Analysis of Phosphine in Dried Foodstuffs via Headspace GC-MSD

Roland Perz, Ellen Scherbaum, Anne Benkenstein, Helmut Köbler, Dieter Köhl, Anja Barth and Michelangelo Anastassiades

E-Mail: ellen.scherbaum@cvuas.bwl.de

Introduction

Globalization has led to an increased trade of goods between countries from different continents. In 2011 maritime trade was estimated at 500 million containers, transporting goods from all parts of the world. However, stowaways such as pests are inevitably carried along with the goods as well. Fumigation of containers is common practice in the export and import of foods, both in order to preserve the foods during the long trip and to eliminate any pests that could be brought into a country with the food. Methyl bromide was previously among the most widely used fumigants but its production and use was restricted by the Montreal Protocol due to its role in ozone depletion. Nowadays phosphine (PH_3) is one of the most widely used, cost-effective and rapidly acting fumigants not expected to leave higher amounts of residues on treated products.

Legal aspects

In Germany several products containing phosphine and its salts aluminum phosphide and magnesium phosphide are registered for use on coffee, cocoa, oily seeds, dried fruit, legumes and stored cereals (Federal Office of Consumer Protection and Food Safety, BVL). Zinc phosphide is permitted, furthermore, as a rodenticide in the form of pellets.

In EU legislation, maximum residue limits for the sum of phosphine and phosphides in foodstuff are set within a range of 0.01 and 0.1 mg kg^{-1}, depending on the commodity.

Analytical method

Due to its high volatility, phosphine is not amenable to common multi-residue methods for pesticide residue analysis in food; thus, special single residue methods have to be applied.

A highly sensitive headspace-GC MSD method (with cryo trapping in a Tenax filled liner at -80°C during injection) was developed achieving limits of quantitation as low as 0.1 µg kg^{-1}. This enabled not only the monitoring of adherence to MRLs, but also the exposure of improper applications.

The chromatographic separation employed was shown to be selective enough to largely exclude any disturbances from oxygen, hydrogen sulfide or other small molecules in the same m/z range.

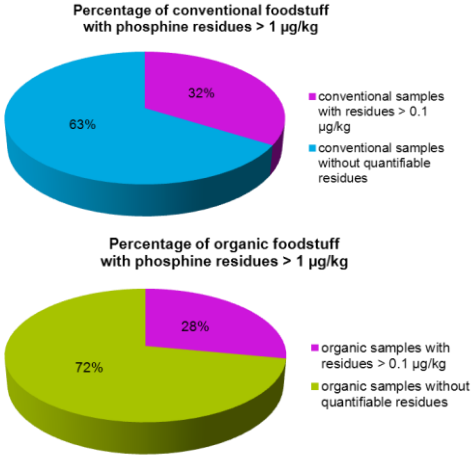
Calibration curves of procedural calibration standards were linear up to at least 50 µg/kg, with good correlation coefficients (R^2>0.99). Due to matrix-dependent signal quenching effects, external non-matrix-matched calibrations are not recommended for final quantification. They are suitable for screening purposes, however. For accurate quantification, positive samples have to be re-analyzed by the standard additions approach or at least calibrated against procedural calibration standards prepared for a similar matrix.

Critical factors

Grinding of coarse samples helps to achieve sufficient homogeneity and accessibility of the residue in well-aged samples, but excessive grinding should be avoided (heat!). For powdery samples the handling is easier when 7 mL water is added, the vial **shaken** and filled up to 15 mL with 10 % sulfuric acid instead of filling it up to 15 mL with 5 % sulfuric acid. After the addition of acid, vials must be closed immediately! Pipettes are not recommended for the dosing of the acid (too slow!).

Results

In all, 115 samples of dried foodstuff from the local market, such as cereals, nuts, and legumes, were analyzed for phosphine residues. In 35 of these samples phosphine in amounts exceeding 0.1 µg kg^{-1} were detected, while 14 samples (12 % of all) exceeded 1 µg kg^{-1}. Interestingly, seven of these 14 samples were labeled as being from organic production, where phosphine application is not allowed.



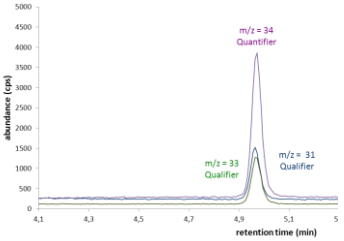
Conclusions

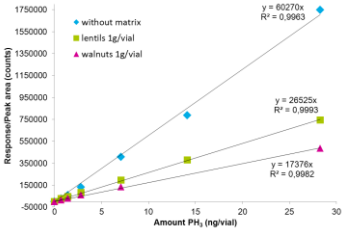
The phosphine concentrations detected in conventional and organic products were in the same range. More research is needed to elucidate the reasons for the findings in organic products, with cross-contamination, blending of organic and conventional products and illegal applications being potential options.

Residual phosphine can be bound tightly to the matrix and survive extended food storage or processing. A few findings in bread indicate that PH_3 residues can even partially survive the baking process. Therefore, phosphine may occasionally occur in a broad variety of processed foods that have not yet been the focus of analytical chemists.

Reference

http://www.cvuas.de,
Aspects of food control and animal health,
Volume 2014 Issue 2 (May)





101

EPRW 2014

Baden-Württemberg