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Article

Testing purity of commonly used marketed insecticides collected from different regions of Bangladesh

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Abstract: The study was made on testing purity of different marketed brands of three insecticide groups such as quinalphos, malathion and fenitrotion in the Pesticide Analytical Laboratory under Division of Entomology, Bangladesh Agricultural Research Institute (BARI), Gazipur using suitable protocols GC-FID. Nineteen marketed brands of these insecticides collected form dealers or retailers of Jessore, Gazipur and Rangpur region were analyzed and estimated their purity in two seasons of 2006-2007 and 2007-2008. In these two seasons, among five marketed brands of Malathion, only one brand (MTF) had 98.95-100% purity which was collected from Jessore in 2007-08 and Gazipur in both the seasons and considered to be standard or acceptable product, but in other regions, this brand contained less AI and was found to be <95% pure which was considered as substandard product. The remaining brands contained 22-92% purity including SRL and MTX having small amount of AI (22-44% purity) and all these were unacceptable and impure. Fenitrothion with five marketed brands showed ≥ 96% purity only in SMT brand in Gazipur and Jessore in 2006-07 and in all the three locations in 2007-08 seasons and this brand considered as standard product. The other four brands of this insecticide had purity at substandard level in all locations in two seasons. Quinalphos with 8 marketed brands, only MLX in 2006-07 and BLX in 2007-08 seasons in all locations had ≥ 95 % purity which was standard product. ALX and CRX in 2006-07 were almost similar and close to MLX except one location, CRX in Gazipur and ALX in Jessore but these two brands were substandard and impure (65-86%) in next season in all locations. The other brands (KNX, QNP, VNR and SLX) were also substandard and impure having 59% to 87% purity.

Keywords: insecticides; quinalphos; malathion; fenitrothion; purity

1. Introduction

Pesticides are one of the major components of plant protection for the farmers of Bangladesh. It will be impossible to grow good quality crops and also the yield would be down by 30-40 percent without the use of pesticides. It is assumed that if pesticides are not used for the management of insect pests and diseases, Bangladesh would lose around 4 million tons of food grains and vegetables every year (Hasanuzzoha, 2004). It is known that there are no practical alternative crop protection technologies which can ensure the substitute for agrochemicals to control the majority of pests, diseases and weeds (Finney, 1990). As there is no other sustainable methods of controlling crop pests, the commercial farmers are depend on the use of insecticides to control insect pests. It was understood from farmers' interview that they use insecticides irrationally and indiscriminately (Anonymous, 2001; Ahmed *et al.,* 2005). Pesticide usage for agriculture in developing countries is constantly increasing, and was estimated to be 36–40% of the world total in 1975 (Alabaster, 1981). Pesticide consumption in Bangladesh has increased day by day as 758 metric tons in 1960 and 3028 metric tons in 1980 to over 19000 metric tons in 2000 (Hasanuzzoha, 2004). The growth rate analysis of pesticide consumption in a period of 24 years shows an average of 9.0% annual increase (Ali, 2004). In the year 2007, over 37,712.20 tones of pesticides were being sold in Bangladesh (Anonymous, 2007). Although field control failure may result from the presence of resistant individual, inappropriate selection of insecticides and doses, poor spray timing and inadequate spray coverage (Phillips *et al.*, 1990), it might also be due to impurity and adulteration of the used insecticides. In Bangladesh, it is assumed that impurity of pesticide is one of the major causes of extensive use of pesticide. Sub standard or little amount of active ingredient (AI) in the formulated pesticides, does not work against insect pests and diseases and the farmers use more pesticide for better result. Impurity and adulteration may be one of the reasons of over and repeated use of pesticides in crops as well as decline in efficacy of applied insecticides (Anonymous, 2009). Considering this, the present study has been initiated to analyze the marketed brands of insecticides for their purity determination and to assure the active materials prescribed in the levels of bottles or packets.

2. Materials and Methods

The purity testing was conducted exclusively in the Pesticide Analytical Laboratory, BARI, Gazipur during 2006 to 2008. The samples were collected from Jessore, Gazipur and Rangpur region where vegetables were grown commercially.

2.1. Materials used in insecticide analysis

Insecticides:

Three insecticides such as malathion, fenitrothion and quinalphos belonging to organophosphorous class all being EC formulation, showing below the technical information in connection with their analysis.

Malathion 57EC

Common name: Malathion (Anonymous, 2000)

Chemical abstract name: Dimethyl [(dimethoxyphosphinothioyl) thiobutanedioate]

Molecular formula: $C_{10}H_{19}O_6PS_2$, Mol. wt. 330.3

Available tested brands: MTF, MTX, ZTN, FNN, HTN, SRL.

Mode of action: Non-systemic insecticide and acaricide with contact, stomach and respiratory action.

Fenitrothion 50EC

Common name: Fenitrothion (Anonymous, 2000)

Chemical abstract name: *O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate),

Molecular formula: $C_9H_{12}NO_5PS$, Mol. wt. 277.2

Available tested brands: SMT, SVT, EMT, FNX, LTN.

Mode of action: Non-systemic insecticide with contact and stomach action.

Quinalphos 25EC

Common name: Quinalphos (Anonymous, 2000)

Chemical abstract name: *O,O*-diethyl *O*-2-quinoxalinyl phosphorothioate)

Molecular formula: $C_{12}H_{15}N_2O_3PS$, Mol. wt. 298.3

Available tested brands: KNX, CRX, MLX, ALX, BLX, SLX, VNR, QNP.

Mode of action: Insecticide and acaricide with contact and stomach action. By penetrating the plant tissues through translaminar action, exhibits a systemic effect.

Chemicals: In the analysis of the insecticides different types of chemicals were used. These are: Acetone, n-hexane, Methanol, Acetonitrile and Insecticide Standard.

Glass wares: Pipette, Beaker, Conical flask, Syringe and Vials with septum.

Others: Spatula, PTFE filter, Knife, Scissors, Forceps, Zipper bag, Zip Stick, Teflon stopcock, Para film, Aluminium foil etc.

2.2. Analytical apparatus used in insecticide analysis

Gas Chromatograph, Model: Shimadzu GC-2010, Auto Injector AOC 20i, Ultrasonic Bath, Ultra low refrigerator, Ultra pure Water Distillation with Deionizer and Reservoir, Vortex Mixture, Solvent Dispenser, Degassing set, Digital Balance and Computer.

2.3. Purity testing

The available brands of tested insecticides were collected from local market of Jessore, Rangpur and Gazipur region where extensive usage of pesticides was recorded. The brands were selected on the basis of their class, mode of action and demand among the farmers from survey and research reports of eight different locations including Jessore, Rangpur, Gazipur in Bangladesh (Kabir *et al*., 1996; Anonymous, 2001; Ahmed *et al*., 2005). All of the formulated products were liquid and dissolved in the respective solvent. The solvents were selected on the basis of the criteria described by Lehotay and Mastovska (2004). The brands of these insecticides varied in two years with at least five brands in each insecticide were tested. There were nineteen brands of three tested insecticides showing individual batch number and expiry date but not mentioning manufacture date in all brands on the label. The purity tests were conducted before the expiry date of each brand of the insecticides. The solutions of different brands of marketed insecticides were prepared in the pesticide analytical laboratory, Division of Entomology, BARI, Gazipur following the procedure compatible with the respective equipment. For color less liquid insecticide the known concentration of the solutions were prepared directly. Thus known and similar concentrated solutions of each of the standard and formulated insecticides were prepared. Methods for testing different brands with GC-FID was developed by setting the instrument parameters suitable for analyzing concerned insecticide selected on the basis of peak sharpness of the chromatogram and retention time for respective compound. The carrier and makeup gas used in the instrument for analysis was helium during 2006-2007 and nitrogen was used in 2007-2008 due to availability of gases. The instrument parameters of Gas Chromatography set for analysis of each group of insecticide are listed in Tables 1 and 2.

Table 1. The instrument parameters of GC-2010 set for analysis of different group of insecticide during 2006-2007.

Pesticide group	Detector	Solvent	Temperature	Carrier gas	Make up gas	Injector	Inj. vol.
Malathion	FID	Hexane	Column-180°C Injection port-200°C Detector-240°C	Helium	Helium	Auto	1 µl
Fenitrothion	FID	Hexane	Column-180°C Injection port-200°C Detector-250°C	Helium	Helium	Auto	1 µl
Quinalphos	FID	Hexane	Column-180°C Injection port-200°C Detector-230°C	Helium	Helium	Auto	1 µl

Table 2. The instrument parameters of GC-2010 set for analysis of different group of insecticide during 2007-2008.

Insecticide group	Detec tor	Solvent	Temperature	Carrier gas	Make up gas	Injector	Inj. vol.
Malathion	FID	Hexane	Column-185°C Injection port- 200°C Detector-220°C	Nitrogen	Nitrogen	Auto	1 µl
Fenitrothion	FID	Hexane	Column-190°C Injection port-220°C Detector-250°C	Nitrogen	Nitrogen	Auto	1 µl
Quinalphos	FID	Hexane	Column-200°C Injection port-220°C Detector-240°C	Nitrogen	Nitrogen	Auto	1 µl

Before the injection of the solutions of formulated products, standard solutions of each pesticide group were injected with the set instrument parameters. Each peak of the chromatogram for formulated products was characterized by the retention time of the concerned standard solution. The similar retention time of the obtained peak of standard solution and the tested brands solution assured the presence of AI (active ingredient) in the tested brands. Sample results were expressed in ppm automatically by the GC software by comparing the peak area of formulated products with that of standard solution. This result represented the actual amount of AI present in different marketed brands and the purity percentage was determined by comparing it with the amount of AI actually required in the concerned insecticide using the following formula

$$\text{Purity (\%)} = \frac{\text{Actual amount of AI present in the insecticide}}{\text{Amount of AI recommended / required}} \times 100$$

3. Results

The results of this study presented here were the purity test of three commonly used insecticides sold by the traders in the local markets of three regions Jessore, Rangpur and Gazipur under different brands. The results were obtained on the chromatograms in tabular form based on the quantification of active ingredient (AI) of the insecticides. Only one chromatogram of standard solution of three insecticides and one chromatogram of marketed brand of each insecticide are shown in Fig. 1 to Fig.6. In this way the results of other marketed brands were also made by in-built GC-2010 software that could not be mentioned here in detail. The lowest detection limit of malathion and fenitrothion was 0.01 mg/kg and quinalphos, it was 0.02 mg/kg in GC-FID.

3.1. Malathion

Six marketed brands of malathion, five from each location viz., Jessore, Rangpur and Gazipur were tested with GC-FID to estimate their purity during 2006-07 and 2007-08 seasons. The standard of malathion was characterized by its retention time (Figure 1) and the marketed brands also showed similar retention time (RT) in Figure 2. The purity percentages of different marketed brands of malathion are presented in the Tables 3 and 4.

Table 3. The percentages of active ingredient (AI) and purity of marketed brands of malathion 57EC collected from different locations during 2006-07.

Malathion brands (Code no.)	Amount of AI present (%) at different locations			Purity (%) at different locations		
	Gazipur	Jessore	Rangpur	Gazipur	Jessore	Rangpur
MTF	56.407	51.517	52.405	98.959	90.360	91.918
HTN	51.779	52.410	50.880	90.820	91.927	89.243
MTX	50.115	45.826	45.662	87.971	80.378	80.091
FNN	47.367	46.419	44.858	83.081	81.418	78.680
SRL	25.247	23.259	22.986	44.283	40.796	40.317

Table 4. The percentages of active ingredient and purity of marketed brands of malathion 57EC collected from different locations during 2007-08.

Malathion brands (Code no.)	Amount of AI present (%) at different locations			Purity (%) at different locations		
	Gazipur	Jessore	Rangpur	Gazipur	Jessore	Rangpur
MTF	56.929	57.00	51.053	99.875	100.00	89.546
ZTN	54.055	52.631	48.476	94.812	92.314	85.026
HTN	40.263	41.195	36.107	70.621	72.256	63.331
FNN	20.750	20.264	18.608	36.395	35.543	32.638
MTX	14.184	14.008	12.720	24.878	24.570	22.310

During 2006-07, among five brands of malathion, only one brand (MTF) 56.40 % AI which showed 98.959% purity form Gazipur sample (Table 3). The similar brand of Rangpur and Jessore had purity less than that of sample. The brand HTN had also similar purity ranging from 89.243 to 91.927% and this was below the standard in respect of purity. The brands MTX and FNN had the purity of ≥80% except the sample of FNN collected from Rangpur. This brand was found to have < 80% purity. The brand SRL showed<50% purity from all the locations and the range of purity was 40.317-44.283%. In 2007-08, only one brand (MTF) of malathion collected form Gazipur and Jessore had the similar level of purity (≥95%) which was higher than in the first year. The same brand of Rangpur showed <90% purity (Table 4). Although the brand ZTN of Gazipur was found to be 94.812% pure but the similar brand of two other locations had less purity. This level of purity is considered substandard. The brand of HTN had the purity ranged from 63.331-70.621% while the brands FNN and MTX were much lower AI and purity of 22.310-36.395%. These levels could be categorized as below sub-standard.

3.2. Fenitrothion

Five available brands of fenitrothion from each location as Jessore, Rangpur and Gazipur were tested with GC-FID to estimate their purity during 2006-07 and 2007-08 seasons. The RT for the standard of fenitrothion was 6.19 min (Figure 3) and the formulated brands also showed similar RT proving the presence of fenitrothion (Figure 4). The purity percentages of the formulated brands of this insecticide are presented in the Tables 5 and 6.

Table 5. The percentages of active ingredient and purity of marketed brands of fenitrothion 50EC collected from different locations during 2006-07.

Fenitrothion brands	Amount of AI present (%) at different locations			Purity (%) at different locations		
(Code no.)	Gazipur	Jessore	Rangpur	Gazipur	Jessore	Rangpur
SMT	49.866	48.289	46.769	99.732	96.578	93.538
EMT	43.341	41.535	40.790	86.682	83.070	81.580
FNX	40.927	39.864	40.384	81.854	79.728	80.768
LTN	40.743	44.003	41.717	81.486	88.006	83.434
SVT	39.719	37.215	40.504	79.438	74.430	81.008

Table 6. The percentages of active ingredient and purity of marketed brands of fenitrothion 50EC collected from different locations during 2007-08.

Fenitrothion brands	Amount of AI present (%) at different locations			Purity (%) at different locations		
(Code no.)	Gazipur	Jessore	Rangpur	Gazipur	Jessore	Rangpur
SMT	50.00	49.822	48.663	100.00	99.644	97.326
LTN	47.274	46.701	45.780	94.548	93.402	91.560
EMT	45.726	47.356	44.156	91.452	94.712	88.312
FNX	43.840	43.800	44.459	87.680	87.600	88.918
SVT	43.840	43.796	44.284	87.680	87.592	88.568

SMT of fenitrothion contained almost same amount of AI as in the original product recording over 96% purity in Gazipur and Jessore but the purity was less in Rangpur in 2006-07 (Table 5). SMT was considered as standard product. The brands EMT, FNX and LTN had the purity of ≥80% except one brand (FNX) that was collected form Jessore. SVT of Rangpur was found to be 81% pure but the same brand of two other locations had 74.430-79.438% purity. In 2007-08, SMT had the similar level of purity (≥97%) which was also satisfactory. The purity levels and AI of LTN and EMT were found to better than in 2006-07 (Table 6) but their purity were <95%. AI and purity of FNX and SVT were similar in all three locations with 87.592-88.918% purity which were substandard and not acceptable.

3.3. Quinalphos

Eight different brands of quinalphos, five from each location viz., Jessore, Rangpur and Gazipur region were tested with GC-FID to know their purity during 2006-07 and 2007-08 seasons. The RT for the standard of quinalphos was 9.67 min (Figure 5). The formulated brands also showed similar RT which proved the presence of quinalphos (Figure 6). The purity percentages of the formulated brands of this insecticide are presented in the Tables 7 and 8.

Table 7. The percentages of active ingredient and purity of marketed brands of quinalphos 25EC collected from different locations during 2006-07.

Quinalphos brands	Amount of AI present (%) at different locations			Purity (%) at different locations		
(Code no.)	Gazipur	Jessore	Rangpur	Gazipur	Jessore	Rangpur
MLX	24.068	23.680	24.882	96.272	94.720	99.528
ALX	23.805	22.768	24.347	95.220	91.072	97.388
CRX	22.887	23.740	23.870	91.548	94.960	95.480
KNX	20.995	19.432	21.965	83.980	77.728	87.860
QNP	15.302	14.831	14.970	61.208	59.324	59.880

In 2006-07, the three brands (MLX, ALX and CRX) showed >95% purity in all locations with some exceptions such as CRX in Gazipur and Jessore and ALX in Jessore (Table 7). The KNX had less AI and QNP had much less AI and as such the purity of these two brands recorded 77.728-87.860% and 59.324-61.208% purity in three locations. During 2007-08, three new brands including CRX and ALX were tested for AI and purity where 100% AI and purity were found only in BLX (Table 8). The brands VNR, ALX and SLX had the purity of ≥81% in all locations which were sub standard. The CRX revealed <70% purity in all locations. The brand CRX showed more impure than in 2006-07.

Table 8. The percentages of active ingredient and purity of marketed brands of quinalphos 25EC collected from different locations during 2007-08.

Quinalphos brands (Code no.)	Amount of AI present (%) at different locations			Purity (%) at different locations		
	Gazipur	Jessore	Rangpur	Gazipur	Jessore	Rangpur
BLX	24.986	25.00	25.00	99.944	100.00	100.00
VNR	21.434	21.216	21.096	85.736	84.864	84.384
ALX	21.240	21.542	21.446	84.960	86.168	85.784
SLX	20.429	20.700	20.429	81.716	82.800	81.716
CRX	16.270	16.562	16.641	65.080	66.248	66.564

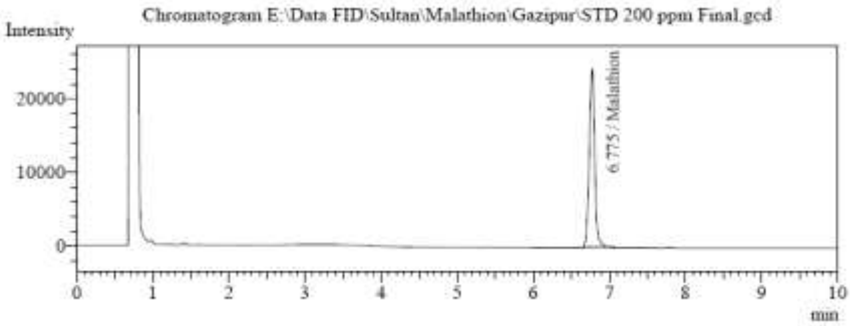

Figure 1. Chromatogram of malathion standard solution.

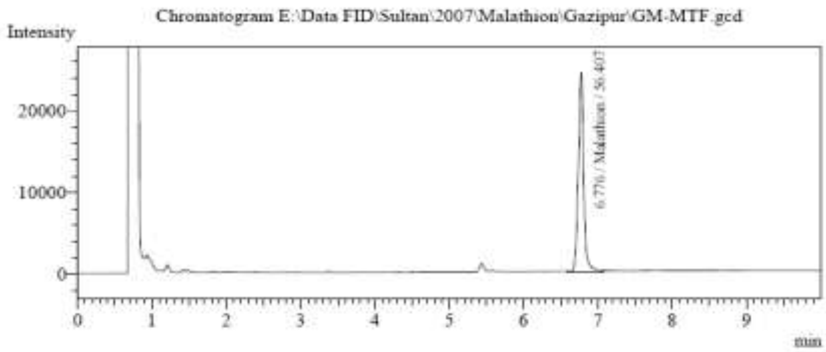

Figure 2. Chromatogram of malathion obtained from the marketed brand of GM-MTF.

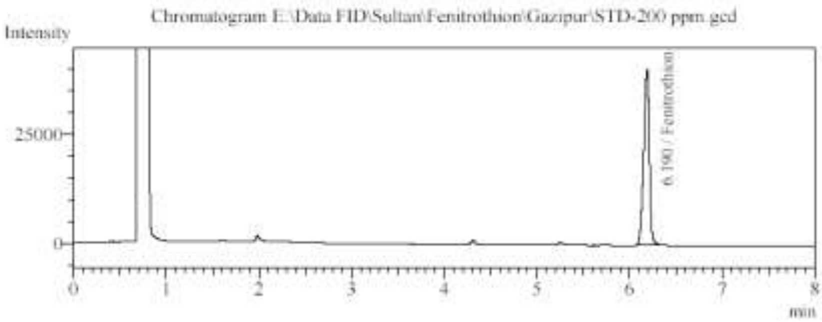

Figure 3. Chromatogram of fenitrothion standard solution.

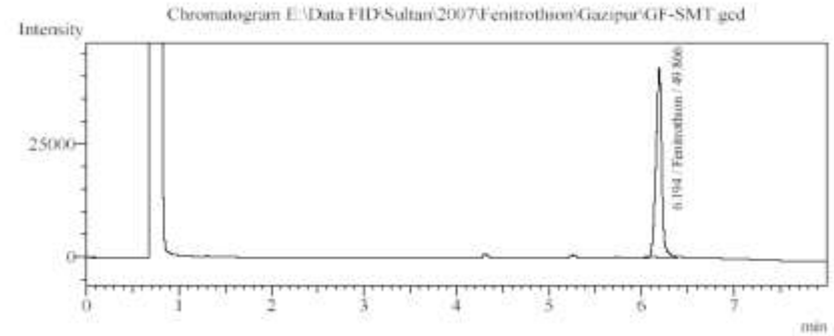

Figure 4. Chromatogram of fenitrothion obtained from the marketed brand of GF-SMT.

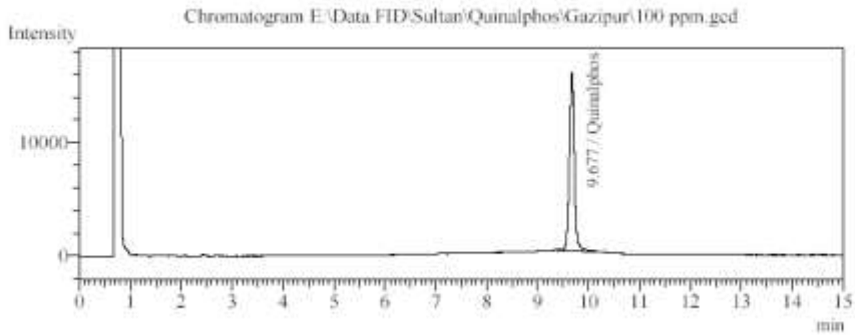

Figure 5. Chromatogram of quinalphos standard solution.

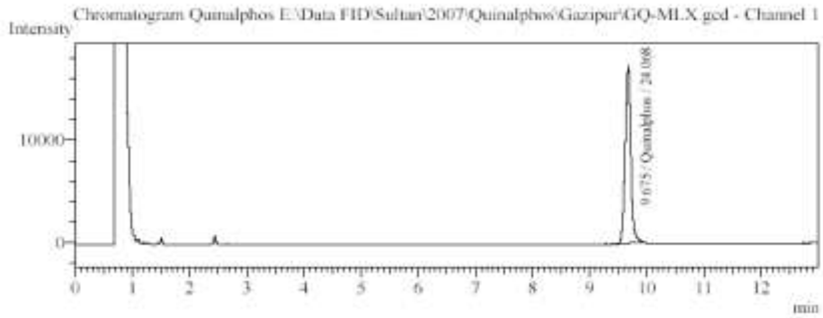

Figure 6. Chromatogram of quinalphos obtained from the marketed brand of GQ-MLX.

4. Discussion

The purity of different brands of selected insecticides were classified in to three categories viz., standard or acceptable level (>95%), substandard (<95-80%) and lower level or little amount (<80%) of active ingredient (AI) present in the product. Different brands of three insecticides were collected from dealers of Jessore, Gazipur and Rangpur region and estimated their purity with GC-FID during 2006-07 and 2007-08 seasons. In these two seasons, among six tested marketed brands of malathion only one brand (MTF) had>98% purity which was collected from Jessore in 2007-08 and Gazipur in both the seasons and considered to be standard or acceptable product but in other regions this brand contained less AI which was sub standard or unacceptable product. The purity of remaining five brands were 22-92% including SRL and MTX having little amount of AI (22-44) and all these are unacceptable. Fenitrothion with five marketed brands showed ≥ 96% purity only in SMT brand in two locations in 2006-07 and all of the three locations in 2007-08 season and this brand might be considered as standard product. The other four brands of this insecticide had purity at substandard level in all locations in two seasons. Of 8 marketed brands of quinalphos the standard brands were MLX in 2006-07 season and BLX in 2007-08 seasons in all locations. These two brands were acceptable level having ≥ 95% purity. ALX and CRX in 2006-07 were almost similar and close to MLX except in one location, CRX in Gazipur and ALX in Jessore but these two brands were substandard and impure (65-86%) in next season in all locations. The remaining brands of quinalphos such as VNR, KNX and SLX were sub standard, but the QNP was the least in quality and was found below the sub- standard level or unacceptable in both the seasons. But in respect of purity of malathion and fenitrothion with emulsifiable concentration in formulation, quinalphos was more pure in quality. The factors such as packing of insecticide in different formulations, storing period and storage facilities (presence of light, temperature, humidity, etc.) handling and transportation of insecticides might be the probable reasons of different degrees of purity of marketed products. Adulteration could be other reason of impurity. Kabir *et al.* (2008) reported 8 brands of malathion of which only two brands showed acceptable level of purity (100%) and another 5 brands had the purity which was substandard (80.11-93.80%) but the remaining one showed very poor purity which was only 59.88%. They also found that the purity of three tested brands of quinalphos ranging from 68.34% to 76.64% active purity which were lower level (<80%) of active ingredient (AI) present in the product. It is reported that some of the marketed brands of malathion and fenitrothion do not contain required amount of active ingredient (Anonymous, 2010). The results of the present study agreed with the works of the above authors.

5. Conclusions

The analytical results of three insecticides with nineteen different marketed brands showed variations in purity. Few brands (three brands of quinalphos and one brand of malathion and fenitrothion) of tested insecticides were found at standard level of purity. Most of the brands of the marketed insecticides were below standard or impure in quality. The purity of malathion was poor which contained <50% purity in some brands. These levels are unacceptable and below standard. It is, therefore, concluded that improper storage facilities and adulteration might be the cause of reduction of the purity.

Conflict of interest

None to declare.

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