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## Organic and Inorganic Bromide Residues in Spices Fumigated with Methyl Bromide

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Two warehouses containing imported spices were fumigated with methyl bromide to eradicate a khapra beetle infestation. Methyl bromide (MB) and inorganic bromide (INBR) residues were determined in spices before and after fumigation by gas-liquid chromatography/electron capture detection (GC/ECD). A private laboratory analyzed spices for INBR with identical lot numbers as those analyzed with GC/ECD by using an ashing-titration method. The highest MB residue found in a before fumigated spice sample was 14.85 ppm in parsley. After the fumigation, the highest MB residue was found in Yugoslavian sage (65.78 ppm). INBR residues in spices before fumigation which were analyzed by GC/ECD showed none with residues in excess of the 200 ppm INBR tolerance for spices. Analysis of fumigated spices revealed two samples with INBR residues greater than 200 ppm. Ashing-titration analysis by the private laboratory showed seven spice samples with INBR residues exceeding 200 ppm before the fumigation and only four fumigated spice samples with residues in excess of 200 ppm. A comparison of residue levels obtained by the two methods is shown. Residues for INBR in selected samples were confirmed qualitatively and quantitatively by gas-liquid chromatography/mass spectrometry (GC/MS).

### INTRODUCTION

In the fall of 1980, two warehouses in the northeastern United States which contained various spices from 27 foreign countries were found to be infested with khapra beetle (*Trogoderma granarium*). Both warehouses were covered with tarpaulins and fumigated with methyl bromide (MB) to eradicate the pest. Before the fumigation, representative spice samples were collected for MB and INBR residues. Seventy-two hours after the fumigation, spice samples were again collected from identical lot numbers as those collected before the fumigation for MB and INBR analysis. The spices were subsampled and one group was shipped in dry ice to the National Monitoring and Residue Analysis Laboratory (NMRAL) for MB and INBR residue determination by GC/ECD. The other group was sent to a private laboratory for INBR residue determination by an ashing-titration method.

**Warehouse Size and Methyl Bromide Fumigation.** The area of warehouse no. 1 was 3 400 000 cubic feet. Methyl bromide was applied to its contents at a rate of 7.5 lbs/1000 cubic ft for 12 h. Warehouse no. 2 contained 312 000 cubic feet and methyl bromide was applied at a rate of 6 lbs/1000 cubic ft for 12 h.

Spice samples were collected according to a biometric design developed by the Technology Analysis and Development Staff (TADS) of Plant Protection and Quarantine of the United States Department of Agriculture.

### EXPERIMENTAL SECTION

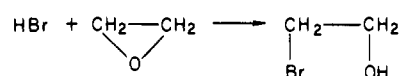
**(1) Methyl Bromide.** Free methyl bromide (MB) was extracted and analyzed by using a modification of a method described by Scudamore and Heuser (1970). Ten

grams of spice was extracted with 30-120 mL (extraction solvent volume was adjusted so that the entire sample was immersed) of a 5:1 V/V, distilled in glass, acetone-distilled water mixture in an amber bottle with a screw cap. All samples were allowed to stand at approximately 8 °C for 24 h before analysis to extract the MB.

Analyses were performed by using two dissimilar columns for qualitative and quantitative confirmation. The analytical instrument used was a Microtek MT-222 equipped with a Ni<sup>63</sup> electron-capture detector. The columns employed were glass 1.8 m long × 4 mm i.d. One column was packed with 15% UCON LB-550X on 60/80 mesh on Chromosorb W-HP; the other was packed with 10% Carbowax 20M on 80/100 mesh, Gas Chrom Q. Instrument parameters were identical for both columns: injection port temperature, 160 °C; oven temperature, 55 °C; detector temperature, 325 °C; carrier gas, 95%/5% argon-methane; flow rate 20 mL/min.

The GC injection port contained a glass insert with a small piece of glass wool inside. The insert was cleaned and glass wool replaced daily since the samples were not subjected to a cleanup procedure before instrumental analysis.

**(2) Inorganic Bromide (GC Procedure) Standard Preparation, Derivatization, and Determination in Samples. (A) Standard Preparation.** 2-Bromoethanol was synthesized by the addition of hydrobromic acid to ethylene oxide as described in the following reaction.



The crude product was vacuum distilled and examined by GC/MS. Bromoethene and bis(2-bromoethyl) ether were formed in addition to 2-bromoethanol. Careful

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Table I. Organic and Inorganic Bromide Residues (ppm) in Spices from Warehouse No. 1 in Northeast United States<sup>a,b</sup>

name of spice	GC/ECD method				ashing-titration method	
	before fumigation		after fumigation		before fumigation	after fumigation
	CH <sub>3</sub> Br	Br <sup>-</sup>	CH <sub>3</sub> Br	Br <sup>-</sup>	Br	Br
Pakistan dundicut chillies	0.06	22.13	3.74	40.70	0.0	13.4
Iranian cumin seed	0.40	7.46	1.78	24.67	39.9	41
Bulgarian wheat no. 2 medium	0.49	<0.01	0.56	28.73	26.6	c
yellow split peas	0.26	4.8	26.55	8.00	289.2	479
Spanish orange peel	0.58	20.61	16.31	<0.01	23.2	10
Egyptian peppermint	0.46	59.69	28.23	148.00	40.5	15
Singapore E. I. mace	1.25	21.54	0.05	22.69	20.0	10.5
Haitian orange peel	0.39	0.60	16.93	9.62	0.0	10.25
Brazil black pepper	0.23	13.81	20.90	64.48	23.2	39.36
Indian cumin seed	0.11	21.45	1.02	26.68	103.0	73.5
Grenada W. I. nutmeg	0.38	27.27	0.94	58.46	20.5	42
Spanish aniseed	0.28	16.94	24.99	35.39	16.7	22.5
Jamacian ginger	0.02	11.92	1.69	65.05	33.4	33.85
Italian juniper berries	3.04	29.80	22.69	0.72	0.0	0.0
Egypt basil	<0.01	19.76	23.31	272.45	674.0	546.0
Greek oregano powder	3.31	0.84	3.07	14.90	51.6	46.1
Ceylon cinnamon	1.63	3.37	6.62	37.33	6.7	3.5
Indian cumin seed	0.35	99.36	11.71	42.26	133.0	36.0
Indian fenugreek	0.11	0.68	22.39	8.96	53.2	206.9
Turkish laurel leaves	0.42	<0.01	1.39	5.13	0.0	0.0
Chinese fennel	0.14	1.92	3.18	51.97	6.6	0.0
Bulgarian savory	3.01	4.80	20.37	38.13	106.4	125.0
Pakistan cumin seed	0.15	12.18	2.90	29.49	13.3	100.0
Indian celery seed	3.70	3.80	23.22	33.68	33.2	26.5
Indian sannam chillies	0.70	48.00	1.69	167.27	425.0	450.0
Guatemalan decorticated cardamon	0.35	1.12	0.55	9.70	0.0	0.0
Indonesian cassia	0.13	2.13	0.28	10.18	50.5	33.5
Egyptian dill weed	<0.01	176.0	0.07	323.32	612.0	c
Moroccan coriander	0.68	7.46	17.97	32.00	43.2	23.5
Cochin (Indian) ginger	0.86	2.67	2.49	23.64	33.2	48.9
Turkish cumin seed	0.03	5.37	1.20	16.82	89.7	75.5
Chinese cassia buds	0.08	<0.01	9.57	30.06	16.7	12.0
Chinese peeled ginger	0.03	46.18	0.11	1.16	40.0	0.0
Spanish thyme	2.52	2.67	22.48	37.45	26.7	30.5
Ground cassia	0.04	1.03	0.48	6.59	53.2	56.1
Greek sage	0.89	10.32	3.39	30.65	39.5	30.9
Ceylon cloves	0.07	4.64	0.20	11.23	10.0	10.0
Telli (extra bold) black pepper	1.70	12.26	9.22	38.97	83.8	73.2
Dutch poppyseed	0.04	3.09	3.09	20.93	40.5	39.7
Egyptian marjoram	8.71	32.0	24.77	117.81	0.0	0.0
Spanish lemon peel	0.48	20.80	15.94	7.84	35.0	12.0
Mexican oregano	9.41	25.60	18.02	46.15	46.5	56.1
Sannam ground blended dundicuts	<0.01	51.20	0.07	55.96	6.6	c
Mexican pimento	0.05	3.20	0.23	37.67	53.2	c
Indian dill seed	0.04	24.88	2.40	40.34	116.0	42.0
Indian fennel seed	1.10	32.0	0.32	44.36	89.8	190.5
Turkish oregano	5.22	4.44	12.90	31.02	96.4	100.0
Honduran pimento	3.11	<0.01	15.35	71.78	33.0	17.4
Guatemalan green cardamons	4.55	5.25	15.03	36.36	0.0	0.0
Holland E. I. nutmegs	0.06	53.33	0.24	55.76	7.0	3.3
Sannam deseeded chillies	0.11	49.77	0.10	45.45	172.9	170.0
Ground red pepper	0.03	38.22	0.06	29.02	315.0	c

<sup>a</sup>Results corrected for recovery from fortified samples. <sup>b</sup>Lower limits of sensitivity = 0.01 ppm. <sup>c</sup>Residues not reported.

fractionation resulted in a product that was  $\geq 99.9\%$  pure. This was then used to prepare standard solutions.

**(B) Derivatization and Inorganic Bromide Determination.** Inorganic bromide (INBR) was derivatized to 2-bromoethanol and extracted with slight modifications of a method described by Stijve (1977). The spices were ground to a powder, and a 2.0-g representative of each was acidified with 1 mL of 6 N plus 10 mL of 0.6 N sulfuric acid in an excess of ethylene oxide in 125-mL amber bottles. After 2 h, 2 g of ammonium sulfate and 25 mL of toluene were added to each sample. Samples were shaken on a mechanical shaker for 5 min, allowed to settle, and then shaken again for 1 min. The mixture was again allowed to settle, and 5 mL of the solvent layer was transformed to a centrifuge tube containing 1 g of anhydrous sodium sulfate.

Quantitation of 2-bromoethanol was achieved with the instrument and columns described previously for methyl bromide analysis. The instrumental parameters, however, were slightly different: injection port temperature, 200 °C; oven temperature, 140 °C; detector temperature, 300 °C.

The carrier gas and flow rate were as described previously.

INBR residues in duplicate samples were also analyzed by a private laboratory by using an ashing-titration method described by Schrader et al. (1942).

**GS/MS Confirmation.** Selected spice extracts were scanned for 2-bromoethanol on a Hewlett-Packard 5982A GC/MS connected to a 5933A data system. The chromatographic column employed was 1.83 m  $\times$  2 mm i.d. glass packed with 5% Carbowax 20M on 100–120 mesh Chromosorb W-HP. The oven temperature was operated

**Table II. Organic and Inorganic Bromide Residues (ppm) in Spices from Warehouse No. 2 in Northeast United States<sup>a,b</sup>**

name of spice	GC/EC method				ashing-titration method	
	before fumigation		after fumigation		before fumigation	after fumigation
	CH <sub>3</sub> Br	Br <sup>-</sup>	CH <sub>3</sub> Br	Br <sup>-</sup>	Br	Br
Peru annato	0.85	16.75	4.95	36.96	139.86	36.63
Dutch poppy seed	0.54	9.22	5.17	13.93	49.5	23.31
Egyptian caraway	0.12	3.11	5.41	10.00	3.33	26.64
Egyptian anise	0.28	<0.01	16.99	11.21	0.0	36.63
Turkish bay leaves	0.08	<0.01	31.87	3.26	0.0	3.33
China star anise	0.10	<0.01	32.09	16.20	23.31	0.0
Madagascar cloves	0.11	<0.01	15.30	1.18	33.3	0.0
Egyptian basil	0.35	36.27	12.56	83.52	0.0	73.26
Turkish oregano	0.70	3.29	50.09	29.44	0.0	13.32
West Indian nutmeg	0.31	29.99	13.56	29.76	77.26	303.03
Indonesian cassia	0.09	0.00	24.98	27.60	59.54	0.0
Egyptian spearmint	0.62	4.04	36.78	113.92	0.0	0.0
Oriental mustard canada	0.15	1.92	3.88	9.49	0.0	0.0
Indian ginger	0.09	3.98	2.24	30.00	66.0	0.0
Turkish cumin	0.45	19.15	4.27	14.23	66.5	16.63
Guatemalan cardamon	0.09	0.0	6.35	15.59	6.66	29.97
Moroccan corriander	0.12	2.44	29.09	51.86	16.65	66.60
Pakistan chillies	1.18	42.41	37.82	63.72	186.48	136.53
Indian tumeric	0.14	4.80	4.24	6.86	49.59	66.6
sassafras	0.16	0.0	3.66	38.28	10.0	0.0
California parsley	14.85	9.87	44.48	79.71	135.20	33.3
W. German peppermint	1.02	66.66	13.60	52.28	99.9	0.0
Canadian yellow mustard	0.09	0.00	2.87	1.98	0.0	9.99
Indian fennel	0.09	51.16	6.73	47.94	103.23	23.31
Yugoslavian sage	0.12	1.10	65.78	10.78	33.2	83.25
Hungarian paprika	0.45	5.17	6.22	64.11	109.80	0.0
Guatemalan allspice	0.06	0.72	18.30	38.30	9.99	13.32
Albanian savory	0.36	0.0	19.43	33.79	0.0	43.29
China chillies	0.21	27.22	24.89	25.17	290.04	3.33
Indian chillies	0.41	90.58	28.02	64.48	26.64	36.63
Canadian brown mustard	0.14	0.50	<0.1	3.18	0.0	0.0
Honduran sesame natural	0.68	36.77	2.06	19.86	36.65	19.98
Indian celery	0.11	6.82	11.94	33.79	83.25	73.26
Israeli fenugreek	0.06	5.31	0.80	8.89	9.9	0.0
Egyptian dillweed	0.19	81.62	3.01	134.74	223.11	0.0
Spanish/Portuguese rosemary	15.42	<0.02	2.80	19.18	6.60	0.0
Spanish thyme	0.18	1.18	29.96	112.10	55.31	0.0
Egyptian marjoram	0.58	31.01	17.10	22.63	0.0	0.0
Brazilian black pepper	0.50	18.60	8.00	15.79	0.0	43.29
Turkish dillseed	0.11	23.28	c	c	33.5	d
Indian dillseed	c	c	6.55	20.74	d	36.63
Brazilian white pepper	c	c	4.11	7.79	c	29.97
Indonesian mace	0.35	49.84	d	d	133.2	c

<sup>a</sup> Results corrected for recovery from fortified samples. <sup>b</sup> Lower limits of sensitivity = 0.01 ppm. <sup>c</sup> Samples not received. <sup>d</sup> Samples not reported.

isothermal at 135 °C. The samples were scanned in the Selected Ion Monitoring (SIM) mode at 70 eV. The ions monitored were 79, 95, 97, and 124.

## RESULTS AND DISCUSSION

Blank solvents (SC), spiked solvents (SFP), blank spice samples (COMP), and spiked spice samples (CF) were analyzed with each group of program samples for quality control.

MB recoveries from spiked samples ranged from 55% to 105%, and INBR recoveries ranged from 68% to 106%. The lower limit of detection for both MB and INBR was 10 ppb.

Exposure of the spices to the 5:1 acetone-water solvent for extraction of methyl bromide for longer than 24 h resulted in diminished recoveries in spiked samples. Presumably, this was due to the N-methylation of proteins as described by Winteringham (1955).

Tables I and II present methyl bromide (MB) and inorganic bromide (INBR) residues in before fumigated and fumigated spices by gas-liquid chromatography at NMRAL, and INBR residues in duplicate samples by the ashing-titration at the private laboratory. Table I results

show residues of the spices collected from warehouse no 1, and Table II shows the residue results of those collected from warehouse no 2.

**Methyl Bromide. National Monitoring and Residue Analysis Laboratory (NMRAL) by Gas-Liquid Chromatography.** Most before fumigated spices showed significant MB residues. This probably indicates that either many of the spices were fumigated before they were brought into the country, or that cross contamination from fumigated spices to those which were not fumigated occurred during shipment to the laboratory. All spices did show an increase in MB residues after fumigation except in Spanish/Portuguese rosemary (15.42 ppm in before fumigated and 2.80 ppm in the rosemary after fumigation) and Greek oregano powder (3.31 ppm in before fumigated and 3.07 ppm in the oregano after fumigation).

**Inorganic Bromide. National Monitoring and Residue Analysis Laboratory (NMRAL) by Gas-Liquid Chromatography.** Five spice samples from warehouse no. 1 revealed higher INBR residues in before fumigated than in fumigated ones. The largest residue difference was found in Indian cumin seed (99.36 ppm in before fumigated and 42.26 in fumigated seed). In ware-

Table III. Comparison of Inorganic Bromide Ion Residues in Six Selected Spices before Methyl Bromide Fumigation

spice name	residues		
	GLC/ ECD	ashing- titration	GC/MS spec
Indian cumin seed	21.45	73.5	22.0
Egyptian basis	19.76	546.0	21.0
Indian sannan chillies	48.00	450.0	45.0
Egyptian dillweed	176.0	a	133.0
Shannon ground blended dundicuts	51.20	a	32.1

<sup>a</sup> Residues not reported.

house no. 2, seven spice samples were found to have higher INBR residues in before fumigated samples than in those which were fumigated. The highest residue difference was in West Germany peppermint (66.66 ppm in before-fumigated and 52.28 ppm in the fumigated spice).

Six before-fumigated samples were randomly selected for GLC/MS analysis of INBR residues. The analyses showed close agreement with the values obtained by GC/ECD (Table III).

In an effort to obtain samples without bromide residues, various spices were purchased from a wholesale warehouse. MB and INBR residues found in these samples are presented in Table IV. MB residues ranged from <0.01 ppm to 1.15 ppm (in oregano leaves). INBR residues ranged from <0.01 ppm to 42.97 ppm (in red pepper). These residues lend credence to our supposition that the spices were fumigated before they reached the United States.

**Inorganic Bromide. Private Laboratory (Ashing-Titration Method).** The ashing-titration analytical method used by the private laboratory is described by Schrader et al. (1940).

There were 47 samples from warehouse no. 1 with data from before-fumigated and fumigated spices. INBR residues determined by the ashing-titration method are presented in Tables I and II. A comparison of residues in before-fumigated and fumigated samples reveals that in the samples from warehouse no. 1 (Table I), 22 of the 47 samples showed higher INBR residues in before fumigated samples than those which were fumigated. In warehouse no. 2 (Table II), 20 of 39 before fumigated spices showed higher INBR residues than fumigated spices. The private laboratory did not report a lower limit of sensitivity and many of the INBR residues were reported as zero.

Some of the higher INBR residues in fumigated spices could be accounted for by decomposition of MB by N-methylation of the protein function of the fumigated commodity. Stijve (1977) found INBR residues of 1550 ppm in fumigated (*Boletus edulis*) mushrooms and reported that further fumigation produced no detectable change in INBR residues. Craske and Reuter (1965) revealed that dried *B. edulis* contained at least 38 water soluble nitrogenous compounds of which several were simple amines that react readily with MB. Obviously, both proteinaceous and alkaloidal components of the spices

Table IV. Organic and Inorganic Bromide Residues (ppm) in Spices from a Warehouse in New Orleans via the GC/ECD Method<sup>a,b</sup>

name of spice	methyl bromide	inorganic bromide
West Indian whole nutmeg	<0.01	40.96
Guatemalan whole cardamon decortigated	0.14	20.35
Indian black pepper, extra bold tellicherry	0.45	11.90
Indian fenugreek, whole	0.0	0.00
Egyptian marjoram, whole	0.19	38.41
Spanish thyme, whole	0.38	0.00
Indian dill seed, whole	0.69	11.61
Indian sannam red pepper, whole	0.84	76.92
Indian celery seed, whole	1.81	14.59
Indonesian cassia cinnamon sticks, whole	0.33	<0.01
Ceylon cinnamon sticks soft	<0.01	<0.01
Dutch poppy seeds	0.14	3.23
Indian fennel seeds	0.42	17.48
Mexican pure ground allspice	0.03	0.77
Indian cominos seed, whole	0.05	12.21
Turkish oregano leaves, whole	1.15	2.41
Yugoslavian savory, whole	0.65	8.04
pure ground red pepper	0.09	42.97
sweet basil, whole	0.62	14.84
Cassia cinnamon, pure ground	0.39	<0.01
Mexican oregano, pure ground	0.05	<0.01
Morraccan coriander, whole	0.25	1.26

<sup>a</sup> Results corrected for recovery from fortified samples. <sup>b</sup> Lower limits of sensitivity = 0.01 ppm.

could undergo N-methylation with concomitant production of bromide ion.

In before fumigated spices, GC analyses showed no INBR residues greater than the 200 ppm tolerance for spices and only two fumigated spices which exceeded the tolerance, Egyptian basil (272 ppm) and Egyptian dillweed (323 ppm). INBR analysis by the ashing-titration method showed seven spice samples which exceeded the tolerance before they were fumigated and four samples after fumigation with residues greater than the 200 ppm tolerance.

Comparison of INBR residues obtained by the GC-ECD method at the National Monitoring and Residue Analysis Laboratory (NMRAL) and the ashing-titration method used by the private laboratory reveals some significant differences. The origin of these differences is obscure but may be technique related. Our experience with fumigant residues indicates that the accuracy of the data using the ashing-titration method is technique dependant.

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