Method development and validation of hydrogen phosphide and inorganic bromide determined as fumigant residues in commercialized rice grains in Thailand

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Abstract

Commercialized rice in Thailand was monitored for assessment of fumigant residues contaminant. Two-hundred eighty-nine rice samples were collected from different parts of Thailand during 2013–2014 and analyzed for hydrogen phosphide (HP) and inorganic bromide (IB) residues. The study was conducted by using gas chromatography–mass spectrometry (GC-MSD) coupled with Headspace and gas chromatography–electron capture detector (GC-ECD) to determine HP and IB. The limit of detection of the methods was 0.02 and 2 mg kg⁻¹ for HP and IB respectively, with recovery 85–108%. Detectable HP residues were found in 30% of the samples in the range of <0.05–2 mg kg⁻¹ and 10% of samples containing IB were traceable in the range of <5–20.6 mg kg⁻¹. The contaminations of HP in 19 samples were higher than the MRL set by the Ministry of Public Health of Thailand but the concentration of IB found in all samples was within the standard limit.

Introduction

Thailand is one of the world's biggest rice *(Oryza sativa)* producers (Maierbrugger, 2013). Traditionally, Thai dietary habits rely mainly on rice. Although the studies of Isvilanonda *et al.* (1995) showed that the rice consumption declined, the kingdom continues to export 10.8 million tons of milled rice in 2014, which was the highest figure in its history (Sarigalaya, 2015). As a result of the economic benefits of rice to the country, Thailand has to meet all international food safety standard requirements. Because there has always been a need to keep crops free from pests, the fumigation of pesticide substances to eliminate insects in rice grains is recommended in several steps of commodities conditioning before trade.

Fumigants are a gaseous element used for pest control in stored products and processed foods. It is possible to control all life stages of the pest. Fumigation is often the quickest way of controlling an infestation, saving time and money. Fumigants can reach where sprays, dusts and aerosols cannot reach and they are used where standards call for "zero insect tolerance" in products or living environments. Cereals and grains, such as milled rice, are mainly disinfected by hydrogen phosphide (HP), commonly known as phosphine, liberated from stable salt, such as magnesium phosphide or aluminum phosphide. In addition, in some cases, methyl bromide in a

gaseous form is used. The application of fumigants is recommended for quarantine and preshipment (QPS) and the prepacked condition. Hydrogen phosphide is a colorless gas that is used worldwide because of its rapid diffusion and extreme volatility (Kevin *et al*., 2000). Despite these desirable properties, a trace amount of hydrogen phosphide persists in commodities several months after treatment (Scudamore *et al.*, 1986) and can cause severe health problems due to its high toxicity. Hydrogen phosphide is toxic to the brain, kidneys, heart, and liver with an end point of cardiovascular collapse. Some investigators have reported pulmonary edema and changes in the kidneys and brain of experimental animals poisoned with phosphine. The maximum residue level (MRL) of hydrogen phosphide is fixed in rice grains at 0.1 mg kg⁻¹ by Thai regulation USFDA and Codex.

Another fumigant often used is methyl bromide (IB). This is a neurotoxic gas that can cause convulsions, coma, and long-term neuromuscular and cognitive deficits. Exposure to high concentrations of pure methyl bromide may cause inflammation of the bronchi or lungs. The studies of laboratory animals showed that methyl bromide causes liver injury in acute inhalation and acted as an alkylating agent of glutathione and other cellular molecules. The over-fumigating, the repeating application process and the others non-following the recommended application

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procedure transform methyl bromide into IB, but this form is much more inert in human organism. IB residue as an inorganic form can show the degree of non-conformation to fumigation procedure. In recent years, the fumigation of methyl bromide has been exempted by the phasing out of the Montreal Protocol (Ogden, 2004; Solomon et al., 2014). But until now methyl bromide has been continually applied in some counties. According to the international standard (Codex) and USFDA, the MRL of inorganic bromide in rice is permitted at 50 mg kg^{-1} by the Thai Ministry of Public Health. Thus, many countries have widely adopted this MRL with the exception of India and China that prohibit hydrogen phosphide residue in rice and the MRL is fixed at 25 and 5 mg kg^{-1}, respectively. These different MRLs set by some countries are not necessarily based on scientific data generated out of clinical studies but on the very low LOD provided only by sophisticated and expensive equipment. This imposes considerable additional costs as a big non-tariff barrier for the exports of developing countries.

The aim of this study was to investigate the presence of residues of HP and IB in rice for food security because there is no data bank available for the whole country and to provide basic information for developing food safety management strategies to protect public health. Therefore, this study assessed the situation of fumigant residue present in milled rice that was sold and consumed in different parts of Thailand. The main objectives of the survey are to create a body of data as a basis for planning and evaluating food-safety strategies and to formulate measures relating to food safety and the prevention of diseases caused by contaminants. Packed and unpacked white rice, Hom Mali rice (Thai jasmine), and brown rice were collected from shops, local markets, and supermarkets and were analyzed from August 2013 to August 2014. Gas chromatographic methods for the determination of HP and IB residues were developed and the methods had to be suitable for their intended use. The method of Musshoff et al. (2008) was used to determine the hydrogen phosphide residue. An aqueous solution of sulfuric acid was directly added to rice and hydrogen phosphide released above the sample in the headspace vial was detected and measured using gas chromatography coupled to mass spectrometry as a detector (GC-MSD). Thus, a modified Stijve (1977) method was used for the quantification of the total inorganic bromide in rice (CRL, 2008). The comminuted ground samples were suspended in an acidified aqueous solution of propylene oxide, with bromide simultaneously extracted and derivatized into 1-bromopropan-2-ol

and 2-bromopropan-1-ol, which were detected by gas chromatography with electron capture detector (GC-ECD) using 3-bromopropan-1-ol as an internal standard. This study presents the results of the control of fumigant residue in food commodities samples in order to ensure the compliance of food with international and Thai standards with regard to the permitted maximum legal limit. In addition, the conclusion provides the outcome of the consumer risk of fumigant residue to authorities that might be concerned and will use this information to devise a national food safety regulation.

Material and Methods

Instrumentation

For the determination of HP residue, a gas chromatography (GC) instrument was used. The equipment was a GC-MSD: Agilent Technology 6890N-5975 inert with a headspace mass detector (MSD) system chromatograph equipped with an Agilent J&W HP-PLOT Q capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). For the analysis of IB, the instrument used was a GC-ECD: Agilent Technologies 6890N with electron capture detector (ECD) equipped with a DB-Wax capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) (both from Agilent technology, USA).

Chemicals

Ethyl acetate (HPLC grade) was purchased from J.T. Baker, USA. Sulfuric acid (AR grade 98%) was obtained from QRёCTM, New Zealand for the preparation of the 3M and 10% V/V aqueous solution. Ammonium sulfate (for analysis), potassium bromide (99.999%), 3-bromopropan-1-ol (for synthesis), and 1, 2-propylene oxide (for synthesis) were the products of Merck KGaA, Germany. Storage at below 11ºC of 1, 2-propylene oxide was required. Zinc phosphide (Zn$_3$P$_2$, 99.998%) was obtained from Sigma-Aldrich, Germany. Anhydrous sodium sulfate (AR grade) was obtained from Fisher Scientific, UK. The sodium sulfate (Na$_2$SO$_4$) with granular 12–60 mesh, was baked for 4 hours at 600ºC in a furnace to remove residual water.

Standard solutions

A hydrogen phosphide standard solution (47 μg mL^{-1}) was obtained from the suspension of 2.35 mg of zinc phosphide (Zn$_3$P$_2$) powder in 50 mL of distilled water. After hand shaking the mixture, the suspension was placed into an ultrasonic bath for 15 minutes. A bromide ion working standard solution (50 μg mL^{-1}) was prepared by diluting the stock solution (1000

µg mL^{-1}) of potassium bromide (KBr) with distilled water. A working internal standard solution (10 µg mL$^{−1}$) of 3-bromopropan-1-ol was also successively prepared by diluting the stock solution (1000 µg mL$^{−1}$) with distilled water.

Calibrations

A calibration curve of HP was established from spiking calibration curves at four levels: 0.05, 0.1, 0.25, and 0.5 µg g$^{−1}$, by adding 16, 32, 81, and 162 µL of zinc phosphide standard solution (47µg mL$^{−1}$) to 4 g of matrix blank in a 20 mL headspace vial. Four levels and one matrix blank without the addition of the standard were shaken vigorously and then 8 mL of 10%V/V of H$_2$SO$_4$ was added in each vial. The headspace vials were capped suddenly to avoid the gas exhausting and placed in a vortex for 30 seconds. After 30 minutes of equilibrium time, the vials were injected and analyzed by the GC-MSD.

For the IB calibration curve, 100 and 500 µL, 1, 2, and 3 mL of the bromide working solution (equivalent to 5, 25, 50, 100, and 150 µg of bromide, respectively) were added to 5 mL of distilled water in screw cap glass vials (size 60 mL). Each vial was equalized to its volume with 8 mL with distilled water. As a reagent blank, an extra portion of 8 mL of water without the addition of the bromide working solution was derivatized. Derivatization was conducted by adding 5 mL of the propylene oxide solution and 1 mL of the 3M sulfuric acid solution. The vials were then closed and shaken briefly, and the mixtures stood at room temperature for 60 min. The mixtures were partitioned by the addition to the suspension of 40 mL of ethyl acetate and 4 g of ammonium sulfate. The vials were closed with screw caps and shaken vigorously by hand for 1 min and then by a shaker at 70 rounds per minute (rpm) for 20 min. Then the decantation of the upper organic phase was performed and it was dried using anhydrous sodium sulfate. One milliliter of the organic extract of the calibration standards was transferred into GC vials. One hundred microliters of internal standard solution (3-bromopropan-1-ol) were added. The resulting solutions were then ready for GC-ECD determination.

Samples

Two hundred and eighty-nine samples of rice consisting of 211 packed (18, 4, 2 and 187 samples of 1, 2, 2.5 and 5 kg plastic sealed bags, respectively) and 78 unpacked were collected from shops, local markets, and supermarkets. The varieties of rice were white rice (170 samples), Hom Mali rice (80 samples), and brown rice (39 samples). The collection was conducted by Regional Medical Sciences Centers (RMSC) to provide the same ratio as the Thai national consumption of rice. The shops, local markets, and supermarkets where the samples were found were located in Bangkok, Ayutthaya, and Nakornsawan, which represented the central region, Chiangmai and Phitsanulok for the northern region, Khon Kaen and Nakorn Ratchasima for the northeastern region, and Surat Thani and Songkhla for the southern region. Over a year, between 20 and 28 of samples were brought to the Pesticide and Veterinary Drug Residues Laboratory (PVRL) of the Bureau of Quality and Safety of Food (BQSF) every month. There were five monthly collections of rice from Bangkok in 2013 (128 samples) and one collection of samples every month from the other eight provinces in 2014.

Sample preparation

After receiving rice samples from RMSC, the sampling procedure was conducted rapidly. Five hundred grams of rice grains were divided into two portions of about 250 g. The first portion of rice grains was sealed in a plastic bag and stored in a freezer at −15ºC or below for hydrogen phosphide determination for at least 24 hours. After one day of freezing, 4 g of the sample was weighed in a 20 mL headspace vial and 8 mL the 10% V/V of sulfuric acid (H$_2$SO$_4$) was added. The GC-MSD analysis procedure followed the same steps as the calibration curve. To determine the inorganic bromide residue, a comminuted ground sample of the second portion was obtained after the homogenization of the rest of the sample (250 g) in a blender. A 2-gram portion of 20 mesh rice powder was weighted into a screw cap vial (size 60 mL) for inorganic bromide analysis. After following exactly the same preparation as the calibration curve for bromide ion, the aliquot was injected into the GC-ECD to determine the trace of methyl bromide in the sample.

Sample analysis

The instruments used for analysis were a GC-MSD and GC-ECD with conditions described in Table 1. After the acquisition of the total abundance chromatogram, peaks were identified by their retention time and mass spectra. The most abundant ion for hydrogen phosphide (34 m/z) that showed no evidence of chromatographic interference and had the highest signal-to-noise (S/N) ratio was selected for quantification purposes, and ion 31 m/z and 33 m/z were the first and second qualifier ions, respectively. The concentration of inorganic bromide was determined by an interpolation of the relative

Table 1. GC-MSD and GC-ECD conditions for hydrogen phosphide and inorganic bromide determination respectively

	Hydrogen phosphide	Inorganic bromide
Instruments	GC-MSD	GC-ECD
	Agilent Technologies 6890N-5975 inert with headspace	Agilent Technologies 6890N
Injection	duration: 0.5min	volume: 1μl
Column	Plot-Q, 30 m x 0.25 mm i.d., 0.25μm film thickness	DB-Wax, 30 m x 0.25mm i.d., 0.25μm film thickness
Temperature	inlet: 150ºC	inlet: 220ºC
	oven: initial 50ºC, hold 1 min, rate 10ºC min^{-1} to 120ºC	oven: initial 50ºC, hold 1 min, rate 15ºC min^{-1} to 180ºC, rate 3ºC min^{-1} to 210ºC
	headspace: 60ºC for 10 min	
	MSD condition: Transfer line 280ºC, MS quadrupole 280ºC, MS source 230ºC	μECD detector: 200ºC pulsed splitless mode
Other	Detection mode: SIM	Flow rate: helium (constant flow): 1.5 ml min^{-1}
	Ionization mode: Electron impact (EI)	
	Target ion: 34 m/z ratio 100%, Qualifier ion 1st: 31 m/z ratio 30±15%, Qualifier ion 2nd: 33 m/z ratio 30±15%	

peak areas to the internal standard (3-bromopropane-1-ol) peak area in the sample on a spiked calibration curve.

Results and Discussion

Method validation

The validation data showing the performance characteristics of the analysis methods for hydrogen phosphide and inorganic bromide in rice are summarized in Table 2. According to the European Guideline: SANCO/10232/2006, recovery of single pesticide residue in quantitative analytical methods should be between 70–120% in terms of 0.01–1 mg kg^{-1}, although lower and higher recovery values might be acceptable if the analyzed compound shows good repeatability. The concentrations of inorganic bromide determined by the method are between 5 and 75 mg kg^{-1} and the recovery were in range of 80–110% is favorable for this method (AOAC, 2012).

Table 2. The validation data showing the performance characteristics of the methods (n=8)

Characteristics	Hydrogen phosphide		Inorganic bromide	
	Criteria	Value	Criteria	Value
Linearity Range	$r^2 \geq 0.995$	$r^2 = 0.999$ (0.05-0.5 mg kg^{-1})	$r^2 \geq 0.995$	$r^2 = 0.999$ (5-75 mg kg^{-1})
Accuracy (%)	70-120	85-108 (at 0.05, 0.1, 0.2mg kg^{-1})	80-110	94-97 (at 5, 25, 50 mg kg^{-1})
Precision(HORRAT)	$\leqslant 2$	0.2 - 0.4	$\leqslant$	0.4 - 0.5
LOD(mg kg^{-1})	-	0.02	-	2
LOQ(mg kg^{-1})	< 0.1	0.05	< 50	5

The first calibration level and the limits of quantitation (LOQs) were lower than the MRLs established by Codex and the Thai authority. These methods are fit for the intended use of the determination of fumigant residue.

To meet the critical detection limits at 0.1 μg kg^{-1} of hydrogen phosphide, an analytical method is needed. Because of its volatility, the residue levels of hydrogen phosphide in food commodities are expected to be very low. However, the result of the GC-MSD determination was excellent with Total Ion Chromatogram (TIC) of 0.5 μg kg^{-1} of hydrogen phosphide in rice, and its mass spectra are shown in Figure 1.(a and b). For inorganic bromide determination, the chromatograms of the rice sample blank, the sample blank spiked with the internal standard (3-bromopropan-1-ol) and with 25 mg kg^{-1} bromide ion, are shown in Figure 1.(c and d). The concentration of inorganic bromide was calculated by summarizing two derivative peaks; 1-bromopropan-2-ol and 2-bromopropan-1-ol, and comparing them with standard peaks. The specificity of both methods could be confirmed. The GC-MSD determination of hydrogen phosphide used the spectra 34 m/z ratio 100% as the target ion, which had its first qualifier ion as 34 m/z ratio 30±15% and the second qualifier ion as 33 m/z ratio 30±15%. In addition, the specificity of the inorganic bromide determination method was expressed by two derivative products (1-bromopropan-2-ol and 2-bromopropan-1-ol), which were isomers and had a 3:1 ratio.

To keep the maximum amount of hydrogen phosphide in the sample required storage in a freezer at below -15ºC for 24 hours. Volatile hydrogen phosphide gas was effectively removed from whole rice grains in an acid solution without blending to avoid the high temperature created by mechanical force in a sample preparation step. The required analytical method was
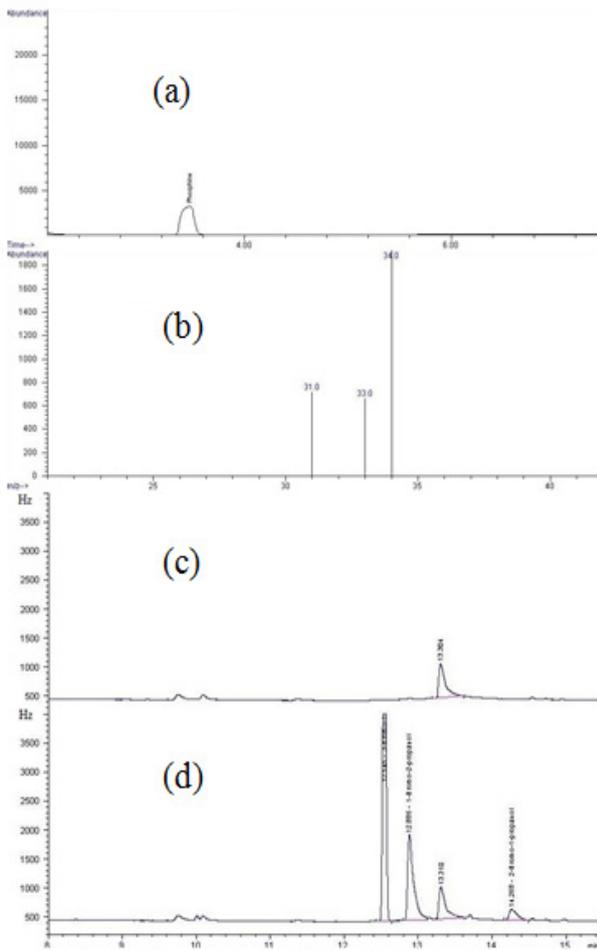
Figure 1. GC-MSD TIC chromatogram of 0.5 mg kg-1 fortified sample of hydrogen phosphide (a). Mass Spectra of the Targets: hydrogen phosphide (b). GC-ECD chromatogram of rice blank sample (c). Spiked rice sample at 25 mg kg^{-1} bromide ion and internal standard (3-bromopropane-1-ol) (d)

improved because zinc phosphide (Zn_3P_2) used as a standard for the quantification of gaseous hydrogen phosphide has difficulty dissolving in an organic solvent and aqueous solution. The preparation of the standard solution by serial dilution of zinc phosphide in glucose has been reported by Hilton *et al.* (1972) to facilitate the solubility, but the mean recovery of the fortified sample was only 33%, which is beyond the criteria of acceptable accuracy (80–110%). Therefore, the suspension of zinc phosphide in water reported by Okuno *et al.* (1975) provided a better result. The methodology developed in this study used the promising preparation of the standard in water with a precaution. Because of the insolubility of zinc phosphide in water, the suspended particles needed to be shaken and homogenized continually during the spiking procedure for each sample. The zinc phosphide solution was placed on a magnetic stirrer to acquire a homogenized solution. The linearity of the calibration curve was found to be excellent, with $r^2 = 0.999$, and provided acceptable precision.

Unlike labile hydrogen phosphide, inorganic bromide is stable and fixed on rice components. Some studies have shown that methyl bromide will react with the protein fraction of wheat (Winteringham *et al.*, 1955) and a numerous studies have indicated that a single treatment at recommended doses has little or no adverse effect on food value (Polansky *et al.*, 1971; Slover *et al.*, 1972). The excess of inorganic bromide residue found in samples can be explained by the non-conforming use of the methyl bromide treatment. Inorganic bromide residue is not likely to be important from the point of view of human health if the foods containing them are consumed in normal amounts. Compared to the method proposed by Mapes *et al.* (1957), our proposed method was more convenient in terms of time and equipment handling. Moreover, the determination of total bromide ion by X-ray fluorescence, neutron activation analysis, and a selective ion electrode were impossible to apply routinely in laboratory analysis (Lindren *et al.*, 1962; Banks *et al.*, 1976). The method development was inspired by the use of gas chromatography published by Heuser et al. (1970) and Stijve (1977). In addition, the blending sample (particle size less than 20 mesh) was primordial for good penetration of the extract solvent and to provide a better result. A statistical test (t-test, p-value = 5%) of the results obtained from the use and non-use of internal standard did not show the difference and the gas chromatography condition can be modified to shorten the analyzing time.

Fumigant residue in rice samples

Hydrogen phosphide

Hydrogen phosphide residue was found in 75 samples (30%) from the total of 289 samples of rice grains in the range of <0.05-2 mg kg^{-1}. Nineteen of the positive samples (about a quarter) had hydrogen phosphide residue of more than 0.1 mg kg^{-1} (Codex MRL). The detection of the over-MRL traces of fumigant were mostly observed in the early period of studies (in 2013: 1 sample in September, 3 samples in October, and 10 samples in November, and in 2014: 5 samples in January). These results were noted because of the detection of hydrogen phosphide residue in samples collected from Bangkok and the surrounding area. The entire samples from the northern, northeastern, and southern provinces did not show an excess of the MRL. The distribution of the varieties of rice and the packaging conditions did not play a major role in the detection of hydrogen phosphide residue. However, the origin of the samples had a different influence on the ratio of detection. More than 80% of positive samples were collected

Table 3. Number of samples presented the residues of hydrogen phosphide and inorganic bromide and their number of over MRL (0.1 mg kg^{-1} for hydrogen phosphide and 50 mg kg^{-1} for inorganic bromide)

Period (year month)	Source of sample (n)	Hydrogen phosphide (n)		Inorganic bromide (n)	
		Detected	>MRL[a]	Detected	>MRL[b]
2013 August	Bangkok (28)	1	0	2	0
2013 September	Bangkok (25)	14	1	2	0
2013 October	Bangkok (26)	18	3	2	0
2013 November	Bangkok (24)	19	10	3	0
2013 December	Bangkok (25)	13	0	5	0
2014 January	Ayutthaya (20)	8	5	0	0
2014 February	Nakornsawan (20)	1	0	2	0
2014 March	Chiangmai(20)	0	0	3	0
2014 April	Phitsanulok (20)	0	0	2	0
2014 May	Khon Kaen (20)	0	0	0	0
2014 June	Nakorn Ratchasima (21)	0	0	2	0
2014 July	Surat Thani (20)	1	0	3	0
2014 August	Songkhla (20)	0	0	2	0
	Total (289)	75	19	28	0

Legend: *(n)* number of sample; (>MRL) results above the maximum residue limits.
[a] MRL value established by Thai legislation for hydrogen phosphide set at 0.1 mg kg^{-1}.
[b] MRL value established by Thai legislation for inorganic bromide set at 50 mg kg^{-1}.

from local markets, but for all the analyzed samples it represented only approximately 50%. An overview of fumigant contamination showed that the residue of hydrogen phosphide was traceable in 30% of samples but not at the same frequency over 13 months. Because the Thai regulation for fumigant residue was established in August 2013 (the beginning of the project), an improvement to the contamination level was observed. Only one year after the start of the studies, hydrogen phosphide was detected on almost none of the samples. The application of the food safety standard recommended by the Department of Agriculture (DOA) was adopted by the packaged rice industry. The varieties, sources, and packaging forms for rice did not influence the level of hydrogen phosphide. The difference in the residue bounded with various constituents was not significant.

Inorganic bromide

Two hundred and eighty-nine samples were analyzed according to the mentioned method for inorganic bromide. Twenty-eight (10%) of the total samples showed contamination with fumigant residue (range of <5-20.6 mg kg^{-1}). The concentrations of inorganic bromide residue in all samples were below the MRL. In addition, 11(40%) samples contaminated by inorganic bromide were under the limit of quantitation (LOQ=5 mg kg^{-1}).

The results in Table 3. showed that rice was contaminated more by hydrogen phosphide than inorganic bromide in a number of positive samples (30% hydrogen phosphide and 10% inorganic bromide) and in terms of the level of contamination (hydrogen phosphide: 19 samples were over the MRL, inorganic bromide: 0 samples). The explanation of this fact is that hydrogen phosphide is available in solid formulations of metal phosphide and the fumigation of hydrogen phosphide is relatively easy compared with methyl bromide. Methyl bromide, which is more versatile, retains its place as the fumigant of choice. Although, the amount of methyl bromide adsorbed by particular commodities is generally important, hydrogen phosphide can efficiently penetrate and fix into commodities. This is why hydrogen phosphide is widely used in most tropical countries such as Thailand. Moreover, the restriction of the use of methyl bromide was deposed by the Montreal Protocol because of its ozone depletion properties. Thailand successively reduced methyl bromide importation before the total ban in 2015, which is why the packaged rice industry did not prefer this gas to hydrogen phosphide.

Conclusion

In this work, the determination of HP and IB residues in rice was performed by using GC-MSD and GC-ECD, respectively. The proposed methods were validated and proved to be sufficiently reliable and efficient for measuring volatile fumigant residues. The LOQs were lower than the MRLs established by the Ministry of Public Health of Thailand. The feasibility of the method for its application in routine analysis was verified. The resulting survey data indicated that the use of metal phosphide to control pests in rice poses some threat of contamination of HP in rice, which should be solved by the public health regulator. On the other hand, the use of methyl bromide was well limited and controlled by the authority. Some IB-positive samples showed the level of contamination lower than the MRL and safe for the consumers.

Acknowledgements

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