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Purity analysis of carbofuran used in tomato (solanum lycopersicum l.) In Bangladesh

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Abstract:

The aim of the present study was to conduct purity analysis of carbofuran, a frequently used pesticide by the farmers in tomato field. All the pesticides available in the markets were found as authorized pesticides and none of them were found to be extremely hazardous according to the WHO recommended classification except carbofuran. Therefore to find out present quality status of carbofuran (5G) products available in market, purity analysis of randomly chosen thirteen samples was done by GC-FID. Among them the highest concentration was found 6.82%. No carbofuran content was found in two samples. Most accurate concentration was 5.04%. The present study indicates that there is a high chance to have residual effects of pesticides in tomato as a result of preharvest or postharvest application. Most of the farmers do not know about health risk issue of using agro-chemicals. In case of purity analysis of Carbofuran, approximately 46% samples showed overconcentration, 30% showed below concentration and two samples showed no concentration of Active ingredient (AI). This variation in results indicates the reason why farmers tend to go with non-judicial application of pesticides. The level of pesticide residues in tomato is affected by washing, preparatory steps, heating or cooking, processing during product manufacturing and post-harvest handling and storage. It is important to aware the farmers to follow the recommended dose of registered pesticides and the consumers to proper handling and processing of tomato for safe consumption. Information on health risk, exposure assessment was also highlighted for public awareness. Suggestions were provided on the handling and processing such as washing, cooking, boiling, packing, storage etc. for the safety of the consumers.

Keywords: carbofuran, GC-FID, pesticide residue, safety, purity analysis;

Introduction

Tomato (*Lycopersicon esculentum* Mill.), which is botanically a fruit and not a vegetable, is loaded with all kinds of health benefits for the body. One of the most well-known tomato- eating benefit is its lycopene content. Tomatoes are equally as nutritious as they are in other variable forms. It plays a vital role in providing a substantial quantity of vitamin C and vitamin A in human diet **[1].** Tomato is the most consumable vegetable occupying the top of the list as canned vegetable having multiple uses **[2].** It is also suitable to grow in our agro-climatic condition. However, our average population has nutritional deficiency due to the traditional rice based food habit and lack of knowledge about balance diet. In addition food adulteration news via media is discouraging us to take fruit regularly. Proper science based risk assessment is essential to evaluate whether the agro-chemicals used for cultivation is actually threat for consumers during the time of consumption. Pesticide poisoning is a global health problem and it is more prevalent in countries like Bangladesh due to the non-judicial use. The incidence of pesticide poisoning is increasing according to the existing reports and it is estimated that about 5 million people die every year as a result of intentional, accidental and occupational exposure worldwide **[3].** To combat insect pests and diseases of tomato and to achieve higher production, many pesticides are used that may leave certain amounts of residues on crops. Farmers tend to spray vegetables up to the time of harvest, and then transport directly to market with no waiting period. These create a very significant potential for pesticide residues causing negative health effects on consumers **[4].** Depending on the situation, pesticides could enter body by any one or all these routes. Typical sources of pesticide exposure include food on which we are giving stress. Because most of the foods we eat have been grown with the use of pesticides. Therefore, pesticides residues may be present inside or in the surface of these foods. In one hand we have food crisis, over population on the other hand we have problem on safety. So, risk assessment (i.e. hazard identification, hazard characterization, exposure assessment and risk characterization) for food safety is a burning national issue. Survey reports conducted **[5], [6] , [7]** at different locations of Bangladesh indicated that the farmers spray pesticide in their vegetable field irrationally, sometimes every day or in each alternate day. Due to the lack of knowledge and non-availability of sustainable alternatives to pesticide, farmers of Bangladesh become dependent on pesticide for crop production. Excessive and non-judicious use of pesticide has raised several environmental and social issues, as well as, destruction of agricultural ecosystem and development of resistance in insect pest, pathogens and weeds **[8].** In Bangladesh, it is assumed that adulteration of pesticide is one of the major causes of such extensive use of pesticide. In the country report originated by FAO **[9]** Corporate Document Repository, it is reported that the regulatory scheme for pesticide registration is systematic. But in practice, there are gaps between policies and implementation. While the intent of the ordinance and rules to monitor formulations and residue is commendable, the lack of facilities and trained analysts does not allow proper monitoring. Thus, specification of pesticides on the market may differ from those registered. So, concern on the purity in respect of active ingredient of the marketed brands of pesticides is therefore, likely key factor for repeated use of pesticides in vegetables. Due to absence or little amount of active material in the formulated pesticides, they do not work against insect pests and the farmers use more pesticide for better result [10]. Due to impurity of pesticide and low amount of active ingredient, farmers use more than recommended dose which are labeled and pest became resistant to that pesticide rapidly. According to this viewpoint, it has become significant to evaluate the brands of pesticide for quantification of their active ingredient (AI). Here the purity analysis was done for carbofuran 5G samples as carbofuran has been classified as highly hazardous by WHO **[11].** It will be helpful for pledge the actual, harmless and safe use of pesticide for healthier harvested crops as well as to ensure safer community. So, the basic research objective was to conduct purity analysis of carbofuran 5G samples by GC-FID and to provide suggestion regarding safety.

Materials and Methods

Purity analysis of carbofuran was conducted by Gas Chromatography-Flame Ionization Detector (GC-FID) in the Agro-Environmental Chemistry Laboratory, Department of Agricultural Chemistry, Central Laboratory, Sher-e-Bangla Agricultural University, Dhaka. Thirteen brand samples of carbofuran 5G were collected from the markets of surveyed areas and code name was given as **Cf** (eg: Cf1, Cf2……Cf13). Preparation of standard stock solution and working sample was done by following procedure.

Purity Analysis Method of Carbofuran by GC-FID

Stock Standard preparation:

18.5 mg of standard carbofuran was taken in 50mL volumetric flask. It was diluted with acetonitrile and vortex for 1hour.The concentration of stock solution was 370 ppm.

Rough:

- 1 mg / 1 L (1000 mL) = 1 ppm
- 18.5 mg / 50 mL
  = (18.5 mg x 20) x (50 mL x 20)
  = 370 mg / 1000 mL
  = 370 ppm

Working Standard preparation:

0 ppm, 25 ppm, 50 ppm, 75 ppm & 100 ppm carbofuran solution were prepared by using the following table: **Table 1.**

Concentration (ppm)	Stock solution (mL)	Acetonitrile (mL)	Total (mL)
0	0	10	10
25	0.676	9.324	10
50	1.351	8.649	10
75	2.027	7.973	10
100	2.703	7.297	10

Table 1: Preparation of Standard Solution

Rough:

V1 x S1 = V2 x S2

Where,

V1 = Required volume?

S1 = Conc. of stock solution

V2 = Final Volume

Sample Preparation:
Take 100 mg of Carbofuran sample in 10mL volumetric flask. Dilute it with acetonitrile and vortex for 1hour (500 ppm). Take 1 mL of above sample in 10 mL Falcon tube then dilute it with acetonitrile (50 ppm).

Rough:

5G means 5%

5% means 5 g Carbofuran active is present in 100 g sample

100 mg in 10 mL = 500 ppm (Since 5 mg active in 100 mg sample)

- **Chromatographic Condition:**
- **Column:** Rtx-624, 0.25mmID, thickness-1.4um, length-30m
- **Detector:** FID (Flame Ionization Detector)
- **SPL (Injection Port) Temperature:** 230^0C
- **Detector Temperature:** 240^0C

Rate	Temp	Hold time
	100^0C	3
10	200^0C	2

Table 2: Column (Column Oven Temperature Program)

Total time program – 15.00 min

Split Ratio: 5
Column flow: 2.5 ml/min.
Retention Time: 12.49 minute.
For safety measurement, various recommended suggestions regarding safe handling and processing were also considered.

Result And Discussion

Purity Analysis Result of Carbofuran:
Thirteen Marketed brands of Carbofuran 5G were tested with GC-FID. The analysis result for the purity testing of the formulated brands has been summarized in the following **(Table 1)**.

Code no.	Formulation type	Amount of AI present (%)
Cf1	5G	5.44

Cf2	5G	3.02
Cf3	5G	5.76
Cf4	5G	6.74
Cf5	5G	5.38
Cf6	5G	4.46
Cf7	5G	5.70
Cf8	5G	4.36
Cf9	5G	2.84
Cf10	5G	5.04
Cf11	5G	0
Cf12	5G	0
Cf13	5G	6.82

Table 1: Percentage of active ingredient presents in thirteen marketed brands of carbofuran 5G.

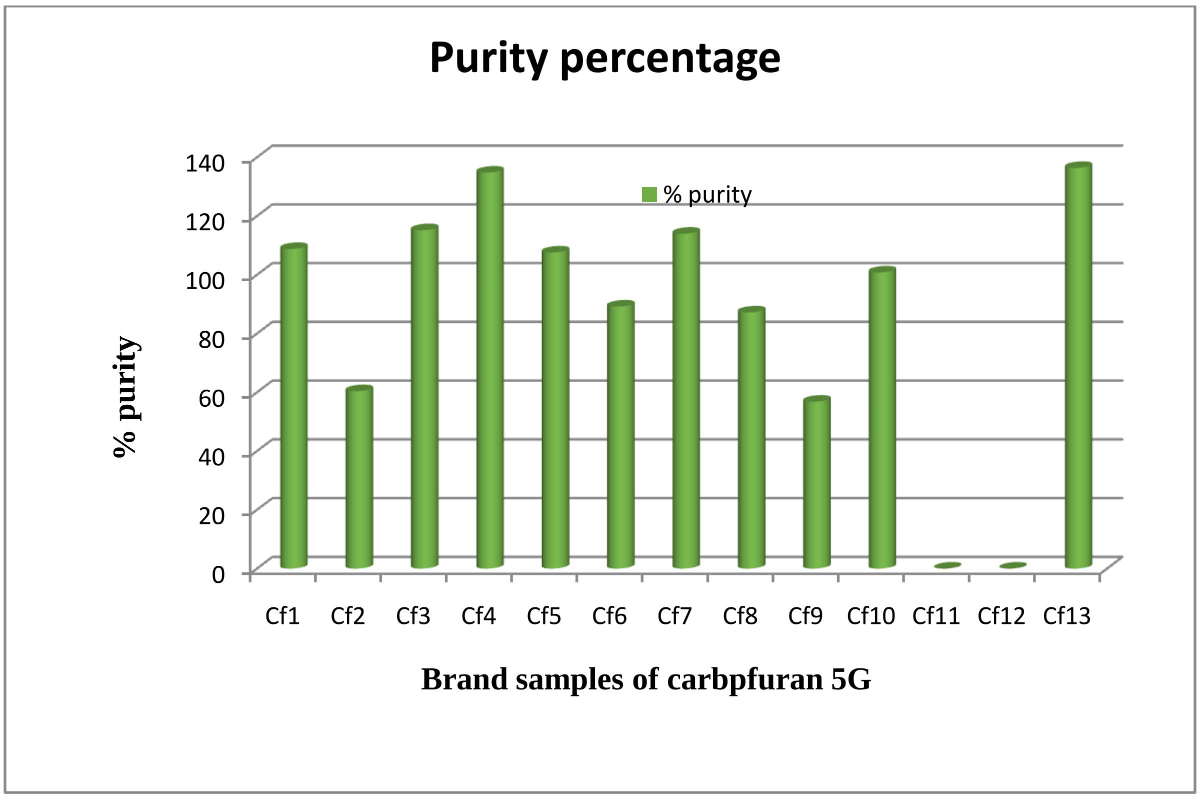

Figure 1: Purity percentage of carbofuran samples.

Results reveal that only Cf10 was almost 100% pure in term of AI presence. No result was found in case of Cf11 and Cf12. 50%-60% purity was shown by Cf2 and Cf9. Over concentration of AI was shown by Cf3, Cf4 and Cf13 **(Figure 1).**

Mitigation Process of Pesticide Residue for Safe Consumption

Effect of handling and processing

Foods after harvest/slaughter are subjected to various handling and processing operations both at home or industry level, involving a simple washing to more multi-step and complex processing aimed to extend shelf-life, add variety, increase palatability and nutrient availability and to generate income. The various techniques and methods applied usually reduce residue levels because of washing or cleaning, peeling, blanching, juicing, cooking, milling baking, pasteurization, canning etc. Thus there is an increasing need for information about the effects of various processes on the fate of pesticide residues in foods both from a regulatory and public concern perspective. The available information has been elaborated under the following heads:

Preparatory steps

The extent of pesticide reduction depends upon the washing operations, nature of pesticide molecule and other preparatory steps used. Loosely held residues of several pesticides are removed with reasonable efficiency by varied type of washing processes **[12].** Moreover, majority of pesticides applied to crops are confined to the outer surfaces and undergo limited movement or penetration of the cuticle. Therefore, they are amenable to removal by washing, peeling and trimming operations **[13].** The effect of different preparatory steps on pesticide residues in food is being described under various subheads.

Washing with water

Fruits and vegetables are invariably washed before consumption. Vegetables are often peeled off and cooked prior to eating. Bindra **[14]** reported 80–83% reduction of carbaryl by washing of tomato. However, only 18–55% endosulfan was reduced by washing. Removal of the fruit stalk, exocarp and tissue around stalk cavity of fruits and fruit-type vegetables and washing of leaves with water or dilute detergent solution were necessary to decrease the intake of pesticide residues from vegetables and fruits. In case of tomato, Singh and Lal **[15]** reported a reduction of 86.20% in malathion deposit by one minute washing only. It was found that washing of tomato fruits in a stream of water for 1–3 h reduced pesticide residues in tomato products; tomato seeds showed higher levels of residues as they were not subjected to processing **[16].** The effectiveness of washing was, however, reduced at later stages of all the insecticides and more specifically on synthetic pyrethroids due to strong bonding between the insecticide molecules and waxy layer of fruit skin and also their non-systemic and non-translaminar movement characteristics **[17], [18].**

Washing with salt solution

Washing with dilute salt (sodium chloride) solution is a convenient method to lower the load of contaminants from food surfaces particularly fruits and vegetables. This method could be equally effective for reducing the pesticide residue from other commodities too. This procedure is recommended as being practical for household use **[17], [18].**

Washing with chemical solutions

Chlorine water and dilute solutions of other chemicals are commonly used for disinfection of fruits and vegetables. These chemicals play an effective role in removing the pesticide residues. The results of Wu **[19]** on the degradation of four pesticides by low concentration of dissolved ozone indicated that initial concentration of 1.4 ppm was effective to oxidize 60–99% of 0.1 ppm aqueous diazinon, parathion, methyl-parathion and cypermethrin shortly within 30 min. Ozonated water was mostly effective in cypermethrin removal (>60%). The efficacy highly depended on the dissolved ozone levels. Higher temperature enhanced the efficacy in pesticide removal with maximal efficacy for diazinon removal detected at 15–20 °C.

Kitchen type and combination processing

Peeling was found to be the most effective way to remove the pesticide from the vegetables followed by frying. Boiling was effective in reducing the level of water-soluble pesticides **[20],[21]** found that plain washing dislodged 20–52% mancozeb residues while washing coupled with cooking led to 53–79% decontamination on cabbage, knoll-khol, tomato, okra and brinjal. Cooking did not help much in reducing the residue below the MRLs of 0.25 and 0.05 ppm for quinalphos and chlorpyriphos respectively. Kadian **[22]** reported that cypermethrin residues declined in tomato, okra, bottle gourd and ridge gourd after all processing steps i.e. about 5–14% by washing, 6–26% by blanching, 6–19% by washing in brine solution and 15–33% by cooking. Lee and Lee (1997) revealed that 45% of organophosphorous pesticide (OP) residues were eliminated when foods were washed in water, 56% with detergent washing, 91% with peeling, 51% with blanching-boiling and 90% in milling and processing. In tomato both the washing and cooking reduced the residues almost to the same extent of 11–30% **[23].**

Thermal Treatment

Foods are invariably subjected to heat treatment during preparation and preservation. The heat treatment is given in many ways including pasteurization, boiling, cooking etc. depending upon the nature of food and aim of processing. The loss of pesticide residue during heat processing may be due to evaporation, co-distillation., thermal degradation which vary with the chemical nature of the individual pesticide **[24].**

Cooking/boiling/Steaming

Incidence and stability of pesticide residues in some vegetable and fruits as affected by food processing was studied by El-Nabarawy **[25].** Processing such as cooking caused marked reduction in insecticides, resulting in complete removal of insecticide residues in some cases.

Product manufacture

A set of processing techniques are used to convert raw materials into a variety of products for consumption. The amount of residue in the final product may be reduced or enhanced depending upon a set of parameters employed and length of processing. In addition, micro-organisms/fermentation, if employed, also contribute to residual degradation of pesticides **[24].**

Drying and dehydration

The drying process could cause an appreciable decline in pesticide residues mainly due to evaporation, degradation and codistillation.The different drying methods have different effect on different pesticides In the production of raisin, the sun drying process caused a 4 times concentration of residue level while oven drying which was preceded by washing lead to decrease in iprodione and procymidone **[26].**

Canning of fruits and vegetables

In most cases, operations leading to canning resulted in a gradual decrease in residue levels in the finished products; the washing, blanching, peeling and cooking stages were particularly effective. Ethylenebisdithiocarbamates were completely removed from tomatoes and spinach by washing followed by hot water blanching. Samples analyzed at each stage of industrial processing of tomato showed a progressive reduction in the contents of the 3 insecticides, only insignificant quantities of dimethoate remaining after the pasteurization stage **[27].**

Juice/concentrate preparation

The distribution of 9 pesticides between the juice and pulp of carrots and tomatoes during home culinary practices was investigated by Burchat **[26].** Tomato and carrot pulp contained a higher percentage of all pesticide residues, except for mancozeb in tomato juice. Although there was a difference in the relative distribution of the pesticides between the commodities with greater amounts present in the pulp of tomatoes, the pesticides followed a similar trend in both. Pesticides with the highest water solubility were present to a greater extent in the juice. An exception was noted in the case of diazinon and parathion, which were present in higher amounts in the pulp than their water solubility suggested. The residue in the pulp ranged from 56.4 to 75.2% for carrots and 49.7 to 95.4% for tomatoes. Washing of the produce removed more residues from carrots than from tomatoes, but it did not affect the relative distribution of the residues. The behavior and fate of the chemical varied with the pesticide as well as the crop. Pesticide residues were greatly decreased in tomato juice under cold or hot break. A sharp decline in profenofos level was noted after treatment by pectinex ultra SP-L and benzyme M during tomato crushing **[28].**

Postharvest handling

Packing

The packing process before shipment to retail outlets was generally effective in removing pesticides that may be present on peel at the time of harvest.

Storage

Gill **[23]** sprayed brinjals and tomatoes with alphamethrin and stored at ambient (40 °C) and refrigerated conditions (5 °C). Dissipation of alphamethrin was observed faster at room temperature as compared to cold conditions in both the vegetables.

Conclusion

Results of purity analysis of Carbofuran revealed that only Cf10 was almost 100% pure in term of AI presence. No result was found in case of Cf11 and Cf12. 50%-60% purity was shown by Cf2 and Cf9. Over concentration of AI was shown by Cf3, Cf4 and Cf13. In case of purity analysis of Carbofuran, approximately 46% samples showed overconcentration, 30% showed below concentration and two samples showed no concentration of Active ingredient (AI). This variation in results indicates the reason why farmers tend to go with non-judicial application of pesticides. The level of pesticide residues in tomato is affected by washing, preparatory steps, heating or cooking, processing during product manufacturing and post-harvest handling and storage.

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