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Investigation of Arsenic Content in Field Pesticides Using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

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Keywords

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Abstract

In this study, Arsenic, which is found in the structure of field medicines, was determined by ICP-OES. For arsenic analysis, Turkey was elected four different commonly used pesticides. These pesticides were commercially named A, B, C, and D samples. These samples were solubilized using the appropriate procedure by microwave digestion method. For arsenic determination, 188.980 nm wavelength measurements were made. The determination of the known acid first with ICP-OES was measured at high sensitivity. Arsenic amounts were measured as approximately 0.46 to 0.81 µg/g as the 95% confidence level in the samples and the average of 5 measurements. The validation process of this method was done according to the reference article. The results of the experiment were made with the electrochemical method, differential pulse polarography (DPP), and the results were found to be in agreement.

Cite

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1. INTRODUCTION

Field pesticides are used to kill harmful insects in the field. Field pesticides affect our health through direct nutrition of drug residues in fruits, vegetables and cereals. It is also known to pollute soil, water and air. Arsenic contained in field pesticides has a toxic effect. Arsenic also has a carcinogenic effect in terms of human health (IARC, 2004).

Pesticides, such asInsecticide, herbicide, fungicide, rodenticide, molluscicide etc. pesticides are widely used in agriculture as well as for non-agricultural purposes, as they provide benefits such as improved product and yield quality (Baksh et al., 2020; Caetano et al., 2020; Dong et al., 2020). They are easily released into environmental areas such as soil, water, edible foods, groundwater, and drinking water, making it nearly impossible to avoid exposure to pesticides in the environment (Baksh et al., 2020; Raju, 2022). With the increase in their amount, it has caused health problems both for the environment and for living things.

Chromatographic, spectroscopic (Caetano et al., 2020) and electroanalytical methods (Demir & Silah, 2020; Demir et al., 2021) are used in the analysis of peptides.

Rapid growing industrialization has caused contamination of heavy metals, agricultural chemicals, pesticides and hydrocarbons. These have significantly damaged the environment and human health. (Maduka, 2006).

Arsenic is an element with high toxicity. The amount of arsenic in natural waters was measured with AAS (Andreae, 1977). Arsenic in agriculture (Christian & Feldman, 1970), in biological samples (Chu et al., 1972), the effect on the environment was studied (Clement & Faust, 1973; Fishman & Spencer, 1977). It has been

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determined that the most effective substance in the pollution of water with population growth is arsenic. (USEPA, 1999; Chauhan & Flora, 2010).

It has been determined that arsenic and pesticides have a possible role in the increase of diabetes. (Bahadar et al., 2014). A similar study was conducted in Pakistan and the use of different types of pesticides has led to an extraordinary increase in the amount of diabetes in recent years. It has been revealed that there are different types of cancer in humans due to the amount of arsenic it contains. In one study, the amount of arsenic in the well reached 620 µg / L in a certain period of time due to the arsenic-containing pesticides placed on the land next to the wells of families (Li et al., 2016).

In one study, heavy metal levels were measured in river creatures. It was determined that the Turia River basin was contaminated with pesticides such as DDT (Bordajandi et al., 2003). In another study, various pesticides contain harmful elements. Some of these drugs have been found to contain arsenic, mercury, chromium and lead (Campos, 2003).

The toxic effect of arsenic is known quality Arsenic has a detrimental effect on plants growing in the field, people and animals eating these foods, irrigation water and groundwater and the environment. It is important to determine the arsenic content in field pesticides. Therefore, arsenic amounts in four different field pesticides were determined by ICP-OES. The verification certificate of the method was measured by analyzing the reference substance. The results of the experiment were made with the electrochemical method, differential pulse polarography (DPP), and the results were found to be in agreement.

2. MATERIAL AND METHOD

2.1. Reagents and Instruments

Field pesticides, Turkey as well as in the world is available in agricultural areas too. In this study, four different brand pesticides were selected as examples. These commercial examples were given the names A, B, C, D. All determinations were performed using an ICP-OES model of Perkin Elmer Optima 5300 Dv. When performing the analysis, the device was made using the conditions in the previous study (Kalayci, 2020). The operational conditionals are presented in Table 1.

Table 1. *The operational conditionals of ICP-OES*

Parameter	**Across**
Auxiliary gas flow rate (L min^{-1})	0.2
Plasma gas flow of rate (L min^{-1})	15
Injector diameter	2.0
View	Axial
Interface	Shear gas
Applied power (kW)	1.3
Nebulization gaz flow of rate (L min^{-1})	0.6

2.2. Solubilization of Field Insecticides Samples

Milestone microwave decoding system was used to dissolve the water-insoluble pesticides. Samples were thawed in a microwave thawing system at specific pressures and temperatures using acid mixtures using the appropriate procedure (Tarla et al., 2020).

The samples were brought to a fixed scale in the oven. Samples were washed and dried at 100^{o}C for 48 hours. The cleaned samples were ground in the grinding machine. Before the amount of metal was determined, a microwave digestion procedure was performed by a Milestone microwave digestion system in order to achieve a total digestion in a short time, thus avoiding loss of metal by volatilization and minimizing the amount of added acid. The digestion procedure was as follows: 0.5 g of sample was placed in a polytetrafluoethylene (PTFE) digestion vessel, 1.5 mL of nitric acid and 2 mL of hydrogen peroxide were added. The samples were then kept at room temperature for 6 hours for homogenization and slow digestion. Afterwards, the containers were closed and the digestion process was carried out by applying a temperature program of 170°C for 18 minutes to the samples inside (Kalayci & Muhammet, 2022).

After the digestion procedure, all digestion vessels were left closed overnight for cooling. The next day, container contents were transferred to vials and the final volume adjusted to 10 mL with ultrapure water.

3. RESULTS AND DISCUSSION

3.1. Determination of the Optimum Conditions of ICP-OES for Arsenic

Prior to arsenic quantification, optimum conditions for analysis were determined. Calibration procedures were done and samples were prepared. The limits of determination were measured. Wavelength, correlation coefficient (R^2), detection limit (LOD) and quality limit (LOQ) of arsenic in ICP-OES are shown in Table 2. Calibration standard contained 0.01-5 mg/L As (Kalayci, 2020).

Table 2. *Analytical criteria of this method*

Element	**λ (nm)**	**R^2**	**LOD (mg/L)**	**LOQ (mg/L)**
Arsenic (As)	188.980	0.9997	0.007	0.022

3.2. Method Validation and Determination of Arsenic in Field Pesticides Using ICP

Validation of the proposed method was carried out by using a NIST-SRM 1547-Peach Leaves certified reference material. The amount of arsenic with certified reference substance is shown in Table 3. It has been observed that the results obtained are very close to the values given in the certified reference material.

Table 3. *Comparison of the measured value with the reference value (µg/g), 95% confidence interval and N=5*

Element	**Certified value**	**Microwave digestion**	**RSD (%)**
Arsenic (As)	0.068 ± 0.011	0.071 ± 0.014	4.56

Field pesticide samples with different brands brought from four different parts of Turkey were solubilized by microwave incineration method. The amount of arsenic in the samples was analyzed with high precision and the results are shown in Table 4.

Table 4. *Arsenic contents (µg/g) in four different field pesticides (A, B, C and D) after microwave digestion, 95% confidence interval and N=5*

Element	**A**	**B**	**C**	**D**
Arsenic (As)	0.52 ± 0.06	0.73 ± 0.11	0.81 ± 0.13	0.46 ± 0.04

Field pesticide samples with different brands brought from four different parts of Turkey were solubilized by microwave incineration method. The amount of arsenic in the samples was analyzed with high precision and the results are shown in Table 4. While arsenic was at a normal level in samples A and D, it was high in samples B and C.

The comparison of the results of our study with the arsenic values obtained in other studies is given in Table 5. It is seen that the sensitivity and selectivity of the applied method are high.

Table 5. *Comparison of arsenic values measured with ICP-OES*

Samples	**LOD (mg/L)**	**Reference**
Spray	2.08	Proch & Niedzielski, 2020
Ketchup	0.5	Massadeh & Al-Massaedh, 2018
Food samples	0.8	Ahmad et al., 2021
Fuel samples	0.05	García et al., 2017
Spinach	0.85	Gonzálvez et al., 2008
Water	0.38	Idris et al., 2017
Pepticides	0.007	This work

3.3. Determination of Arsenic Using DPP

The most sensitive result of arsenic determination in polarography was made by using the catalytic hydrogen peak. 10 ml of 0.25 M HAc buffer (pH = 3.5) electrolyte was placed in our cell and its polarogram was taken. Approximately 1000 times Mo (VI) was added on it and its polargram was taken. Then, when 0.2 mL of our pesticide samples were added, it was seen that the peak at -1.1 V grew. The peak in Figure 1 is the catalytic arsenic peak.

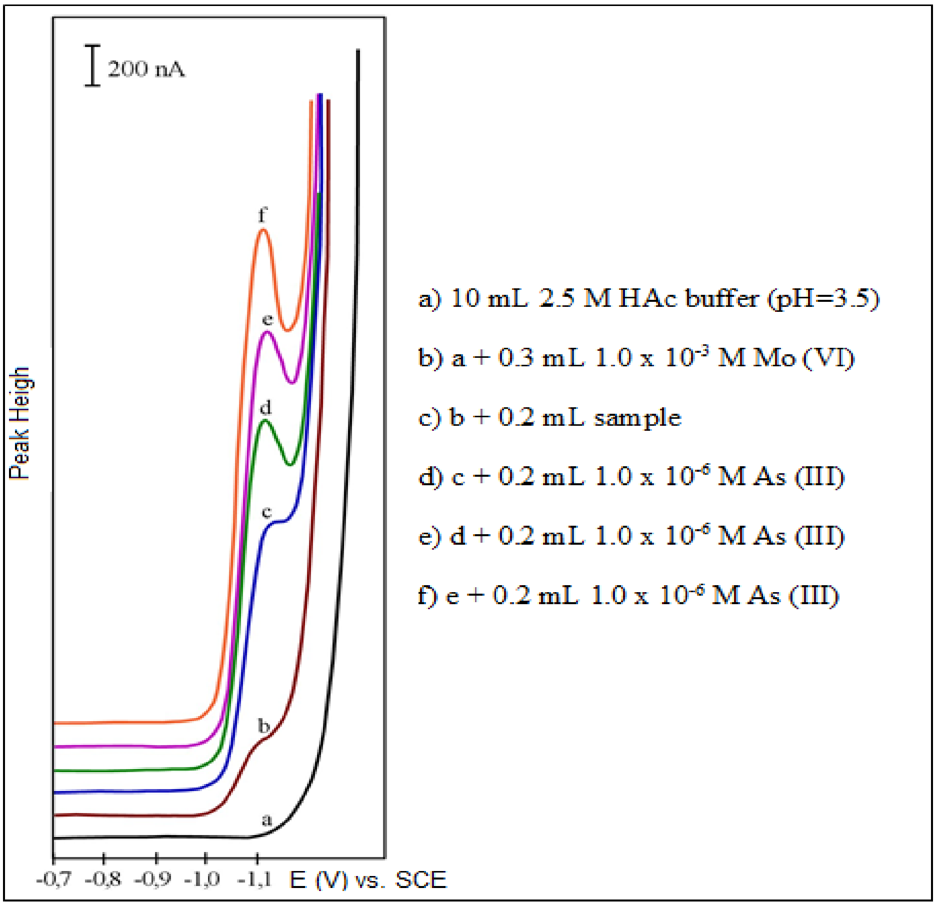

Figure 1. *Determination of arsenic using DPP*

When arsenic standard solution was added on it, arsenic concentrations were calculated by using the peak heights (Somer & Almas, 2006; Somer & Kalayci, 2014). The amounts of arsenic found by this method are given in table 6. The t test was applied to the results obtained from both methods and it was seen that they were compatible with each other.

Table 6. *Comparison of arsenic amounts with ICP-OES and DPP, 95% confidence interval and N=5*

Methods	**A**	**B**	**C**	**D**
ICP-OES	0.52 ± 0.06	0.73 ± 0.11	0.81 ± 0.13	0.46 ± 0.04
DPP	0.52 ± 0.07	0.74 ± 0.14	0.80 ± 0.25	0.47 ± 0.11
t-test ($t_{Critical}$=3.18)	2.15	2.68	2.72	1.96

4. CONCLUSION

Field pesticides are used to kill harmful insects in the field. Field pesticides affect our health through direct nutrition of drug residues in fruits, vegetables and cereals. It is also known to pollute soil, water and air. Arsenic contained in field pesticides has a toxic effect. Therefore, in this study, we used to define the amount of arsenic in Turkey in the field of pesticides. We identified four different field pesticides (A, B, C and D) as samples. We solved these samples with microwave digestion system. Arsenic analyzes were done with ICP-OES. The validation process for the method used in the measurements was carried out with the reference material. Then, arsenic amounts in samples were determined. The results of the experiment were made with the electrochemical method, differential pulse polarography (DPP), and the results were found to be in agreement. While the amount of arsenic in samples A and D was between normal values, the amount of arsenic in samples B and C was excessive.

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CONFLICT OF INTEREST

The authors declare that they have no competing interests.

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