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LABORATORY FUMIGATION OF WHEAT FLOUR WITH SULFURYL FLUORIDE – PENETRATION AND FLUORIDE RESIDUES

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ABSTRACT

Research on sulfuryl fluoride (SF) in the recent past has been focused on its potential in applications, which were covered by methyl bromide formerly. The fumigation of flour mills is one of the areas of SF use. A lot of publications are focusing the efficacy of SF against stored product pests. However, there are only few data on its behaviour on flour. The present work wants to add some more information about the property of SF to penetrate flour and, in consequence of the SF break down, the fluoride residues. Two different experimental set ups were chosen. In a larger scale experiment different amounts of wheat flour, densely packed in a glass column were exposed to SF. The glass column was connected to a SF reservoir of 2.5 m^3. Heights of 110 cm, 30 cm and 15 cm of flour were investigated. In the headspace and on the bottom of the flour the SF concentration was recorded during an exposure of 50 h. In a second experimental set up the SF was pumped through flour in a circuit array, changes in the SF concentration were observed. For both, an initial concentration of 50 gm^{-3} was chosen. The concentrations were determined with FTIR-spectroscopy methods. After aeration, the fluoride content of the flour samples was determined using a fluoride-selective electrode. The time – concentration curves during the fumigation of flour indicate a decline in the initial concentrations. In case of the first set up, the concentration on the bottom of the flour column increased in a time period, depending on the depth of the flour. It leveled off within a certain time but remained less than the head space concentration on the top. The fluoride contents of the fumigated samples ranged from 7 mg kg^{-1} to 31 mg kg^{-1}. The results are discussed.

Key words: fumigation, sulfuryl fluoride, fluoride residue, flour, fluoride-selective electrode.

INTRODUCTION

Sulfuryl fluoride (SF) is used worldwide and is in Germany in stored product protection currently registered for the control of insect pests. Along to the phase out of methyl bromide (MeBr), which includes the ban of MeBr in Germany since 2005, the pest control companies as well as the millers have adapted to alternatives like heat treatment or SF fumigation. Moreover some millers decided to invest in fixed installed fumigation-systems (Böye and Mück, 2011). Apart from tree nuts as commodity only, the use of SF relates to empty rooms, before storage of products. All other stored products are excluded from treatment. The authorization includes empty silo bins, rooms, stores and storehouses as well as empty mills. Conditions are 128 g m^{-3} maximum concentration and 1500 g h m^{-3} maximum dosage with no more than three applications a year and 4500 g h m^{-3} a year in total. As a further application SF is registered for mills with the reduction to only one treatment per year and with 128 g m^{-3} maximum concentration and 1500 g h m^{-3} maximum dosage. This meets the situation of mills, which have to disrupt the running process for the time of the SF fumigation. Restrictions take care, that no food or feed comes into contact with the fumigant: grain, stored in the mill has to be enclosed gastight before the treatment. Silos and tubing systems have to be emptied before the treatment. It has to be avoided, that all grain - exposed to the fumigant because of technical reasons - comes into the further processing or delivery-chain as food or feed. Finally, the presence of grain or milling products during the treatment has to be excluded.

Mills consist of many process units like grain cleaning, grain preparation, roller mills, sifter and purifier, flour collection, separation of flour (different types) and other milling products, packaging and storage. There are several transporting-tubes in between. It takes time and causes production loss to empty all these units but it is essential. It might concern, if flour or other milling products have been forgotten and remained unintended in the mill during fumigation.

There are only few studies, which describe the penetration of SF into flour (Bell et al., 2003), the residues of SF itself (Sriranjini and Rajendran, 2008) and of fluoride (Guogan et al., 1999, Scheffrahn et al., 1989). The penetration study of Bell et al. (2003) aimed at a sufficient gas concentration in various depths of flour, because of the insect pests, which may be hidden in the flour. However, there was evidence, that SF penetrates thick flour layers in a short time.

MATERIALS AND METHODS

All trials[1] were carried out on wheat flour type 405 ("Diamant"; the type number corresponds to the ash content: 405 g per 100 kg) using SF by Dow Agroscience (Vikane™, 99.8%). There were two different fumigation set ups. In the larger scale experiment, a glass column of 130 cm height and 20 cm diameter with closed bottom was used. There was a perforated plastic tube fitted across the whole diameter in the inner of the glass column near to the bottom. The ends of the perforated tube were connected in a closed set up. The gas in the inner of the perforated tube was continuously pumped through. The flow was recorded using a flow controller. The SF concentration was measured using an infrared spectrometer (Gasmet Cr-1000, Temet Instruments, Finland). In order to prevent flour getting into the spectrometer, a filter was used in the gas line from the glass column to the spectrometer. A dessicator top fixed on the top of the glass column was sealed gastight with vacuum grease. The headspace of the glass column was connected to a 2.5 m^3 fumigation chamber in a closed set up. This was carried out by means of a gas wash-bottle head and teflon gas tubes. The gas was pumped through in this second loop continuously. The fumigation chamber was filled with SF to a concentration of 50 g m^{-3} directly from the gas cylinder. There was a second infrared spectrometer (Gasmet Cx-1000, Gasmet Technologies, Finland) between the glass cylinder

[1] Sulfuryl fluoride is a toxic, colourless and odourless gas, the handling requires extreme caution. The TLV is 10 mg m^{-3}. The described experiments were conducted in the Berlin fumigation laboratory with safety equipment and by certified employees.

and the chamber for determining the concentration in the chamber and in the headspace of the glass column.

The cylinder was filled with the flour in different heights. To make sure that there were no empty holes or cavities, the cylinder was put on a laboratory shaker, originally for sieving (Fritsch analysette 3) and fixed during the shaking procedure. It has been shaken until no drop in the height of the flour was noticed. Three different heights were investigated, 110 cm, 30 cm and 15 cm. The corresponding amounts of flour were 26 kg, 15 kg and 7 kg, respectively. During fumigation the gas from the chamber was pumped continuously over the headspace of the flour. The gas concentrations on the top and on the bottom of the flour were observed simultaneously for 50 h at room temperature. Spectra were recorded in intervals of 20 – 60 seconds and the concentration was calculated with the software Calcmet vers.11 (Ansyco GmbH, Germany).

In the second, smaller experiment, a plexiglas tube of 5 cm diameter and 30 cm length was filled with flour. The tube was connected at both ends to teflon tubes in a circuit array. To prevent flour pouring in the tubes, a piece of filter paper in the plexiglas tube and an additional filter were used. A fitted 2.5 l bottle with ground glass stopper and septum served for the injection of the SF. The gas was pumped through the flour in the upright positioned tube. A concentration of 50 g m^{-3} was chosen. The change in concentration in the gas stream during 50 h was observed by means of FTIR spectrometry, as described above.

After the fumigation and aeration the content of the glass column, or the plexiglas tube respectively, was removed and mixed. Per condition the samples were taken out of the mixed flour. The flour-samples were analyzed for residual fluoride by a potentiometric method with a combined ion-selective electrode (Mettler Toledo, perfectION™ comb F^-) according to an official method (BVL, 2012).

RESULTS

During the fumigation of different layers and consequently different amounts of flour in the glass column, an initial concentration of 50 g m^{-3} SF was provided in the headspace. As shown in Figure 1, in all cases a decrease of the headspace concentration of about 10% in 48 h took place. The SF concentration at the bottom of the flour layers (30 cm and 110 cm) increased and got to a constant level depending on the thickness. The SF concentration at 15 cm was not recorded. In comparison to the 30 cm thick layer, the SF concentration increased at the bottom of the 110 cm layer slowly and got near to a level of about 8% of the headspace concentration in about 15 h. The concentration at the bottom of the 30 cm layer increased faster and showed a constant level of 36% after about 5 h. In both cases, the concentration remained at a level lower than the headspace concentration during the observed exposure time.

The trials with flour in the plexiglas tube in the circuit array were accompanied with some difficulties in keeping up the system without fluctuations in pressure. Reliable results were achieved using about 100 g flour in the tube in upright position with a gas flow from the bottom to the top. As presented in Figure 2, the initial gas concentration decreased continuously. Only 24% of the SF has been found after 50 h. However, there was a slight concentration drop in the empty system (without flour).

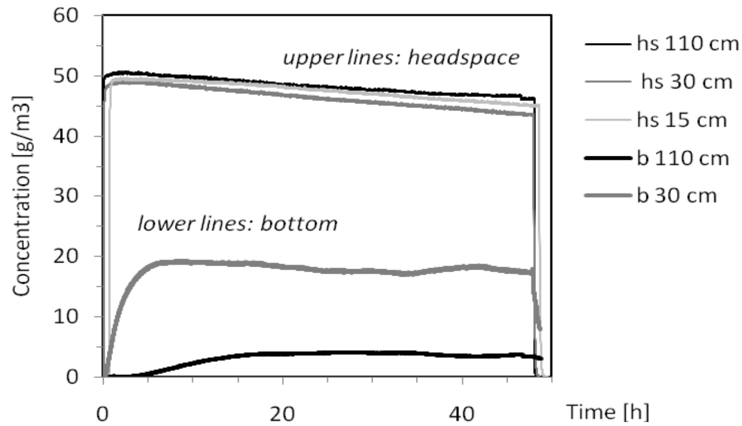

Fig. 1- Sulfuryl fluoride concentration by time depending on the height of flour in the glass column. Fumigation at room temperature.

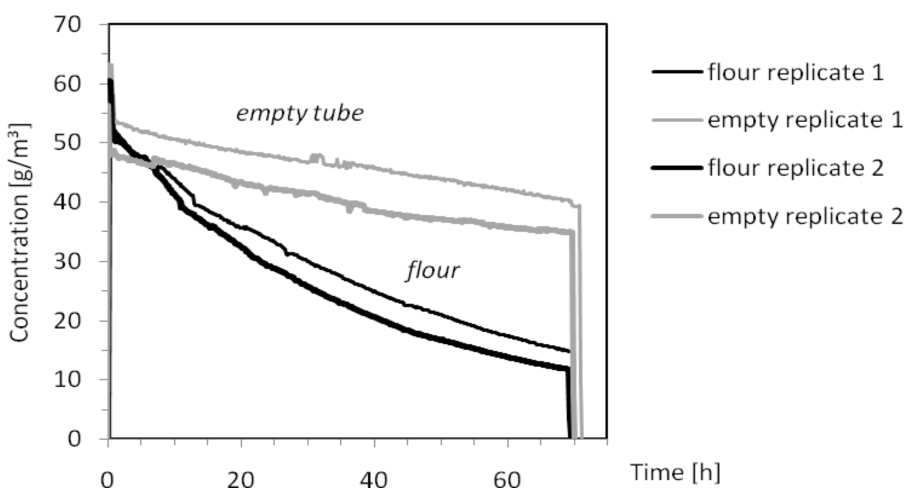

Fig. 2- Sulfuryl fluoride concentration by time under recirculation. Fumigation at room temperature.

The residual fluoride contents are listed in the table. The highest amount of fluoride was found in the 30 cm thick layer, followed by the 15 cm layer sample. In the large amount of flour (110 cm layer) 7.3 mg kg^{-1} fluoride was determined. The second experiment resulted in 17.1 mg kg^{-1} and 8.3 mg kg^{-1} fluoride in both replicates of the fumigation trials. The total dosage of SF was a bit higher in the first replicate.

Table 1. Fluoride residues [mg kg^{-1}] following fumigation of flour with sulfuryl fluoride in different experimental set up

Fluoride content in flour following fumigation by gravity penetration			
		Dosage [g h m^{-3}]	Fluoride [mg kg^{-1}]
Penetration in glass column	Thickness of flour		
110 cm (26 kg)	110 cm	2317	7.3 ± 0.2
30 cm (7 kg)	30 cm	2231	31.1 ± 0.2
15 cm (4 kg)	15 cm	2303	25.3 ± 0.4
Flour exposed to sulfuryl fluoride under recirculation			
100 g	Replicate 1	2008	17.1 ± 0.1
	Replicate 2	1795	8.3 ± 0.03

DISCUSSION

The penetration of flour by sulfuryl fluoride, the sorption and the formation of fluoride is complex. In contrast to Bell et al. (2003), who investigated 30 cm layers and assumed equal concentrations in any depth of flour for appropriate long times, the present study found that the concentration of SF at the bottom of the flour layer did not reach an equilibrium to the head space concentration. The diffusion of gases is driven by the concentration gradient. During its diffusion through the flour, there are other processes likely, i.e. sorption and desorption as well as the break down into fluoride and other compounds. An attempt to explain the findings could be the part of the sulfuryl fluoride-breakdown as the predominant process during its dispersion through the flour. This hypothesis is supported by the results of the second experimental set up, the continual decrease in concentration in the flour streamed by the sulfuryl fluoride.

Fluoride residues have been found, as expected, following the sulfuryl fluoride exposure experiments. Sulfuryl fluoride is known to form residual fluoride on various commodities. It is caused by the break down either by a potential hydrolysis of the molecule or, as formerly described by Meikle (1964) on flour, by reaction with proteins and amino acids. Scheffrahn et al. (1989) found fluoride on flour ranging between 60 – 450 mg kg^{-1} depending on the fumigant concentration (36 – 360 g m^{-3}) in 20 h exposure. According to this background, it has to be found out which maximum residue amounts (and the causing conditions) are principally possible. The present study tried to give an idea of a worst case scenario, an unintended fumigation of milling products in a mill. The potential contribution to the daily fluoride intake and the significance to a risk of overexposure due to this pathway have to be discussed.

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