Arab Gulf J. scient. Res. **3** (2), pp. 727-734 (1985)

A Preliminary Study of Pesticide Residues in Some Vegetables and Fruits in Saudi Arabia

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ABSTRACT. Although the application of pesticides is important for crop production, it is just as important for its impact on the environment. A rapid and efficient laboratory system has been established for the purpose of multi-residues analyses, *e.g.* Malathion, Diazinon, Dimethoate, Phenthoate, Methidathion, and DDVP. The basic instrumental methodologies are based on GLC. The analytical results and their significance for the different procedures are discussed and compared. In addition to the laboratory tests, the levels of pesticide residues in some vegetables and fruits from the market are presented.

Organophosphorous pesticides are widely used on vegetables and fruits for the control of insect pests. These chemicals are generally of short persistence and do not accumulate in the animal tissues and environment. The rapid development of agriculture in Saudi Arabia has necessitated the use of a wide number of pesticides on crops. Based on many reports, it is evident that the haphazard and careless use of pesticides have created a health hazard to consumers. To monitor the status of multiresidues in vegetables and fruits, methods of analysis need to be investigated for their relative efficiency and quick determination.

A large number of organic solvents are being used for the extraction of pesticides from crops. The use of acetonitrile (Getz 1962, Coffin and Savary 1964, Nelson 1966), ethyl acetate (Watts and Storherr 1965, and Watts *et al.* 1969), chloroform (Laws and Webley 1961), and acetone have been reported. Sissons and Telling (1970a) extracted hexane-soluble insecticides with acetone-hexane and water-soluble with water. Johanson (1978) used a mixture of toluene and hexane for extraction of organochlorine, organophosphorous, dinitrophenyl and carbamate pesticides from apple. He used florisil column for clean-up. For the routine analysis of hexane-soluble organophosphorous and organochlorine pesticide residues in crops, Ferreira and Fernandes (1980) used acetone as the extracting solvent. Methylene chloride has been used for the simultaneous extraction of polar and nonpolar pesticides from acetonitrile or aqueous acetone (Storherr *et al.* 1971). Chloroform (Abbot *et al.* 1970), in addition to its use for the extraction of polar and nonpolar pesticides from acetonitrile or aqueous acetone has been used by Sissons and Telling (1970b), for the extraction of water-soluble organophosphorous pesticides from aqueous solutions. Ferreira and Fernandes (1980) used absorption chromatographic method for clean-up of the hexane extract on a column of florisil and a mixture of attapulgus-clay and carbon, using three different solvent systems for elution. Laws and Webley (1961) extracted organophosphorous pesticides from plant materials and separated them into water-soluble and petroleum-soluble groups by partitioning between petroleum ether and 15% methanol in water. The water-soluble fraction was cleaned-up by elution with chloroform through carbon. The petroleum ether portion was chromatographed on aluminium oxide with petroleum ether as the solvent. Elution of malathion and Azinphos-methyl required 15% diethyl ether in petroleum ether (Laws and Webley 1961).

This paper will present a comparison between the efficiencies of three different methods in the recoveries of six organophosphorous pesticides from lettuce, tomatoes and cucumbers and their application in routine analyses.

Material and Methods

Three different methods were compared for their efficiencies in the extraction of Diazinon, Dimethoate, Malathion, Phenthoate, Methidathion, and DDVP. Tomatoes, cucumber and lettuce vegetables were used as test crops.

Pesticides

1. Diazinon	*0,0*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate. Purity 99.2%, CIBA-GEIGY
2. Dimethoate	*0,0*-dimethyl S-(*N*-methylcarbamoylmethyl) phosphorodithioate. Purity 99.5%, American Cynamid
3. DDVP	2,2-dichlorovinyl dimethyl phosphate. Purity 99%, Shell Chem. Company
4. Malathion	*0,0*-dimethyl-S-1,2-di(ethoxycarbamyl) ethyl phosphorodithioate. Purity 98.0%, Conwood Corporation, Memphis, TN
5. Methidathion	*0,0*-dimethyl-S-2-methyloxy-1,3,4-thiodiazol-5(4-H)-onyl- (4)-methyldithiophosphate(4). Purity 99.6%, CIBA-GEIGY
6. Phenthoate	ethylmercaptophenyl acetate (*0,0*-dimethyl) phosphorodithioate. Purity 99.0%, American Cynamid

Method I

A sample of 100 g of each vegetable was taken and fortified with 5 μg pesticide. The sample was blended well with 200 ml aqueous acetone (1:1). The extract was filtered through glass-wool on Buchner funnel and transferred to a Separatory funnel. The aqueous acetone filtrate was extracted three times by shaking 3 min each with 40, 20, and 20 ml chloroform, using 10 ml of saturated sodium chloride solution for breaking the emulsion. The chloroform extracts were collected through anhydrous sodium sulfate and evaporated to dryness on vacuum rotary evaporator and diluted to suitable volume with acetone for analysis.

Method II

A sample (100 g) fortified with 5 μg of pesticide was blended with 200 ml of chloroform for 3 minutes. The mixture was filtered through anhydrous sodium sulfate and evaporated to dryness on vacuum rotary evaporator at 40-50°C temperature. The sample was then cooled in the refrigerator and transferred to a separatory funnel by washing five times with 5 ml portions of cold aqueous acetone (1:1) on filter paper and allowed to reach the room temperature. The aqueous acetone washings were extracted by shaking for 3 min with 15 ml of chloroform. The layers were allowed to separate and the organic solvent layer was received and dried over anhydrous sodium sulfate. This procedure was repeated three times. The chloroform extract was evaporated to dryness and used for the analysis.

Method III

A sample of 100 g was blended well with 200 ml chloroform. The mixture was filtered through anhydrous sodium sulfate and concentrated on vacuum rotary evaporator (40-50°C). A chromatographic column (30 × 2 cm) was prepared by filling with anhydrous sodium sulfate (2 cm) followed by alumina (10 cm) and an additional sodium sulfate (1 cm) on the top of alumina. The column was prewashed with 50 ml of petroleum ether and the washings discarded. The concentrated (5 ml) sample extract was transferred to the column and allowed to penetrate the upper portion of alumina. The sample was then eluted with successive and separate portions of 200 ml petroleum ether + diethyl ether (1:1), followed by 200 ml portion of chloroform.

Gas Chromatographic Technique

Samples were analysed on gas chromatograph (Hewlett-Packard 5830A) equipped with alkali flame ionization detector (AFID). A 1.8 m × 4 mm i.d. glass column packed with 3% OV-17 on 100-120 mesh cromosorb W-HP was used. Temperatures used for all tested compounds except DDVP were: column 220°C, injection port 250°C, and detector 300°C. For DDVP the column temperature was 150°C. The flow rate of gases were N_2 38ml/min, H_2 3ml/min, and air 50 ml/min.

After adoption of the Procedure 1 as the most suitable method, samples of vegetables and fruits (1-5 kg) each were collected from the market and analysed for pesticide residues, using aqueous acetone for extraction as mentioned in Method I.

Results and Discussion

To test and compare the efficiency of the three methods of extraction and recovery, samples of tomatoes, cucumber, and lettuce were fortified with known amounts of pesticides and carried through the methods described. The percent recovery of each pesticide is presented in Table 1, which showed that the highest recoveries of all the added pesticides to cucumber, and tomatoes were obtained by extraction with aqueous acetone (Method I). Extraction with chloroform and clean-up by precipitation (Method II) gave equally good recovery of Dimethoate from tomatoes, and cucumber, and Malathion from lettuce and cucumber. Lettuce extracted with chloroform and clean-up by column chromatography (Method III) yielded satisfactory recovery of Dimethoate, Malathion and Phenthoate. The recovery of Diazinon, Malathion, Phenthoate, and Methidathion eluted by using petroleum ether + diethyl ether (1:1) as the eluent on aluminium oxide column chromatography are shown in Fig. 1A. The average percent recoveries of Diazinon, Malathion, Phenthoate and Methidathion for these pesticides were 62, 81, 80, and 65, respectively. When chloroform was used as eluent after the previously eluted pesticides on the column, additional quantities of Malathion (14%) and Dimethoate (80%) were obtained (Fig. 1B).

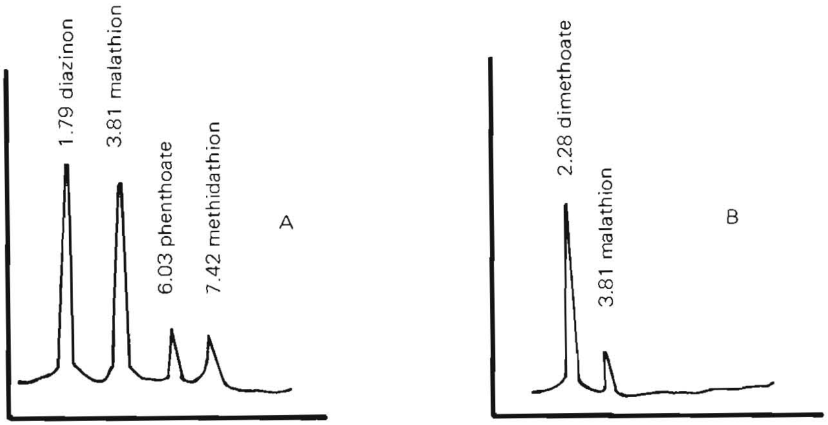

Fig. 1. Recovery of different organophosphorous pesticides. Extraction with chloroform, clean-up by column chromatography (A)-elute-petroleum ether + diethyl ether (1:1), (B)-elute-chloroform.

Table 1. Recovery of some organophosphorous pesticides from various vegetables using different methods.

Method	Crop	% Recovery of pesticides					
		Diazinon	Dimethoate	Malathion	Phenthoate	Methidathion	DDVP
I	Cucumber	86 (70-100)	80 (75-86)	104 (95-113)	95 (92-100)	81 (77-104)	–
	Tomatoes	83 (76-98)	67 (60-75)	99 (90-105)	96 (75-110)	65 (57-75)	95 (92-100)
II	Lettuce	23 (20-25)	65 (64-65)	90 (85-92)	51 (50-51)	62 (60-63)	–
	Tomatoes	21 (20-22)	83 (80-90)	71 (69-75)	56 (55-58)	30 (30-31)	–
	Cucumber	13 (11-14)	94 (82-106)	104 (90-108)	43 (40-45)	53 (50-55)	–
III	Lettuce	62 (60-66)	80 (74-90)	95 (90-100)	80 (75-90)	56 (50-60)	–

I: Extraction with Aqueous acetone.
II: Extraction with Chloroform. Clean-up by Precipitation Method.
III: Extraction with Chloroform. Clean-up by Column Chromatography.

These results suggest that Method I is suitable and efficient for the quick monitoring of most of the organophosphorous insecticides in fruits and vegetables. Furthermore, the method is rapid and the solvents required are inexpensive. Adoption of Method III (extraction with chloroform, clean-up by column chromatography) for the analysis of Dimethoate, Malathion, and Phenthoate in lettuce proved to be promising.

The levels of pesticide residues in some vegetables and fruits are presented in Table 2. The data indicated that all the tested vegetables (squash, tomatoes, potato, cucumber, spinach, and lettuce) and fruit (apple) carried pesticide residues, different in kind and quantity. The residues of Malathion, DDVP, and Dimethoate were detected. However, their amounts were well below the 'established tolerance levels'.

Table 2. The level of pesticide residues in some vegetables and fruits.

Crop	Source	Known Pesticides		Unknown Compounds		Column T°C
		Compound	**Residue (ppm)**	**Rt (mn)**	**Height of Peaks (mm)**	
Lettuce	Riyadh Market	–	–	1.52	13	150
		–	–	2.87	20	150
		Malathion	0.004	2.15	26	220
Spinach	Riyadh Market	DDVP	0.0015	0.59	32	150
				1.14	21	150
				1.35	9	150
				1.82	51	150
Cucumber	Riyadh Market	DDVP	0.005	0.59	70	150
				1.57	28	150
				2.84	22	150
				5.26	9	150
				0.99	10	220
		Malathion	0.001	2.15	10	220
				5.57	25	220
Squash	Riyadh Market			0.51	12	150
				1.17	14	150
				1.45	55	150
				2.73	20	150
		Malathion	0.24	0.49	111	220
				2.25	4	220
				3.33	27	220
				6.71	15	220
Tomatoes	Riyadh Market	DDVP	0.006	1.47	30	150
		Malathion	0.058	–	–	220
Potato	Riyadh Market	Malathion	0.0037	–	–	220
Apple (USA)	Riyadh Market	Malathion	0.007	7.88	–	220
Apple (French)	Riyadh Market			1.13	25	150
				1.39	85	150
				1.81	9	150
		Malathion	0.01	–	–	220
Squash	Qasseem Area	DDVP	0.015	–	–	150
		Malathion	0.0016	–	–	220
		Dimethoate	0.002	–	–	220
Tomatoes	Qasseem Area	Malathion	0.0044	–	–	220

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(Received 25/02/1984;
in revised form 12/08/1984)

دراسة تمهيدية على متبقيات المبيدات في الخضروات والفواكه الشائعة بالمملكة العربية السعودية

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في الوقت الحالي ، تُستعمل المبيدات على نطاق واسع لمكافحة الآفات في المملكة العربية السعودية . ومع أن استخدام المبيدات مهم من ناحية إنتاج المحاصيل ، فإن هذه الأهمية تتساوي مع أهمية الحفاظ على البيئة من التلوث . إذ يجب ألا تحتوى المحاصيل المحصودة على مستوى من متبقيات المبيدات أكثر من «الحد المسموح به» .

وقد وضعت طريقة معملية سريعة ودقيقة لتحليل عدد من المبيدات مثل الملاثيون ديازينون ، داى مثويت ، فنثويث (سيديال) ، مثيداثيون (سوبراسيد) ، DDVP وتبنى الطريقة على استعمال طريقة كروماتوجرافية الغاز في التحليل .

وقد نوقشت نتائج التحليل للطرق المختلفة التي استعملت وقورنت .

وتتضمن النتائج - بالإضافه إلى الاختبارات المعملية السابقة - تقدير مستوى متبقيات المبيدات في الخضروات والفواكه المحلية والمستوردة .