Technical Aspects of An Automated Chromatography Based Greenhouse Gas Analysis System

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SYSTEM JUSTIFICATION
Several large-scale research programs associated with the Great Lakes Bioenergy Research Center (GLBRC) and Long-term Ecological Research (LTER) at the Kellogg Biological Station in SW Michigan require intensive year round gas sampling to quantify the greenhouse gas footprint of different crop management practices. A very large number of gas samples (approximately 30,000/yr) are routinely generated and require a quick, accurate, and reproducible analysis. This instrumentation allows research to continue uninterrupted without a loss of analytical accuracy.

SYSTEM ADVANTAGES
Robotic sampling and analysis of up to 440 samples. Stable and reproducible analysis with low CV’s. Flexible method development and user interface. Easy to understand post report summary. Automated calibration standard builder. Relatively simple design. Nondestructive analytical procedure. Samples may be reanalyzed. Compiles results in Excel via a post data analysis hook macro for easy data handling.

Chromatography System

Gas Sampling

Fig. 1 Static chamber sampling in a miscanthus plot. For a 54-60 minute flux cycle, the chambers are closed creating an airtight headspace. While closed, samples are extracted via syringe every 10-20 minutes and injected into an airtight test vial. The vials are returned to the laboratory and analyzed for CO₂, N₂O, and CH₄. Lid clamps assure a complete airtight seal. The chamber is also vented.

Fig. 2 Visual comparison of the three types of static chambers employed at KB.

Fig. 3 Static chamber sampling in a miscanthus plot. For a 54-60 minute flux cycle, the chambers are closed creating an airtight headspace. While closed, samples are extracted via syringe every 10-20 minutes and injected into an airtight test vial. The vials are returned to the laboratory and analyzed for CO₂, N₂O, and CH₄. Lid clamps assure a complete airtight seal. The chamber is also vented.

Fig. 4 A Gerstel MPS2XL autosampler configured with a custom valve allows for up to 440 samples per run. A 0.25 ml static headspace syringe draws a one ml sample for each of the GC inlets.

Fig. 5 A 7890A gas chromatograph analyzes CH₄ with a FlameIonization Detector (FID) and N₂O with an Electron Capture Detector (ECD). A backflush system allows the ECD columns to purge any remaining moisture or highly retained compounds.

Fig. 6 A Licor Li-6400 Infrared Gas Analyser (IRGA) analyzes the sample for CO₂. The sample is split after the FID inlet with one third of the injected sample diverted to the Licor. The Licor results are analyzed on the Agilent analog/digital (AID) channel and displayed in real time.

Fig. 7 The CH₄/CO₂ Instrumentation Schematic

Fig. 8 The N₂O Instrumentation Schematic

Table 1: Gas Chromatograph Parameters

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<th>Parameter</th>
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<td>Sample Heater – Gerstel MPS2XL 3.5 ml vial</td>
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Table 2 and 3: Air Sample Coefficient of Variation Results.

Fig. 9 Standard Agilent ChemStation chromatogram of N₂O, CH₄, and CO₂

Fig. 10 Developed Calibration Curves of a suite of six gases

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