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Detection of phosphine residues in organic cereals

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Introduction

Phosphine (PH_3) is a fumigant frequently used for the control of insect pests in stored cereals. Tablets containing an inorganic metal phosphide (aluminium or magnesium phosphide) are mixed with the cereals and gaseous phosphine is formed by reaction of the metal phosphide with the humidity of the cereals. Appropriate concentrations of phosphine are lethal for insects and rodents. Although highly toxic to man, it is considered to be safe for human health because it is assumed that, after due airing and physical cleaning of the fumigated product, no significant residues remain in the cereal. The Swiss tolerance value of 100 µg/kg for cereals is easy to fulfil.

Several authors have studied the behaviour of phosphine residues in cereals using colorimetric or photometric methods (1–5) with detections limits down to 1 µg/kg. By application of more sensitive gas chromatographic methods, the degradation of phosphine was monitored down to levels below 1 µg/kg (11). In the range of 1 µg/kg, the degradation curve in wheat becomes very flat, indicating that the residual amount of phosphine is less easily lost and seems to be more firmly bound to the cereal matrix. By means of fumigation using phosphine labelled with radioactive ^{32}P and monitoring its decrease, it was shown that part of the ^{32}P remains in the outer layers of the grains in spite of airing (12).

The kinetics of phosphine desorption depends on parameters such as nature and amount of cereal, intensity of fumigation, fat contents, temperature, humidity and airing. Under usual conditions phosphine decreases below the detection limit within a few weeks or months. The detection method most frequently used in Switzerland, Dräger tubes (6), has a detection limit between 5 and 10 µg/kg. Therefore, in most cases a fumigation of cereals with phosphine can not be detected unless the delay after fumigation is short enough (a few weeks) or a more sensitive method is used.

Fumigation with phosphine is not admitted in organic food. There are different possibilities to react to the occurrence of insects in organic cereals:

- Fumigation with carbon dioxide. This method is time consuming and requires special equipment.
- Fumigation with phosphine or another toxic fumigant and selling the product as conventional food. This method is very expensive due to the large price difference between organic and conventional foods.
- Fumigation with phosphine or another toxic fumigant and still selling the product as organic food. This method is cheap, but illegal. If the cereal is fumigated with phosphine and subsequently duly cleaned and aerated, the fumigation can not be recognized by food control authorities if they use the insensitive Dräger tube method.

To check for illegal application of phosphine in organic cereals a more sensitive and more selective method (7–10) was adapted in our laboratory. Phosphine is desorbed from the sample with dilute sulphuric acid, injected into a headspace-GC system, separated on a porous layer open tubular (PLOT) capillary column and detected with a flame photometric detector. The method is fast, easy to apply and reaches a detection limit of 0.1 µg/kg. The recovery was found to be in the range of 89 to 98 %.

The method was applied to 47 organic cereal or cereal product samples from the Swiss market. Phosphine residues were found in five of ten rice samples and in one of three maize samples. An example of the obtained chromatograms is given in figure 1.

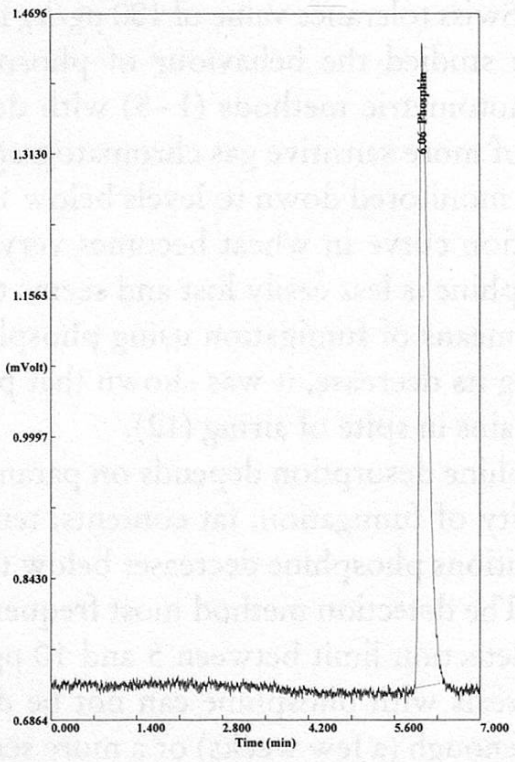

Figure 1 **Gas chromatogram of a rice sample containing 0.23 µg/kg of phosphine**

Experimental

Samples

500 g of each sample were drawn in local mills, food producing companies, and on the retail market. The samples were stored in the original packing or in polyethylene bags at room temperature. The phosphine concentrations in the samples did not decrease upon one month of storage. Entire grains were not ground prior to analysis.

Analytical method

Put 10 ml of water into a 20 ml GC-headspace vial and mark the vial at the height of the water surface with a permanent marker (=10 ml mark); discard the water; mark all the vials to be used for this analysis at the height of 10 ml.

Weigh 5 g of sample into the vial; add sulphuric acid (5 mg/100 ml) up to the 10 ml mark; close the vial tightly and immediately with a septum cap; shake for 10 min at 80 °C; and inject 1 ml of headspace vapour into the GC.

GC System

Gas chromatograph	Fisons HRGC Mega 2 series equipped with a Combi Pal headspace autosampler and a flame photometric detector in the P mode
Column	Chrompack CP-Poraplot Q length 25 m, ID 0.53 mm, phase layer thickness 20 µm (PLOT capillary)
Carrier gas	Hydrogen 50 kPa
Flame gases for FPD	Hydrogen 150 kPa, air 60 kPa
Split liner	5 mm
Split	24 ml/min
Septum purge	0.2 ml/min
Injection volume	1 ml
Injector temperature	220 °C
Detector temperature	Basis 250 °C, FPD 180 °C
Oven temperature	Isothermal 50 °C
Syringe	Hamilton 2.5 ml gastight

Calibration

The system is calibrated by injecting gas phase dilutions of phosphine in nitrogen. Add 10 ml of sulphuric acid (5 ml/100 mg) to an empty 20 ml-headspace vial; close the vial tightly with a septum cap; by means of a gastight microliter syringe, add 5, 20, 50, 200 and 400 µl of phosphine in nitrogen (96.2 mg/m^3) (Linde, Dresden, Germany), corresponding to 0.096, 0.385, 0.962, 3.846 and 7.692 µg/kg, respectively; inject into the GC; and plot the calibration function (figure 2). The response is linear in this range.

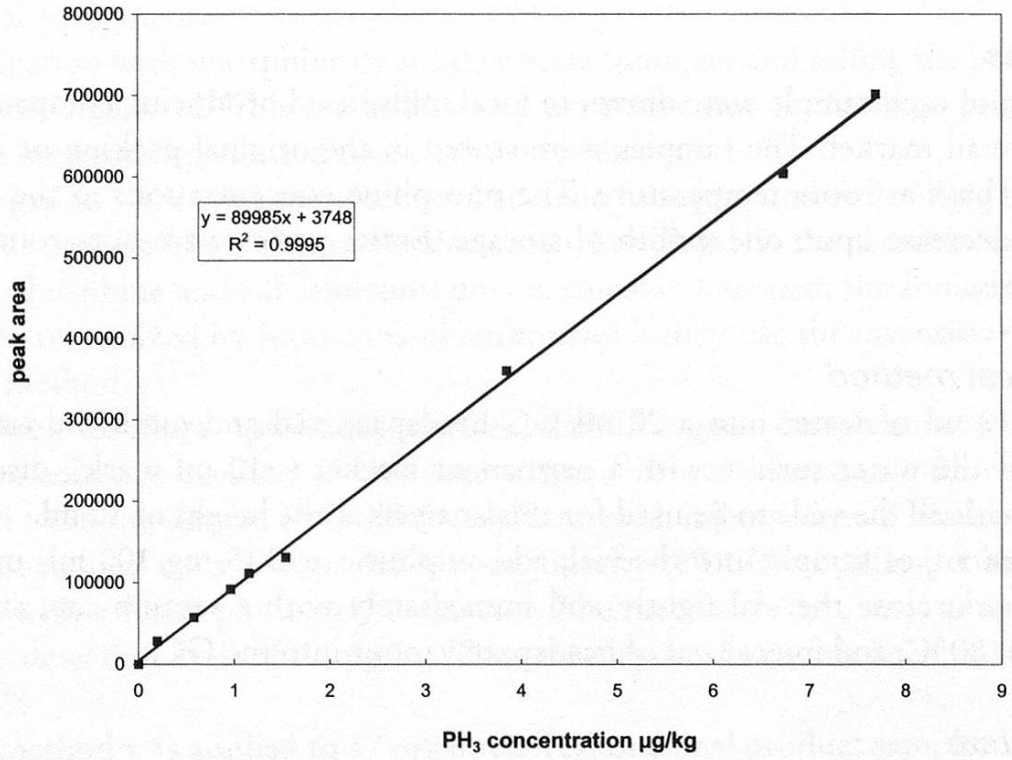

Figure 2 **Calibration plot**

Results and Conclusions

47 samples of organic cereals or cereal products were analysed for phosphine residues using the method described above. The results are presented in table 1.

Table 1
Samples of cereals analysed for phosphine and number of positive samples

Cereal	*Total number of samples*	*Number of positive samples (PH_3 > 0.1 µg/kg)*
Barley	4	0
Cereal mixture	6	0
Maize	3	1
Millet	4	0
Oats	4	0
Quinoa	1	0
Rice	10	5
Rye	3	0
Wheat	12	0
Total	47	6

Phosphine residues in the range of 0.3 to 2.5 µg/kg were found in rice and maize samples. Half of the ten rice samples contained phosphine. All other samples contained no detectable phosphine (detection limit 0.1 µg/kg). The difference between

rice and the other cereals (except for maize) is highly significant. At present we have no explanation for this fact. It is not likely that rice exhibits a residue behaviour which differs strongly from other cereals or that rice contains natural phosphine. Further investigations on these issues are planned.

Summary

Cereals are usually checked for residues of phosphine fumigation with Dräger tubes. The detection limit of this method lies between 5 and 10 µg/kg. After sufficient cleaning and airing of the fumigated cereals no residues can be detected any more. A more sensitive and specific headspace GC/FPD method was adapted and applied to 47 samples of organic cereals. With a detection limit of 0.1 µg/kg, phosphine was found in five of ten rice samples and in one of three maize samples. The concentrations lied in the range of 0.3 to 2.5 µg/kg. All the other kinds of cereals were free from detectable phosphine. Further investigation is planned to clear up these findings.

Zusammenfassung

Getreide wird üblicherweise mittels Dräger-Röhrchen auf Begasung mit Phosphorwasserstoff geprüft. Die Nachweisgrenze dieser Methode liegt zwischen 5 und 10 µg/kg. Nach genügender Reinigung und Belüftung sind keine Rückstände mehr nachweisbar. Eine empfindlichere und spezifischere Headspace-GC/FPD-Methode wurde angepasst und auf 47 biologische Getreideproben angewendet. Bei einer Nachweisgrenze von 0,1 µg/kg konnte in fünf von zehn Reisproben und in einer von drei Maisproben Phosphorwasserstoff in Konzentrationen zwischen 0,3 und 2,5 µg/kg nachgewiesen werden. Alle übrigen Getreidearten waren frei von nachweisbarem Phosphorwasserstoff. Zum besseren Verständnis dieser Befunde sind weitere Untersuchungen vorgesehen.

Résumé

Pour doser la phosphine, les céréales sont habituellement analysées avec des tubes Dräger. La limite de détection de cette méthode se situe entre 5 et 10 µg/kg. Si les céréales sont suffisamment nettoyées et aérées, la phosphine n'est plus décelable. Une méthode headspace-GC/FPD plus sensible et plus spécifique a été adaptée et appliquée à 47 échantillons de céréales biologiques. Avec une limite de détection de 0,1 µg/kg la phosphine a été mise en évidence dans cinq échantillons de riz sur dix et dans un échantillon de maïs sur trois à des concentrations de 0,3 à 2,5 µg/kg. Toutes les autres sortes de céréales ne contenaient pas de phosphine décelable. D'autres recherches sont envisagées pour mieux pouvoir expliquer ces observations.

Key words

Phosphine analysis, organic foodstuffs, cereals, fumigation, residues

References

1 *Rangaswamy J.R.:* Phosphine residue and its desorption from cereals. J. Agric. Food Chem. **33**, 1102–1106 (1985)

2 *Noack S., Reichmuth Ch. und Wohlgemuth R.:* Rückstandsverhalten von Phosphin in begasten Lebensmitteln in Abhängigkeit von der Lagertemperatur und der Belüftung. Z. Lebensm. Unters. Forsch. **178**, 31–37 (1984)

3 *Suckow P. und Meuser F.:* Rückstände von Phosphorwasserstoff und Methylbromid in Getreide und Getreideprodukten. Deutsche Forschungsgemeinschaft, Bericht über das Kolloquium am 12./13. Oktober 1978, S. 62–75 in Boppard and Boldt (eds.), Verlag Chemie, Weinheim (1981)

4 *Meuser F., Rajani Ch. und Suckow P.:* Sorption von Phosphin durch Weizenkörner und Weizenkeime in Abhängigkeit von den Begasungsbedingungen. Mühle & Mischfuttertechnik **114** (30) 435–438 (1977)

5 *Mayr G.E.:* Einfluss der Mühlenbegasung mit Blausäure, Methylbromid und Phosphorwasserstoff auf die Mehlqualität. Getreide, Mehl & Brot **28** (4), 91–95 (1974)

6 Schweizerisches Lebensmittelbuch, Kap. 46 Pestizidrückstände, Methode 4.7.2.

7 *Brunner U., Chasteen Th.G., Ferloni P. and Bachofen R.:* Chromatographic determination of phosphine (PH_3) and hydrogen sulfide (H_2S) in the headspace of anaerobic bacterial enrichments using flame photometric detection. Chromatographia **40** (7/8), 399–403 (1995)

8 *Nowicki T.W.:* Gas-liquid chromatography and flame photometric detection of phosphine in wheat. J. Assoc. Off. Anal. Chem. **61** (4), 829–836 (1978)

9 *Allen S.E., Ren Y.-L. and Desmarchelier J.M.:* Comparison of six methods for determining aged phosphine residues in wheat. JAOAC Int. **81** (3), 633–637 (1998)

10 *Desmarchelier J.M. and Ren Y.-L:* Modifications of a method for determining multifumigant residues. JAOAC Int. **81** (3), 638–644 (1998)

11 *Scudamore K.A. and Goodship G.:* Determination of phosphine residues in fumigated cereal and other foodstuffs. Pest. Sci. **37**, 385–395 (1986)

12 *Disney R.W. and Fowler K.S.:* Phosphorus-32-labelled phosphine in the determination of fumigation residues in grain. In: Proc. IUPAC 2nd Int. Congress of Pesticide Chemistry. Tahori A.S. (ed), pp 423–425. Tel Aviv 1971, Gordon and Breach, New York (1972)

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