

Pesticide Analysis and Method Validation with GC/MSD Instrument in Environmental Water Samples

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Abstract

In this study, a rapid and multiple method has been proposed which can be used in determination of more than 130 pesticide residues at ppb ($\mu\text{g/L}$) level in water samples. For this purpose, a Kuderna-Danish Evaporative Concentrator, which was used for enrichment of the analyte concentration in the samples and gas chromatography coupled mass spectrometry in the selective ion monitoring (SIM) mode was developed and validated for the multi-class determination of pesticides. In the analysis, a 30m HP-5 MS UI capillary GC columns was used. The high sensitivity of chromatographic analysis was necessary, due to that these pesticides must be determined at low concentrations. The method presented quantification limits between 1.8 and 29.2 ng.L^{-1} . Most of the compounds presented mean recoveries between 70.1-116.5 % and 70.7 – 114.0% at 10 ppb and 50 ppb levels, respectively. Although the difference in chemical natures of the pesticides made difficult to attain good recovery for all of the compounds evaluated, the precision of the results was excellent. The selectivity of the method was evaluated through the relative intensity of quantification and qualification ions and was considered adequate. Analysis in real samples met criteria for instrumental qualification and the system suitability evaluation. Thus, qualitative and quantitative determinations of 130 pesticide were done.

Keywords: Pesticide, Water, Aldrin, Validation, GC/MSD

Çevresel Su Örneklerinde GC/MSD ile Pestisit Analizi ve Metot Validasyonu

Öz

Bu çalışmada, su numunelerinde 130'dan fazla pestisit kalıntısının ppb ($\mu\text{g/L}$) düzeyinde belirlenmesinde kullanılabilecek hızlı ve çoklu bir analiz yöntemi önerilmiştir. Bu amaçla, analit konsantrasyonunun zenginleştirilmesi için bir Kuderna-Danish Evaporatif Konsantratör ve SIM (Selective Ion Monitoring) modunda çalışan gaz kromatografisi (GC) ile birleştirilmiş kütle spektrometresinin (MSD) kullanıldığı bir yöntem geliştirildi ve çoklu pestisit analizi için validasyonu yapıldı. Kromatografik analizde, pestisitlerin düşük konsantrasyonlarda dahi yüksek hassasiyetle tespit edilebilmesi gerektiğinden dolayı 30m HP-5 MS UI kapiler GC kolonu kullanıldı. Geliştirilen yöntemle miktar tayin limitleri 1.8 ve 29.2 ng.L^{-1} olarak belirlendi. Yöntem, bileşiklerin çoğunda sırasıyla 10 ppb ve 50 ppb seviyeleri için 70.1-116.5 % ve 70.7 – 114.0% aralıklarında ortalama geri kazanım sağladı. Pestisitlerin birbirinden çok farklı kimyasal yapıları, analizi yapılan tüm bileşikler için iyi bir geri kazanım sağlamayı zorlaştırmış olmasına rağmen sonuçların hassasiyetinin mükemmel olduğu değerlendirilebilir. Metodun seçiciliği, hesaplama ve tanımlama iyonlarının bağlı oranı yoluyla değerlendirildi ve değerlendirme sonucunda yeterli kabul edildi. Gerçek numunelerdeki analizler, enstrümental yeterlilik kriterlerini ve sistem uygunluğu değerlendirmesini karşılamıştır. Böylelikle, 130 pestisitinin nitel ve nicel tayinleri yapılmıştır.

Anahtar Kelimeler: Pestisit, Su, Aldrin, Validasyon, GC/MSD

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1. Introduction

Pesticides, chemical substances used for the prevention, development and proliferation of undesirable insects, rodents, plants, mosses and other harmful substances, and to provide better quality and more efficient products in agricultural production [1]. The use of pesticides to protect crops against pests is a common and important part of agricultural practices all over the world.

The usage of pesticide has increased significantly in order to provide the growing nutrition need for the world population [2]. The use of pesticides helps to avoid a 65% loss in food production. In addition to this, it is advantageous to cultivate the product more frequently in the correct conditions, such as keeping the products for a long time and bringing more economic benefit to the producer together with it [3]. The pesticides used extensively worldwide are about 3 million tons per year. The average annual sales amount is around 30 billion euros [4].

On the other hand, these chemicals disrupt the ecological system balance due to pollution of water, air, soil and nutrients with the remains left behind in large areas, while the use of pesticides provides benefits for public health and hunger. In addition, some of them are toxic to the only specific living species because of their selective properties, while others are harmful to people, domestic animals and wild animals which are outside the target of the pesticides. In such cases they can cause acute and chronic poisoning [5].

Pesticides also play a very important role in the contamination of water resources. Since herbicides and nematicides are applied directly to the soil, they are considered to be the most important pesticides that pollute environmental waters [6]. The ways for pesticides to interfere with the aquatic environment can be listed as; direct inputs from the agricultural industry, industrial effects, waste water effects, spraying of cattle and sheep, dust and flooding, and atmospheric transmission (wind effect, evaporation from application areas, erosion of pesticide applied lands in various ways) [7].

Pesticides, which can be dissolved in water or can be sediment in the case of exceeding the solubility criterion, pass through aquatic organisms in various ways through the food chain and cause bioaccumulation [8]. Pesticides, which are transmitted to waters in different ways, are a threat with the adverse consequences of reaching people through water ecosystems and food chains [9]. The fact that a person is a living creature that feeds on both plant and animal nutrients, and that it forms the last ring of the food chain, causes such compounds to appear in large measure in humans [10-12]. Compostable compounds such as pesticides or heavy metals can enter the human body first with fish consumption [13]. In many studies, the relationship between the concentration of pesticides in the mother's milk and fat tissue and the frequency of application of certain pesticides in a particular area has been clearly demonstrated. For example, the high DDT amounts in the fat tissue of people in Costa Rica and Zaire as well as in the mother's milk in Hong Kong, are the results of continuous use of DDT in these countries [14].

Accurate and reliable analysis of these waters should be carried out and their current status should be monitored to prevent or reduce the adverse effects of pesticide residues in the environmental waters which is the source of life. In this study, a rapid and multiple method has been proposed which can be used in determination of ppb ($\mu\text{g/L}$) level of 130 pesticide residues in water samples.

2. Material and Methods

2.1.1. Materials and Chemicals

Pesticide reference standards were of analytical grade, and were purchased from either Dr. Ehrenstorfer (Augsburg, Germany). The names of the tested pesticides were shown in Table 2. Acetonitrile, methanol, acetic acid, sodium chloride, anhydrous sodium sulfate, toluene were supplied by Sigma-Aldrich. Dichloromethane used for extraction was of extra pure (EP) grade, whereas acetone and ethyl acetate were of pesticide grade obtained from E. Merck (Darmstadt, Germany).

2.1.2. Standard solution preparation and quantitative analysis

All pesticide standard substances Certified Reference Standards from Dr. Ehrenstorfer Turkey. The pesticide standards were weighted in a 50 mL volumetric flask approximately 10 mg with a precision of 0.01 mg and the volume was completed with methanol. Main stock solutions are stored at -18 °C.

2.1.3. Extraction of Pesticide Residues

A Kuderna-Danish Evaporative Concentrator was used for enrichment of the analyte concentration in the samples.

A liter of water sample is added to the separation funnel. 60 mL of dichloromethane (CH_2Cl_2) is poured on water and is subjected to liquid-liquid extraction by shaking for 10 minutes. 30 minute is waited for the separation of phases after shaking. 20 mL of a saturated aqueous NaCl solution is added to facilitate phase separation. This process is repeated two more times. Extraction is done using by 180 mL of dichloromethane in total. The organic phases are combined and water is removed with anhydrous sodium sulfate (Na_2SO_4). Then the solvent is evaporated with the help of Kuderna-Danish Evaporative Concentrator.

The residue is dissolved in 1 mL of toluene and injected on Agilent GC/MSD instrument. In the analysis, a 30m HP-5 MS UI capillary GC columns was used. Qualitative and quantitative determinations of 130 pesticide were made in total.

2.1.4. Instruments and Analytical Conditions

We applied gas chromatograph (Agilent Technologies 6890-GC) with mass spectrometry (Agilent 5975C-MSD), equipped with a HP-5MS column (Agilent HP-5MS UI, 30 m, 0.25 mm, 0.25 μm) for pesticides separation.

The gradient analysis of the gas chromatograph was followed as: temperature 70°C, maintain temperature rising rate of 25°C /min to 150°C for 2 min, temperature rising rate of 3°C/min to 200°C, a temperature rising rate 8°C/min, and an end temperature 280°C, maintained for 10 min.

Operation condition settings of mass spectrometer components were followed as: the temperature ion source, 230°C; the quadrupole temperature, 150°C; the mass spectrometer and gas chromatograph transfer line temperatures, 280°C; the ionization energy, 70 eV. Helium was used as carrier gas.

Using selected ion monitoring mode (SIM) to scan the ions, we set the retention time (RT), precursor and fragmentation ions, entrance voltage and dwell time.

3. Results and Discussion

3.1.1. Method Validation

An analytical method is a series of procedures from preparing the sample to issuing the final report. The validation method is the process of verifying suitability. The validity of the methods is often established based on the performance of inter-laboratory studies. However, this process is a high cost and very slow, or limited in scope. Validation in a single laboratory can also provide a practical and cost-effective alternative approach [15].

The identification, validation, calculation of an analyte in the Agilent Technologies 6890-GC gas chromatography 5975C-MSD quadrupole mass spectrometry system takes place in the SIM mode with at least one precursor ion and at least two product ions. The specificity of validation procedure is an ability to verify precisely an assay even in the presence of other components (such as impurities, disruptive products, matrix components, etc.). Selectivity of the method is that a method analyses the matrix of a given compound without interfering with the matrix components [16].

Accuracy is a qualitative term that is used to express the true value of the measurement results and their closeness to each other [17,18]. For recovery and repeatability parameters, as it is specified in European Commission Directive [19], representative water matrix were spiked by pesticide analytes at 10 ng/ml and 50 ng/ml concentrations as 10 repeats for three days.

3.1.2. LODs and LOQs

In this study, the validation of 130 pesticides analyzed according to Regulation [19] was carried out in the water matrix and included in the method. 130 of pesticides were optimized in GC/MSD. To perform this operation, intensive work has been done on instrument. In the method validation studies, LOD - LOQ parameters were determined in the water matrix. The limits of detection (LOD) and of quantification (LOQ) were established from the signal-noise (S/N) ratio of quantification ions and qualification ions selected for each compound studied.

The limit of detection (LOD) is the lowest residual concentration limit that can be measured but not necessarily quantified under validated conditions. The limit of quantification (LOQ) is the lowest residual concentration limit that can be determined with acceptable accuracy under validated conditions [20]. The European Union has determined the MRL (maximum residue limit) values of the European Union by reference to LOQ [17,21-23].

In accordance with the European Union directive [23,25], water matrix which is contaminated with pesticide standards such that each pesticide was 10 ng/g were studied by 10 parallel for the LOD and LOQ parameters. The standard deviations were calculated. The minimum detection limit (LOD) is calculated as 3s value, while the minimum quantitation limit (LOQ) is calculated as 5s value (Table 1).

3.1.3. Recovery and Repeatability

While the highest recoveries at 10 ppb were found to be for methoxychlor (p,p'-o,p') (116.5%), endosulfan sulfate (111.3%) and chlorfenprop-methyl (110.7%), minimum recoveries were calculated in disulfoton (70.1%), tefluthrin (74.4%), γ -HCH (Lindane) (77.7%) and tetrachlorvinphos (78.3%). On the other hand, alachlor (114.0%), methoxychlor (p,p'-o,p') (109.3%) displayed highest recoveries, but β -endosulfan (70.7%), heptachlor exo-epoxide (isomer B) (71.2%) showed lowest recoveries at 50 ppb. The method performance values are in accordance with European Commission Directive [19,25].

Table 1. LODs, LOQs, recoveries at 10 ppb and 50 ppb levels of the 130 pesticides in the GC/MSD

Name of Pesticide	LOD	LOQ	%Rec 10 ppb	%Rec 50 ppb
2-Phenylphenol	2.3	3.8	82.7	97.1
3,4- Dichloraniline	7.5	12.5	103.6	74.5
3,5- Dichloraniline	4.9	8.2	97.4	93.8
Acrinathrin	6.8	11.3	86.0	85.1
Alachlor	1.6	2.7	104.6	114.0
Aldrin	2.3	3.8	98.1	80.2
Allethrin	7.1	11.8	91.5	72.4
Azinphos-ethyl	3.8	6.3	95.3	81.9
Azinphos-methyl	6.5	10.8	101.4	88.2
Benfluralin	5.4	9.0	82.5	77.0
Bifenthrin	2.1	3.5	95.4	80.0
Bromocyclen	1.3	2.2	94.5	82.1
Bromophos-ethyl	6.6	11.0	89.7	79.9
Bromopropylate	1.2	2.0	100.8	81.9
Captafol	4.7	7.8	102.5	97.2
Carbophenothion	5.1	8.5	94.3	81.8
Chinomethionate	17.5	29.2	105.0	100.5
Chlorbenside	3.3	5.5	103.8	76.4
Chlordane (<i>cis, trans</i>)	0.6	1.0	97.8	82.4
Chlorfenapyr	1.6	2.7	99.6	81.5
Chlorfenprop-methyl	6.3	10.5	110.7	76.4
Chlorfenson	1.6	2.7	105.8	97.5
Chlorfenvinphos	5.0	8.3	94.5	84.6
Chlorfenvinphos	2.6	4.3	98.4	93.9
Chlorobenzilate	2.1	3.5	98.4	93.8
Chloroneb I	1.1	1.8	94.5	83.0
Chlorothalonil	2.2	3.7	96.5	84.9
Chlorpropham	2.4	4.0	103.2	88.7
Chlorpyrifos	1.9	3.2	93.0	98.3
Chlorpyrifos methyl	1.9	3.2	93.3	97.0
Chlorthal-dimethyl	1.9	3.2	100.5	95.2
Chlorthiamid	3.0	5.0	92.5	94.9
Chlozolate	2.1	3.5	99.4	93.9
Cyanophos	3.0	5.0	97.6	99.3
Cyfluthrin	4.0	6.7	109.0	102.3
Cyfluthrin I,II,III,IV	3.9	6.5	93.6	100.1
λ -Cyhalothrin	2.7	4.5	90.8	86.4
Cypermethrin	5.0	8.3	96.6	101.0
Dazomet	2.1	3.5	97.9	96.8
o,p'-DDD	2.0	3.3	100.4	90.6
p,p'-DDD	2.0	3.3	96.5	84.0
o,p'-DDE	2.2	3.7	97.6	99.2
p,p'-DDE	2.3	3.8	94.3	95.1
o,p'-DDT	2.0	3.3	94.9	84.2
p,p'-DDT	2.8	4.7	86.9	82.3
Deltamethrin	2.8	4.7	102.7	78.0
Demeton-S-methyl	1.7	2.8	106.3	81.9
4,4-Dibromobenzophenone	2.3	3.8	96.7	85.8
Dichlobenil	1.9	3.2	97.8	101.7
Dichlofenthion	1.9	3.2	89.3	100.7
4,4-Dichlorobenzophenone (Dicofol)	2.3	3.8	93.1	98.5
Diclofop-methyl	3.2	5.3	88.3	103.1
Dicloran	3.5	5.8	97.4	87.0
Dieldrin	2.0	3.3	100.0	75.1
Dinitramin	3.5	5.8	92.4	77.6
Diphenylamine	2.3	3.8	104.0	82.8
Disulfoton	2.4	4.0	70.1	79.4
Endosulfan sulfate	2.4	4.0	91.2	80.4
α -Endosulfan	1.7	2.8	89.2	73.3
β -Endosulfan	2.3	3.8	81.6	70.7
Endosulfan-sulphate	2.4	4.0	111.3	79.2
Endrin	2.9	4.8	105.3	75.5
Esfenvalerate	3.2	5.3	105.7	92.0
Ethion	1.5	2.5	101.9	81.5
Etridiazole	1.8	3.0	92.2	80.1
Etrimfos	1.8	3.0	105.0	74.9
Fenchlorphos	1.6	2.7	107.5	87.9
Fenitrothion	1.8	3.0	88.1	82.7
Fenson	2.4	4.0	106.0	93.9
Fenvalerate (I-II)	3.6	6.0	98.8	84.6
Fipronil	2.4	4.0	99.6	80.2

Table 1 (continue). LODs, LOQs, recoveries at 10 ppb and 50 ppb levels of the 130 pesticides in the GC/MSD

Name of Pesticide	LOD	LOQ	%Rec 10 ppb	%Rec 50 ppb
Fluchloralin	11.4	19.0	86.4	90.2
Flucythrinate (I-II)	3.7	6.2	103.4	77.5
Flumethrin	3.8	6.3	94.4	81.3
Fluvalinate- τ (I-II)	3.3	5.5	108.1	81.6
Formothion	3.8	6.3	84.2	77.3
Furalaxyl	3.3	5.5	105.9	83.1
Halfenprox	1.4	2.3	91.9	86.7
α -HCH	2.1	3.5	90.1	83.8
β -HCH	2.3	3.8	102.4	71.3
γ - HCH (Lindane)	2.1	3.5	77.7	87.5
δ -HCH	2.4	4.0	99.4	90.5
Heptachlor	2.3	3.8	88.4	78.1
Heptachlor endo-epoxide (isomer A)	3.5	5.8	98.8	105.1
Heptachlor exo-epoxide (isomer B)	2.1	3.5	103.4	71.2
Hexachlorobenzene	3.1	5.2	85.5	80.4
Iodofenphos (Jodfenphos)	2.1	3.5	93.3	84.1
Isodrin	2.3	3.8	82.7	79.4
Isofenphos	2.4	4.0	100.9	87.3
Methacrifos	2.3	3.8	89.5	81.6
Methidathion	2.1	3.5	96.8	80.0
Methoxychlor (p,p`- o,p`)	1.7	2.8	116.5	109.3
Mirex	2.3	3.8	106.9	103.0
Nitralin	2.8	4.7	87.1	87.2
Nitrapyrin	3.2	5.3	102.9	88.3
Nitrofen	4.4	7.3	85.2	93.4
Nitrothal-isopropyl	3.3	5.5	102.4	89.7
Parathion (-ethyl)	1.9	3.2	98.4	85.9
Parathion methyl	2.7	4.5	82.3	96.1
Pentachloroaniline	2.0	3.3	95.8	83.9
Pentachloroanisole	2.4	4.0	109.2	85.1
Permethrin	3.2	5.3	95.2	87.9
Perthane	2.0	3.3	95.4	87.6
Phorate	4.4	7.3	92.6	82.7
Phosmet	4.2	7.0	101.1	86.0
Phthalimide (Folpet)	2.2	3.7	87.1	86.4
Procymidone	2.0	3.3	106.8	98.5
Profluralin	3.2	5.3	101.6	99.0
Propham	3.7	6.2	86.6	84.0
Prothiophos	3.4	5.7	89.5	95.4
Pyraflufen-ethyl	2.0	3.3	89.8	90.3
Pyrimidifen	4.0	6.7	89.4	95.0
Quinalphos	1.8	3.0	92.6	89.2
Quintozene	2.9	4.8	97.5	94.0
Resmethrin	2.4	4.0	84.9	94.6
S421	3.0	5.0	89.8	99.5
Spiromesifen	3.6	6.0	87.8	93.3
Sulprofos	1.6	2.7	100.0	95.5
Tecnazene	2.2	3.7	87.0	94.8
Tefluthrin	2.3	3.8	74.4	87.5
Terbacil	3.6	6.0	87.9	103.9
Terbufos	3.3	5.5	89.9	97.6
Tetrachlorvinphos	3.3	5.5	78.3	88.6
Tetradifon	2.1	3.5	100.9	100.3
Tetrahydrophthalimide (Captan)	3.0	5.0	92.6	96.6
Tetrasul	2.4	4.0	99.5	95.7
Thiometon	2.4	4.0	95.7	95.5
Tolclofos-methyl	2.0	3.3	87.2	93.1
Trifluralin	2.9	4.8	87.2	92.7
Vinclozolin	2.1	3.5	83.9	75.8

LOD: Limit of dedection, LOQ: Limit of quantitation

Method selectivity showed to be adequate for the determination of the pesticide studies. All the pesticides presented signals greater than their limits of quantification. Table 1 shows the limits of quantification and the MRL values from Regulation. The limits of quantification achieved with the proposed method are also adequate for the control of pesticide residues in drinking water in accordance to the EURACHEM Guide [25]. All the pesticides presented signals greater than their limits of quantification

4. Conclusion

In the developed method, several factors were varied in order to increase sensitivity and robustness significantly. The present method was shown to be adequate for the determination of most of the pesticides in water. The GC-MS in the SIM mode proved to be essential for quantification with adequate sensitivity and selectivity for pesticide residues in samples from a number of origins. Moreover, high recoveries were obtained.

The design of the Agilent 6890 GC-5975 Quadrupole GC-MS enables pesticides to be determined at lower detection limits when combined with an inert sample path and GC column backflushing. The high sensitivity Electron Impact (EI) Ion Source with improved thermal characteristics delivers confident trace analysis even in complex matrices.

The simple, easy, economical and efficient method was developed for the determination of 130 pesticides in water. The method demonstrates good sensitivity, precision, accuracy and allows for rapid analysis. The results demonstrate that pesticide residues can be detected below the current maximum residue levels required by the Regulatory specifications. The method is ideally suited for use in a regulatory laboratory for the determination of pesticides in surface, drinking and packaged drinking water.

For the reason of importance of pesticide analysis in the water should be carried out in a precise manner by optimized and validated methods and risk analysis should be done in the most accurate way.

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