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Quantitative method for detection of formic acid in beehive air samples

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Formic acid is utilized as a natural biocide in bee hives, offering an environmentally friendly alternative to synthetic chemicals. However, the quantitative determination of formic acid in air samples presents a significant analytical challenge due to its low concentrations and the complex nature of the sample matrices. To address this challenge, we employed a sophisticated hyphenated system that integrates gas chromatography (GC) with a mass-selective detector (MSD). Our setup includes a gas valve box featuring two gas valves, which enhances the efficiency of sample handling and minimizes contamination. The system utilizes a PE-5ms column, known for its ideal separation capabilities, along with a deactivated capillary to prevent any chemical reactions that could lead to the degradation of formic acid during analysis. In this analysis, the air sample is passed through a heated transfer line, which facilitates the rapid vaporization of volatile compounds, ensuring that formic acid is effectively introduced into the gas chromatograph. For the mass analysis, formic acid was specifically quantified using the mass-selective detector in Selected Ion Monitoring (SIM) mode. This approach allows for the selective detection of specific ions associated with formic acid, enhancing the sensitivity and specificity of the measurement. To further minimize errors related to sample introduction and ionization variability in the mass-selective detector, we employed chloroform as an internal standard. The internal standard compensates for potential fluctuations in detector response and sample variability. In addition to establishing the calibration curve, we conducted comprehensive investigations to determine the limits of detection (LOD) and quantification (LOQ) for the method. These measures are critical for assessing the analytical method's sensitivity and reliability, particularly when detecting formic acid at trace levels that may be present in environmental samples. This study provides a reliable framework for the quantitative analysis of formic acid in air samples, contributing valuable information to the field of environmental monitoring and assisting in the management of bee health through more precise assessments of biocide usage.

Used Equipment:

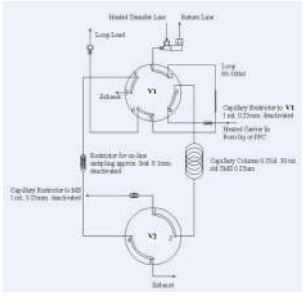
Hyphenated system PerkinElmer TGA4000 connected with RedShift gas valves to PerkinElmer Clarus 680S/Clarus SQ8S GC/MSD.

Instrument Control, Data Acquisition and Data Processing were performed by GC/MSD software TurboMass v.6.1.0.1963.

GC/MSD Conditions:

- GC Columns:
  - GC Injector to Valve1 - Fused silica capillary SGE (1.0 m x 0.25 mm).
  - Valve1 to Valve2 – PE-5MS (30 m x 0.25 mm x 0.25 µm).
  - Valve2 to MSD - Fused silica capillary SGE (1.0 m x 0.25 mm).
- Mobile Phase – Helium 5.0.
- Mobile Phase Mode - Constant Flow – 1.0 ml/min.
- GC Injector Temperature – 260°C.
- Transfer Line Temperature – 270°C..
- Valve Box Temperature – 270°C.
- GC Oven Temperature Program:
  - 35°C – hold 2.0min.
  - ramp 4°C/min to 70°C – hold 0min.
  - ramp 12°C/min to 280°C – hold 3.0min.
- VALVE 1 Program: 0.1min – ON; 2min – OFF.
- MSD Transfer Line Temperature – 280°C.
- MSD Ion Source Temperature – 220°C.
- MSD mode – 1.0 to 7.0min. - SIM - m/z 46 - 50ms, 83 - 50ms,
  7.0 to 30.0 min. - SCAN - m/z – 45 ÷ 450 amu.

Flow Diagram:

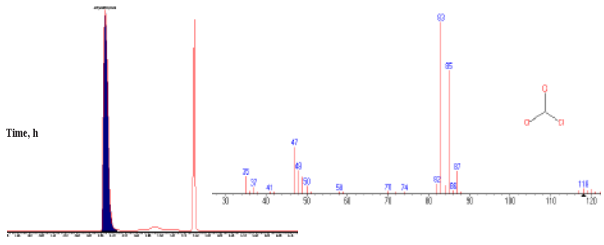


Calculation:

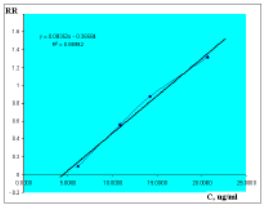
In order to minimize the analytical errors from gas valve filling, MSD ionisation, etc. a calculation of relative response (RR) have been done.

$$RR = \frac{AreaST * MassISTD}{AreaISTD}$$

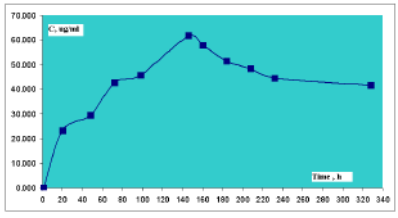
ISTD Response



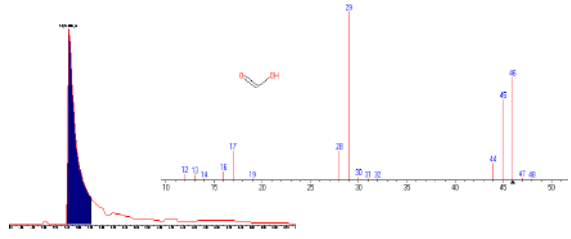
FORMIC ACID Relative Response Calibration:



FORMIC ACID concentration in beehive atmosphere – two weeks sampling.



Formic Acid Response:



Conclusions

A new feasible analytical method for quantitative determination of formic acid in bee hives has been developed. Calculation by specific response of selected ions from mass-selective detector allow us to make very good calibration curve - correlation factor 0.9899. Limit of detection of formic acid is less than 4 ug/ml. Calculated LOQ is 12 ug/ml.

Acknowledgment

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