Analysis of Fumigants in Cereals and Dried Fruit, Using GC-MS/MS

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Introduction

We present a method for the simultaneous analysis of 14 different fumigants in cereals and dried fruits using GC-MS/MS. Fumigants consist mostly of small molecules which diffuse quickly and are gaseous at 20 Grad C.[1] They are mainly used to counter two problems of globalized trade. First is the protection of goods from spoilage during long transports through different climatic zones. Second is Prevention of the introduction of (harmful) organisms via export/import between countries.

Legal aspects

Most of these substances have toxic effects, so maximum residue limits (MRLs) of fumigants have been established to protect the consumer from these health hazards. They are classified as pesticides; therefore, the default MRL of 0.01 mg kg^{-1} is given (only for chloropicrin in tea and spices the MRL is set at 0.02 mg kg^{-1}).

Analytical method

5 – 20 g of the samples were weighed into 50 mL PP tubes. X mL of n-Hexane followed by 50 µL of the internal standard working solution (1 µg mL^{-1} Chlorobenzene D5) were added to the samples. The tube was shaken for one minute and then centrifuged for 5 min at 4000 rpm and filtered through a syringe filter (0.45 µm), if necessary. 1 mL of the extract was transferred into vials. The extracts were measured via GC-MS/MS. Example chromatograms of fumigants in wheat extracts (0,1 mg kg^{-1}) are shown below.
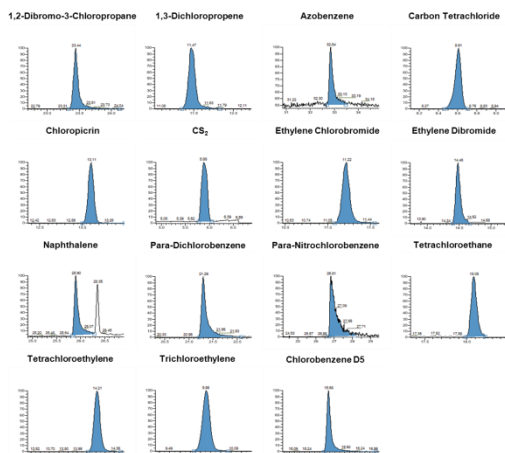

GC-Conditions:
Column: 30 m; 0,20 mm; 1,12 µm Agilent HP VOC column
Pre-Column: 10 m; 0,25 mm Fused-Silica precolumn
More Method Details[3]

Results

Most of the substances had a linear detection range of between 0.01 and 2 mg kg^{-1}. All substances except Trichlorethylene showed a lower detection rate in the presence of a matrix. Matrix matched calibrations are thus necessary for more accurate quantification (see graph on matrix effects below). In raisins an overlay exists at the matrix peak with the substance Azobenzene. In further analyses we found the same effect in dried apricots (see chromatograms below).
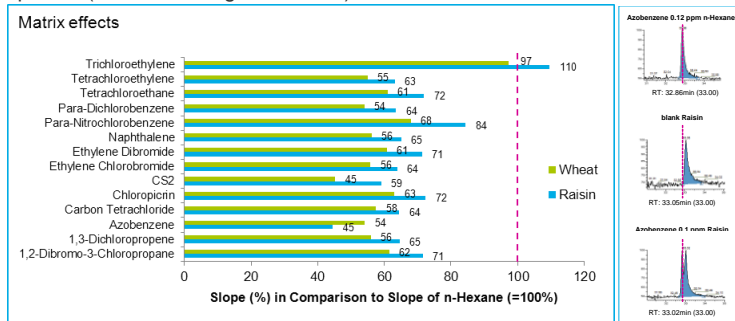
The method was validated at a level of 0.01 and 0.1 mg kg^{-1} for raisin and wheat matrices, showing average recoveries (n=5) at both levels for wheat of between 79% and 106% and for raisins between 86% and 106%. In both matrices CS_2 had lower recoveries at the level of 0.1 mg kg^{-1} than the other substances (55% wheat and 52% grain).
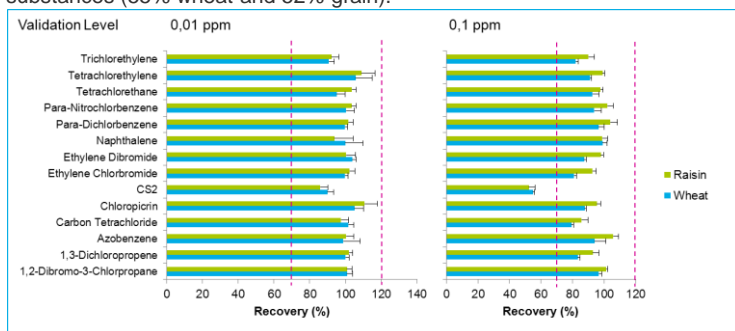
Summary

Our study demonstrates that several fumigants can be analyzed simultaneously applying an n-Hexane extraction method and GC-MS/MS analysis. The validation of the method showed satisfactory recoveries and RSDs in wheat and raisin matrices. We recommend the use of matrix matched calibration standards or isotopically labeled internal standard to compensate for matrix effects. Besides it is advisable to prepare fresh calibration standards anew. Further validations of fumigant analyses of additional matrices and concentrations are in process. The first samples (13 dry fruits) analyzed were without any residues.

Reference
1. Begasungsmittel - Mögliche Anwendungen. Reichmuth, Christoph. [Hrsg.] Umweltbundesamt. Berlin, 2006. S. 179-186. ISSN 1862-4808.
2. http://www.cvuas.de
3. Method-Details http://www.eurl-pesticides.eu/ Search: Fumigants

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