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Quantification of Some Pesticide Residues in Milk Powder in Iraq by Gas Chromatography/ Mass Spectrometry

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Pesticides are widely used on a global scale to improve productivity, but the persistent chemical residues they leave behind contaminate the environment and pose health risks to people. As a result, the current investigation was carried out to QuEChERS procedure adapted to gas chromatography coupled with mass spectrometry (GC–MS), to monitor the amounts of several organochlorine pesticides (OC), organophosphorus pesticides (OP), and pyrethroid in milk brand powder samples that were collected from Sulaimani market. About ten milk brand samples were analyzed to detect and quantify BHC, Chlorpyrifos, α-Cypermethrin, 2,4-D, Diazinon, and Endosulfan sulphate. Analytes provided acceptable responses at validation levels of 0.05 to 1 mg/kg. The linearity correlation coefficient R^2 was ≥ 0.9441, and limits of detection (LOD) value ranged from 0.18-0.49, limit of quantification (LOQ) value ranged from 0.54-1.49. Recovery

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percentage was obtained for all spiked levels (72.57-119.3) with acceptable relative standard deviation (RSD). The compounds α-Cypermethrin and Endosulfan sulphate found in most of the milk brands after that 2,4-D was found in brands but no one of them exceeded the MRL in all milk brands.

Keywords: Dairy science; milk products; pesticide; milk powder; GC–MS; spectrometry; gas chromatography.

1. INTRODUCTION

Milk powders are produced by spray drying of liquid milk to turn the liquid perishable raw material into a product without loss of its quality with longer shelf life [1]. Moreover, it needs less storage space, and reduced transportation costs. Milk powder production has grown to be a significant sector of the dairy industry and is predicted to continue expanding [2]. However due to potential contamination from the chain production of the raw material (the liquid milk), milk powders may contain toxic substances such as pesticides.

Pesticides are synthetic compounds that have been commonly used since the 1960s to manage agricultural pests and disease vectors. These pesticides are chemicals with a strong resistance to degradation, it may accumulate, making up a significant class of persistent organic pollutants [3]. Several classes of pesticides, such as organo-chlorines, organo-phosphorus, carbamate, and pyrethroids, have been detected in milk and milk products [4]. Consuming milk contamination with pesticides cause serious threat to human health such as reproductive disorders, diabetes, neurological dysfunction, cancer and respiratory disorders [5]. Hence Maximum residue levels (MRL) for pesticides have been established by the European Union and other countries to safeguard the health and safety of consumers. To guarantee effective consumer safety, reliable techniques have been used for quantification of pesticides in milk and milk product [6]. The most frequent, approaches to determine of pesticides are based on the use of liquid chromatography and_GC with selective detectors including electron capture detection (ECD) [7] and mass spectrometer (MS) detectors which are more sensitive and selective [8].

The use of mass spectrometry, with its information-rich content and explicit confirmation, is recommended for monitoring pesticide residues in different kinds of food [9,10] including milk powder [11]. Ideal technique for quantification of pesticides should be fast, easy to reproduce, have good recovery of the analytics, which need a good method for pretreatment of samples. Among the various available method used for this purpose, QuEChERS (quick, easy, cheap, effective, rugged, and safe) approach was the most popular due to its ability to extract wide range of polarity compounds [12].

The purpose of this paper was evaluating the occurrence of six selected pesticides residue in different brands of milk powder collected from Sulaimani province market through a QuEChERS-based extraction coupled to GC-MS.

2. MATERIAL AND METHODS

2.1 Sampling

Samples of ten different brands of powder milk collected from markets of Sulaimani province in Iraq which were: Altunsa, Bani Khellan, Mahmood, Holland Street, Anchor, Al-Modhish, Amazon, Nido, Puck and Dielac. All samples were supplied as powder milks. Infant containers (cans or bags) were stored in dark at room temperature until analyses were performed. For determination of pesticides 13g of powder-milk samples were suspended in 87ml of deionized water according to the manufacturer instructions. The studied pesticides were (BHC, Chlorpyrifos, α-Cypermethrin, 2,4 D, Diazinon and Endosulfan sulphate). Also, Blank milk samples free of the pesticides was acquired to use for sensitivity test, recovery studies and to produce standard and matrix matched calibration curves.

2.2 Chemicals and Apparatus

Pesticides standards (Benzene hexachloride, Endosulfan sulfate, Cypermethrin, Chlorpyrifos, Diazinon, Dichlorophenoxyacetic acid) with purity more than 99% purchased from Sigma-Aldrich (Germany). Furthermore (n-hexane, Dichloromethane “99.9%”, Acetonitrile “MeCN 99.5%”, methanol, primary secondary amin “PSA” 40 mM, sodium chloride (NaCl), and

anhydrous magnesium sulphate "$MgSO_4$" were purchased from (Merck Co Ltd).

2.3 Gas Chromatography Analysis

The pesticide residues were detected using GC/MS (Shimadzu Corporation- Japan) the separation process performed with capillary column of a 25m, with 0.25mm and 0.5 µm film thickness. The injector, interface, and ion source temperature were kept at 250℃.

Split less injection (1.0 min) was also performed using helium as a carrier gas with a flow rate of 1.0 ml/min. The oven temperature was set at 4 /min from 100 to 180, then temperature was increased from 18 /min to 300, and held 4 min for cleaning and restart again.

2.4 Extraction and Clean Up

Extraction was performed according to Rejczak and Tuzimski [13], by taking milk samples, 20 mL which were placed in polypropylene (PP) centrifuge tubes for extraction. Then, 16 mL acetonitrile (MeCN) was added to the tube and to be well mixed it was manually shaken for around 1 min; subsequently, 2 g NaCl and 8 g anhydrous $MgSO_4$ was added into the tube and immediately shaken well. The tube was centrifuged for 5 min at 6000 rpm. To make the result dry the supernatant acetonitrile (12 mL) of tube was collected with a pipette, and evaporated under a fume hood. Then, the residue was reconstituted in 1.2 mL MeCN and transferred into 12-mL PP tube containing 125 mg PSA, 25 mg Z-Sep, and 5 mg Z-Sep Plus. The tube was shaken vigorously for 1 min and centrifuged (6000 rpm/5 min). The supernatant (800 µl) was collected and dried under a fume hood. Afterwards, remaining residue was reconstituted in 1 ml MeCN and transferred into a vial. Final extract was stored at 6±2 before the analysis via GC-MS [13].

2.5 Method Validation

The method was validated according to the internationally accepted SANTE/11813/2019 in term of accuracy, linearity, precision and sensitivity (LOD and LOQ). The accuracy of the GC/MS technique was validated by evaluation of recovery performance. Blank milk samples were spiked with six known concentrations (0.05, 0.2, 0.3, 0.35, 0.5 and 1 µg/kg) of each pesticide, and then pesticide residues were extracted and detected.

The recoveries % = concentration found/concentration added*100

From six-point scale calibration curve, correlation coefficient R^2 and y-intercept(slope), of the regression line were used to assess the acceptability of the linearity data**.** Method sensitivity was determined by calculating the LOD and LOQ to meet the acceptance requirements for method performance. LODs and LOQs were computed using the formulas: LOD = 3.3 * (SD/b) and LOQ = 10 * (SD/b), respectively, based on the standard deviations (SD) of detector responses at the lowest concentration level and the slope of the calibration curve (b) [14]. By comparing the chromatograms of the solvent blank and control milk sample to the working mix standard using six replications for their separation and resolution from analyses.

3. RESULT AND DISCUSSION

3.1 Sample Extraction and Recovery

3.1.1 Assessment of the extraction method

It is challenging to achieve good recovery in the field of multiresidue food analysis, due to the large variances in characteristics of target analytes and effects of various matrices on the those analytes, [15]. In this study QuEChERS technique was used, due it is the most economical, good recovery and less time-consuming procedure. It was also was applied in pesticide residue analysis of milk [16, 17, 18], as well as from other various foodstuffs such as vegetables [14], fruits [19] cereals [20], honey [21] and meat [9].

In terms of the chemical components utilized in the QuEChERS technique Acetonitrile (Me CN) was used due to its ability to extract diverse target analytes including polar and non-polar analytes including pesticides from a variety food matrices [9, 15]. Addition of an inorganic salt (salting out) such as magnesium sulfate (MgSO4) was used to remove of water from extracted analytes, due to its high water absorption capacity, and to co-extracting some undesirable polar compounds from sample matrix like sugars [22]. Moreover, addition

Sodium chloride helps to increases selectivity of extraction [23].

A solid phase extraction (SPE) cartridge containing primary secondary amine (PSA), and octadecyl saline (C18) were used for this purpose which can strongly interact with acid compounds and remove various co-extractive interferences such as organic acids, sugars, fatty acids, lipid and some pigments.

Regarding to octadecyl silane (C18), it was added to the usual sorbents primary secondary amine (PSA), to maximize extraction efficiency, and peak resolution, [24] by strongly interact with acid compounds and remove various co-extractive interferences such as organic acids, fatty acids, and some pigments.

3.1.2 Validation methods

Several guidelines for validation have been proposed by the world's regulatory agencies, including Eurachem Guide: (2014), the World Health Organization (WHO) (2016), and the International Council for Harmonization (ICH) [25]. ICH was used in this study for the validation of GC/MS technique for determining pesticides in Milk in term of accuracy, Linearity, sensitivity (limit of quantification and limit of detection), and precision.

Accuracy was assessed by the percentage of recovery (Table 1) which were ranged from 79.46% to 112.81% for BHC; 75.61% to 116.97% for chlorpyrifos; 72.57% to 119.3% for α-Cypermethrin; 74.9% to 90.4% 2, 4_ D; 84.62% to 115.4 for Diazinon and 73.54% to 88.25 for Endosulfan sulphate. These values are within the acceptable ranges of recoveries that provided by EC No. SANTE/11813/2019, which ranged from 70-120% [16].

In the study of Zheng et al., [26] in analysis of 30 organochlorine pesticides in milk powder using GC-Ms/MS, the average recoveries were in the range of 70.1 to 114.7% at 3 spiked concentration levels.

To assess the acceptability of the linearity data; correlation coefficient R^2 and y-intercept of the linear regression line were used. R^2 ranged between 0.9441 to 0.9936 (Table 2), which considered as appropriate fitting the data to the regression line of EC No. SANTE/11813/2019 [37].

Many researchers used R^2 and y-intercept for the acceptability of the linearity data [27, 9].

The sensitivity of the method was determined by limit of detection (LOD) and limit of quantification (LOQ). LODs and LOQs were estimated based on the standard deviations (SD) of detector responses for the lowest concentration level and the slope of the calibration curve (b) according to the formulas: LOD = 3.3 * (SD/b) and LOQ = 10 * (SD/b), respectively.

LOD values of the assay as presented in Table 2 by µg/kg, was 0.492 for BHC; 0.284 for Chlorpyrifos; 0.410 for Cypermethrin; 0.203 for 2,4_D; 0.368 for Diazinon; and 0.180 for Endosulfan sulphate. the LODs of GC–MS in this study was close to that of Jadhav et al. [18] which was 0.2 µg/kg even he used GC–MS/MS, in determination of 66 pesticide residues in milk. And lower than the LODs obtained in the study of Tripathy et al. [16], who used the same technique (GC–MS) which was 20 µg/kg. The LOD will acceptable since it should be lower than the MRL that established by EU.

The LOQ values were ranged between 0.547 (for Endosulfan sulphate) to 1.492 for BHC. Validation parameters and recoveries values of GC–MS technique for determination of different types of pesticide residues in milk and dairy products also reported by Manav et al, [28].

3.1.3 Powder milk samples analysis

Out of the ten brands samples investigated, all samples were contaminated with the studied pesticides residues, and however all of these samples were not exceeded the MRL. Results of table 3 revealed the ratio of the six studied pesticides that detected from brands milk powder samples collected from Sulaimani markets. The pesticide residue BHC and Diazinon were recorded only in one (10%) of the studied samples which were Mahmood and Nido respectively (Table 3), meanwhile residue of Chlorpyrifos was found in 3 samples (30%) (Holland Street, Anchor, and Dielac) and their value were 3.038, 2.600 and 0.900 respectively. Regarding to the pesticide residue 2, 4-D and Endosulfan sulphate both of them found in 5 studied brands of milk powder (Table 3).

Table 1. Recovery and relative standard deviations (RSD %) in different spikes milk samples

Spiked level (mg/kg)	Recovery ± (RSD%), n=3					
	Milk samples					
	BHC	Chlorpyrifos	α-Cypermethrin	2,4-D	Diazinon	Endosulfan sulphate
0.05	95.21 ± 0.08	112.66 ± 1.54	87.57 ± 1.7	83.08 ± 1.32	90.73 ± 0.11	86.4 ± 1.11
0.2	99.42 ± 0.07	116.97 ± 0.11	112.15 ± 0.01		85.32 ± 0.23	84.09 ± 0.1
0.3	112.81 ± 0.05	101.4 ± 0.12	119.3 ± 0.63	84.09 ± 0.05	86.86 ± 0.05	83.75 ± 0.07
0.35	104.42 ± 0.1	99.3 ± 0.12	100.6 ± 0.09	90.4 ± 0.18	115.4 ± 0.97	88.25 ± 1.64
0.5	112.31 ± 0.05	79.79 ± 0.13	72.57 ± 0.24	78.38 ± 0.07	103.64 ± 0.05	83.67 ± 0.02
1	79.46 ± 0.75	75.61 ± 0.06	94.92 ± 0.05	74.9 ± 0.08	84.62 ± 0.05	73.54 ± 0.96

Table 2. GC-MS analysis presenting, linearity range, regression equation, coefficients, limits of detection (LOD) and quantification (LOQ) for milk samples (µg/kg)

Pesticides	Regression equation	r^2	LOD	LOQ
BHC	y = 764988x + 71690	0.9441	0.4925	1.4924
Chlorpyrifos	y = 676609x + 69187	0.9806	0.2845	0.8621
Cypermethrin	y = 816272x + 18448	0.9606	0.4102	1.2432
2,4 D	y = 717957x + 28405	0.9936	0.2032	0.6159
Diazinon	y = 720916x + 28928	0.9679	0.3686	1.1172
Endosulfan sulphate	y = 827156x + 36491	0.9921	0.1807	0.5477

Table 3. Levels of the pesticide residues in milk powder in Sulaimani markets

Brand	BHC	Chlorpyrifos	α-Cypermethrin	2,4-D	Diazinon	Endosulfan sulphate
Holland street	0.000 b	3.038 a ± 0.082	0.000 f	7.000 a ± 0.082	0.000 b	2.000 b ± 0.082
Al-Modhish	0.000 b	0.000 d	3.800 a ± 0.082	0.000 f	0.000 b	2.200 a ± 0.082
Anchor	0.000 b	2.600 b ± 0.082	0.000 f	2.000 d ± 0.082	0.000 b	1.800 c ± 0.082
Amazon	0.000 b	0.000 d	2.700 c ± 0.082	4.400 c ± 0.082	0.000 b	0.500 f ± 0.082
Mahmood	1.900 a ± 0.082	0.000 d	0.000 f	1.200 e ± 0.078	0.000 b	1.400 d ± 0.091
Dielac	0.000 b	0.900 c ± 0.147	0.800 e ± 0.082	0.000 f	0.000 b	0.800 e ± 0.082
Nido	0.000 b	0.000 d	0.951 e ± 0.008	0.000 f	0.900 a ± 0.082	0.000 g
Puck	0.000 b	0.000 d	0.000 f	6.367 b ± 0.094	0.000 b	0.000 g
Altunsa	0.000 b	0.000 d	2.900 b ± 0.163	0.000 f	0.000 b	0.000 g
Bani Khellan	0.000 b	0.000 d	2.200 d ± 0.082	0.000 f	0.000 b	0.000 g

The highest percentage of the studied samples were contaminated with the pesticide residue α-Cypermethrin, which was detected in 6 of the ten studied samples (60%) including Al-Modhish, Altunsa, Amazon, Bani Khellan, Nido and Dielac.

The levels of studied pesticides in milk powder were below the MRL values for these pesticides set by the European Commission (EC) [36] and Codex Alimentary Committee (CAC) [35].

The result of research about milk powder showed four samples trademark of (Nido, Dialac, Al-Mudhish) contaminated by organochloride pesticide residue that samples most commonly used by consumers, overtime residue of organochloride pesticide will accumulate, which lead to high concentration in the body [29]. The GCMS method was ideal for regular analysis and had the advantages of excellent accuracy and precision, easy operation, and speed [30].

OCPS and OPPS pesticide residue were also detected in milk powder in Romania using gas chromatography–mass spectrometry (GC-MS) with LOD ranged between 0.001–0.320 µg/kg [31]. The average values of 13 OPPs measured were below established MRLs (Salas et al., 2003). Chlorpyriphos was detected in 20 samples, all exceeding the MRL [32].

Organochlorine pesticide residue determined in milk powder. After simple processing samples for extraction and injection into the mass spectrometer for analysis, results showed that in the correlation coefficient were >0.998, and the method detection limits (MDLs) were <0.5 µg/kg [30]. 84.6% of milk powder samples were contaminated with pesticides and o p-DDD was the major contributor in milk powder (0.15 of 0.30 µg/kg). DDT was the major metabolite in milk powder in the study of Dos Santos et al. [33]. The highest mean concentration of DDTs was also found in the study of Zhou et al. [34], followed by DDTs were the most abundant pesticides, followed by HCHs and HCB. These concentrations of DDTs and HCHs dramatically declined with time.

4. CONCLUSION

Analysis of six kinds of pesticide residues in some imported brands of powder milk samples collected from Sulaimani markets in Iraq using GC/MS, revealed detection of these pesticides in most of them. However, the residue levels of the studied pesticides were not exceeded MRLs set by EC. These results obtained after validation of the technique in term of accuracy, linearity, sensitivity (limit of quantification and limit of detection), and precision.

All the validation parameters are within the acceptable range that set by the EC. Due to the risk of the pesticides on human health, hence it is very necessary to reduce consumer exposure to them by continuous monitoring of the pesticide's residue in food stuffs especially in milk which is more consumed by children than other age groups. It is worthwhile to extend this study to detect other pesticides residue in milk using more sensitive detectors of GS with the capability of full automation.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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