirming the fermentation was a success.



Conclusions

- The inlet system presented here coupled to a Shimadzu QP2010 mass spectrometer addresses problems associated with real-time MS and incorporates solutions into a user-friendly prototype.
- The innovative design has enabled the development of real-time high definition MS (RTHD-MS) as a new tool for characterizing living systems.
- The inlet provides for on-the-fly adjustments to reveal high definition profiles of metabolic processes.

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