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Improved Analysis of Propylene Oxide, Propylene Chlorohydrin and Propylene Bromohydrin

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Abstract

The benefits and deficiencies of several methods of analysis for PPO and PXH, including the aqueous extraction used in ASTA method 23.1 and the MTBE extraction method previously reported by the authors, will be discussed. Novel methods utilizing dynamic headspace extraction and solid phase microextraction (SPME) will also be reported with particular emphasis on preventing artefactual effects. Preliminary experiments have found that dynamic headspace sampling can lower detection limits by up to 3 orders of magnitude.

Keywords: Propylene Oxide, Fumigation, Sterilent, Headspace-SPME, Pesticide Degradants.

Introduction

The importance of propylene oxide (PPO) treatments for stored product protection has only increased in recent years, especially as the implementation of FSMA in the US puts pressure on tree nut producers to pasteurize their product. In the search for post-harvest methyl bromide replacements; PPO/SF blends, with PPO overcoming the ovicidal deficiencies of sulfuryl fluoride, have been shown to be effective against several stored product pests.

With the increasing variety in PPO treatments across commodity types and a "deharmonized" global MRLs comes an increasing need for the quick and accurate quantification of PPO residues. Analysis is complicated by the ease with which PPO will undergo nucleophilic reaction with water to form propylene glycol, or with chloride and bromide to form propylene chloro and bromo- hydrin, which can artificially lower the detected PPO residue. Avoiding the formation of these halohadrins (PXH) is of particular importance as they face regulatory scrutiny as carcinogens.

Materials and Methods

Jimenez et. al. Method:

Almonds or walnuts are added to an explosion proof blender along with chilled, deionized water and MTBE and homogenized. 45mL of the homogenate is centrifuged and a 1 mL aliquot of the MTBE supernatant is transferred to a 2 mL amber glass vial for analysis. A 10x concentration (10 mL to 1 mL) of the MTBE supernatant could be performed to increase detection of PBH-1 and PBH-2. Analysis was performed via cool on-column injections in an Agilent 6890 gas chromatograph (GC) equipped with a 5973N mass spectrometer (MS).

Dynamic Headspace Extraction Method:

Three almonds or walnuts are chopped roughly, transferred into a 20 mL headspace vial and sealed. The vial is then incubated at 80C for 42 min in a Perkin-Elmer Turbomatrix dynamic headspace autosampler, and three cycles of pressurizing the vial to 15 psi and allowing it to vent through an adsorbent trap are performed prior to ballistically heating the trap and directing the sample flow into a Perkin-Elmer Clarus SQ8 GCMS.

SPME-Headspace Method:

An approx. 50g sample of almond or walnuts is cryogenically milled under liquid N2 and a 2g subsample is transferred to a 20 mL headspace vial and sealed. SPME extraction is performed with

a Carboxen / DVB / PDMS fiber at room temperature and 30min sorbtion time. Analysis is performed on an Agilent 7890B GC with a LECO Pegasus BT TOF-MS.

For each methods, % recovery and LODs were determined by spiking known amounts of each analyte onto the surface of a walnut or almond and extracting. The amount of side reaction (amount of PCH or PBH formed during extractioin and analysis) was determined by spiking PPO-treated nuts with d6-PPO and measuring the amount of deuterated PCH (PCD) and PBH (PBD) formed. The reaction kinetics between PPO and chloride / bromide will be examined by spiking PPO onto the surface of nuts or nut grounds and measuring the amount of PCH and PBH formed at varying reaction times and temperatures.

Results

Negative chemical ionization MS (NCIMS) was not found to improve analyte sensitivity for the target analytes when compared to electron impact MS (EIMS). GC-ECD (electron capture detection) demonstrated improved sensitivity for PBH-1 and PBH-2 in non-concentrated MTBE extracts (approx. 0.7 mg/kg compared to 50 mg/kg for EIMS). Ten-fold concentration of the MTBE extract yielded a 10x improvement in detection limits for PBH, but recoveries for PPO and PCH, respectively, dropped below 50% and ranged from 50 to 72%.

The use of dynamic headspace extraction demonstrated a great improvement in the simplicity, speed and sensitivity of analysis compared to MTBE extraction, with detection limits for PCH and PBH around 10 ng/g (ppb). The incubation temperature required for the sensitive detection of PBH, however, was shown to also cause further reaction of PPO into PCH and PBH. Results from the the use of a saturated KI solution to preemptively react with PPO will be reported.

Preliminary experiements show that SPME-Headspace extraction has been shown to have excellent sensitivity for each target analyte, able to detect as little as 1.5 ng of material, dissolved in 5 µL H_2O, and spiked into an empty 20 mL HS vial. Spiking approx. 20 µL of PPO into almond grounds and analyzing with SPME-headspace analysis has shown that PBH and PCH begin to form in as little as 20 min at room temperature.

Tab. 1 Limits of detection for each target analyte for the MTBE extract and dynamic headspace methods.

Compound	Matrix	LOQ - Solvent Extract	LOD - Head Space Trap
PPO	Almond	0.85 ug/g	0.54 ug/g
	Walnut	0.81 ug/g	0.08 ug/g
PCH-1	Almond	2.10 ug/g	10.0 ng/g
	Walnut	2.31 ug/g	12.1 ng/g
PCH-2	Almond	2.22 ug/g	N/A
	Walnut	1.95 ug/g	N/A
PBH-1	Almond	75.1 ng/g	6.01 ng/g
	Walnut	74.8 ng/g	19.0 ng/g
PBH-2	Almond	75.3 ng/g	4.92 ng/g
	Walnut	77.3 ng/g	N/A

Discussion

Preliminary experiments have demonstrated that while headspace sampling methods can significantly improve sensitivity for PPO, PCH and PBH, great care must be taken to avoid aretfactually raising PCH and PBH levels. The use of autosamplers (either dynamic headspace or L-PAL3 with SPME attachment) can greatly reduce injection to injection variability and reduce the number of person-hours required for analysis, but to fit walnuts or almonds into headspace vials they must be chopped or ground exposing further chloride or bromide to react with PPO. Future experiments using manual SPME sampling will allow the use of glassware that can accommodate whole nuts. The use of iodide, or other nucleophiles, to compete with chloride and bromide for the reaction with PPO will also be examined.

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Monitoring of post-harvest fumigation with Gasmet Multikomponent FTIR gas detection systems

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Keywords: Post-Harvest, Fumigation, Fourier Transform Infrared (FTIR), Fumigant, Library Search Tool

Fumigation business has changed dramatically after the Montreal protocol came into effect on January 1st 1989. Methyl Bromide had to be replaced in all its widespread application. A lot of fumigators having experience with Methyl Bromide are still mourning in regards of its outstanding fumigation performance. Today, almost 30 years after, we are having a big variety of different alternatives to Methyl bromide, developed by research institutes around the world.

Focusing on new gaseous alternatives to Methyl Bromide, FTIR technology is an extremely versatile detection principle, offering a widespread use in the fumigation industry.

Fourier transform infrared (FTIR) is a powerful gas measurement technology that offers true multicomponent capability. This technology that was originally used for challenging research applications has since proven to be very reliable and versatile and has become the industry standard in many challenging emissions monitoring applications.

Most gases absorb infrared light at some wavelengths in the infrared spectrum. The position and intensity of the absorptions are determined by the molecular structure of the gas and this means that each gas will have a unique absorption pattern. This unique pattern can be used like a fingerprint to identify and measure each gas in the sample.

An FTIR analyzer works by simultaneously scanning the entire infrared spectrum and then calculating the concentrations of each gas in the sample based on their characteristic absorptions. The fact that the entire infrared spectrum is scanned at once means that all the gases in the sample can be measured simultaneously. This allows for very quick multicomponent measurements and for compensation for any cross-interference.

As all gases are measured by scanning the same infrared spectrum, adding new compounds can be done easily in the software without requiring any changes to the hardware. The recorded spectra are also unaltered by the analysis performed on them and can therefore, always be re-analyzed at a later point. This allows for traceable data and facilitates for instance retrospectively checking the measurements for new gases.

All this makes FTIR the ideal solution for a variety of applications where multiple gases need to be measured quickly, accurately and reliably.

Working on approving, registering, developing or applying new fumigation procedures has become much more demanding than what experienced for Methyl Bromide. The need for an ideal gas detection device is enormous.

FTIR technology brings some outstanding advantages for the fumigation industry as listed below:

1. Detection of several different fumigants with the same instrument
2. No changes of sensors required for change in gases
3. Extremely easy and low cost calibration
4. Detection of complex gas mixtures