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A REVIEW ON ANALYTICAL METHODS FOR DETERMINING METHYL PARATHION IN ENVIRONMENTAL SAMPLES

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ABSTRACT

Methyl Parathion is an organophosphorous pesticide and is classified by the Environmental Protection Agency as a class I toxicant. It is sprayed on crops to kill insects. Methyl parathion partitions mainly to air and soil in the environment, with lesser amounts in plants and animals. In human body, the liver breaks some of the methyl parathion down to a more harmful chemical, methyl paraoxon. Methyl parathion and methyl paraoxon bind to enzyme acetylcholinesterase in nerves and interferes with the normal functioning of nerves and brain. This review paper presents an overview of some chromatographic methods reported for the analysis of methyl parathion in environmental samples. The review has also explored the analysis of MeP by optical, fluorescent biosensors whose practicability was tested in real environmental samples and extended Raman Spectroscopy approaches for pesticide analysis.

KEYWORDS: Methyl parathion**,** acetylcholinesterase, chromatography, biosensors, raman spectroscopy.

INTRODUCTION

Methyl Parathion, also called Dimethyl parathion or Parathion-methyl, is among the most toxic organophosphate pesticides, generally sprayed on rice, cotton and fruit trees to kill insects. The ready-to-use solutions of methyl parathion have concentrations of 0.05 to 0.1%. The chemical is banned for use on many food crops as it does not meet the safety standard as currently registered. Parathion acts on the enzyme acetylcholinesterase, but indirectly. Once ingested, the methyl parathion gets oxidized to give methyl paraoxon.

Exposure to high levels of methyl parathion or methyl paraoxon for a short period may cause sweating, cramps, vomiting, blurred vision, diarrhea, wheezing, difficult breathing, chest tightness, headaches, confusion, tremors, dizziness, loss of consciousness, and death. In human body, the liver breaks some of the methyl parathion down to a more harmful chemical, methyl paraoxon. Methyl parathion and methyl paraoxon can bind to enzyme acetylcholinesterase in nerves within minutes or hours. Methyl parathion interferes with the normal functioning of nerves and brain. Exposure of methyl parathion to levels below those that affect nerve function cause few or no health problems.[1]

Methyl parathion stays for a few days to several months in the environment. It is generally degraded to other chemical compounds by water, sunlight, and bacteria that are found in water and soil. In case of soil, methyl parathion sticks to it, and then is rapidly degraded by bacteria. It generally does not leach to the groundwater through the ground. In case of water, methyl parathion breaks down quickly by the action of bacteria in the water, and sunlight. In water and air, methyl parathion is broken down by sunlight to form a more toxic product which is methyl paraoxon.[2] Presence of large amounts of methyl parathion in soil, such as landfills and hazardous waste sites, degradation rate is retarded.

Determination of Methyl Parathion by Chromatographic Methods.

Sample Matrix	*Extraction Method*	*Analytical Method*	*Sample Detection Limit*	*Reference Number*
Marine sediment	10 g homogenized sediment added to 50 ng deuterated parathion-methyl in soxhlet extraction thimble which was wetted prior with extraction	Combined Capillary Column Gas Chromatography	1.7 ppb	[3]

	mixture acetone : n-hexane (4: 1). After extracting overnight, organic phase partitioned with 0.5 M sodium hydroxide, concentrated, and applied to column consisting of 10 g activated charcoal, magnesium oxide and Celite 545 (1:2:4). The column was eluted with 120ml ethyl acetate saturated with water and then with 150ml of ethyl acetate/acetone/toluene (1 : 1 : 2). The extract was concentrated to dryness and redissolved in 1 ml n-hexane	Negative Ion Chemical Ionization Mass Spectrometry		
Water	600.0 µL dispersing and extraction solvents mixture, acetonitrile : toluene (5:1) mixture injected rapidly into water samples (5.0 mL) free or fortified with parathion-methyl by a microsyringe of 1000.0 µL. The resulting cloudy solution was vortexed for 30 seconds followed by centrifugation at 6,000 rpm for 5.0 min.	Dispersive Liquid Liquid Microextraction – Gas Chromatography with Electron Capture Detector	0.083 ppb	[4]
Rice	On-line SPME procedure: 1 mL standard solution of 10mg/L, prepared by dilution of stock solution (methyl parathion pesticide dissolved in methanol) in deionised water. Then extraction and preconcentration of MeP was done by direct extraction, in which the fibre was immersed in the aqueous sample for a certain time. The SPME fibre was preconditioned for 1 h at 250 ∘C before analysis, and subsequently thermally desorbed into GC injector for 15 min at 240∘C. During microextraction, a constant volume of standard solution was used in a flask-type confined space (headspace) of 20 mL capacity, having a butyl rubber septum faced with Teflon, under constant magnetic agitation. The optimized conditions of the method : sample volume in the vial 10 mL; addition of 0.5 g of sodium sulphate to the vial; agitator temperature 70 ∘C; needle size 2 cm; total extraction time20 min; thermal desorption at 280 ∘C for 30 min; fibre desorption temperature 240 ∘C for 5 min; agitation at 250 rpm.	Headspace Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry	0.026 ppb	[5]
Honeybees	3 g lyophilized honeybees previously pounded in a glass mortar in 250 mL flask; shaken vigorously for 10 min with 100 mL of acetone. The mixture was filtered through a Buchner funnel packed with a layer of Celite (~5 mm). A coagulate solution of 1% (w/v) ammonium chloride and 2% (v/v) orthophosphoric acid was added to above filtrate, allowed to stand for 30-40 min with occasional stirring, and then filtered. The filtrate was diluted with 200 mL of 2% aqueous NaCl (w/v) and extracted twice with 100 mL of dichloromethane. Organic extracts were then passed through anhydrous sodium sulfate and evaporated to ~10 mL in a rotary evaporator at 35 °C. Five milliliters of methanol was added, mixture evaporated to 5 mL using a gentle stream of nitrogen gas.	Liquid Chromatography Atmospheric Pressure Chemical Ionization Mass Spectrometry	1 ppb	[6]
Mango and Grapes	20 g fruit cover was collected from the sample. The covers were kept in a cone flask and thoroughly mixed with dichloromethane (30 ml) and sodium carbonate (15 g). The mixture was allowed to stand for 12h in well-sealed cone flask	High Performance Liquid Chromatography	0.005 ppm	[7]

	and later filtered through filter paper. The dish was washed with dichloromethane, filtered liquid phase was contained in an open watch glass. Once dichloromethane dried out, methanol (5 ml) was added to extract the MeP. The extraction was repeated twice with methanol (2 ml) and later mixed and diluted by methanol to 10 ml and then filtered for analysis.			
Bottle Guard Matrix	15 g sample weighed, homogenized and chopped into a centrifuge tube. Ethyl acetate (30 ml) added for extraction and shaken for 1 min. Na2SO4 (10g) added and shaken for 30 min by rotospin and centrifuged for 5 min. Cleaning of 6 ml upper layer extract by adding 0.9 g anhydrous MgSO4, 0.25 g PSA and 0.25 g activated charcoal: shaken for 1 min in 15 ml centrifuge tube. Supernatant 4 ml was dried and finally make up to 1 ml.	Gas Chromatography	0.1 ppm	[8]

Determination of Methyl Parathion by Biosensors

Arjmand, M. *et al.* developed non-adiabatic tapered fiber optic biosensor for real time, free detection of methyl-parathion pesticide (MeP) in presence of acetylthiocholine iodide (ATCh). From series of experiments conducted with NATFOBS it was found that the enzyme substrate does not interfere with or has little impact on the detection of pesticide especially when the MeP concentration is higher than 5 μM. On the contrary, it was observed that, for the MeP concentrations lower than 0.1 μM, ATCh is the predominant substance in the complex and prevents the effective reaction of MeP with the enzyme. Monitoring of real time reaction between enzyme AChE and MeP was done and detection limit of MeP was found to be 23nM in solutions containing 1 mM acetylthiocholine iodide. For practical applicability the sensor was explored for MeP detection in real samples, indicating excellent recovery of MeP in the tap and river water. Two specific concentrations of MeP (1 μM and 10 μM) spiked in the tap water and river water samples (both filtered by filter paper) were taken and the detection of MeP was done through screening the wavelength shift corresponding to sensor response from interferometric spectrum and from calibration curve reading the corresponding concentration of MeP. The experiments were carried out both in the presence and in the absence of 1 mM ATCh. The experimental results show acceptable values for the MeP recoveries ranging from 96.5% to 103%.[9]

Li, Y. *et al.* reported a highly sensitive and selective method for UV–vis spectrophotometric as well as fluorimetric determination of organophosphorus pesticides (OPs) that uses silver nanoparticles (AgNPs) modified with graphitic carbon nitride (g-C3N4). The AgNPs reduce the fluorescence intensity of g-C3N4. The enzyme Acetylthiocholine (ATCh) was firstly hydrolyzed by Acetylcholinesterase to form thiocholine, which would further induce aggregation of the AgNPs. This aggregation yields the recovery of the blue fluorescence of g-C3N4, which has excitation/emission peaks at 310/460 nm. This fluorescence intensity was again reduced in the presence of OPs because they have inhibitory effect on the activity of enzyme AChE. It was found that degree of reduction was proportional to the concentration of the OPs, and the limit of fluorimetric detection was 0.0324 μg/L (S/N = 3). The mechanism of the experimental method was confirmed by a series of characterizations using TEM images, the fluorescence spectrum, UV–vis absorption spectroscopy, fluorescence lifetime measurements, and zeta potential measurements.

This method was successfully applied to the analysis of methyl parathion in real samples. A series of different concentrations of parathion-methyl in water, apple, and carrot samples were analyzed. From the results, the percentage of recovery from both spectral methods was in the range 79.2% to 120% and the relative standard deviation (RSD, n = 3) values were found to be < 5.3% which indicates the feasibility of the method.[10]

Tan, X. *et al.* devised a sensitive and rapid electrochemical sensor that is based on pillar.[5] arene (CP5) reduced graphene (rGO) nanohybrid-modified glassy carbon electrode CP5-rGO/GCE serving the purpose of trace detection of methyl parathion (MeP) by differential pulse voltammetry (DPV). These nanocomposites were further characterized by fourier transform infrared spectrometry (FTIR), charge transfer resistance (R_{ct}) and zeta potential. This method was successfully applied to MeP detection in soil and tap water samples. The detection of MeP in soil and waste water practical samples was carried out by standard addition methods. Percentage recoveries were in the range of 98.6% to 101.2% and RSDs were in the range of 2.1% to 4.3% for MeP.[11]

Govindasamy, M. *et al.* developed a highly sensitive methyl parathion sensor for the determination of MeP in cabbage, green beans, strawberry, and nectarine samples using silver@graphene nanoribbons nanocomposite modified screen printed electrode (Ag@GNRs/SPCE).

The Ag@GNRs was successfully prepared through simple wet chemical method and its structure was confirmed by Transmission Electron Microscopy (TEM), Energy Dispersive X-Ray Analysis (EDX), X Ray Diffraction (XRD), Raman, UV-visible and EIS techniques. It was observed that the synergic combination of GNRs and Ag greatly reduced the overpotential and enhanced the sensitivity. The modified electrode was shown to have excellent sensor performance and achieved low detection limit. The advantages of SPCE technology in combination with electrocatalytic trait of Ag@GNRs has made the composite highly suitable for electroanalytical applications and the composite provides better pesticide sensing in real samples.

From the amperometric responses the LOD for detection of MeP in cabbage, green beans, strawberry, and nectarine fruit samples was found to be 1.0nM, 2.0nM, 2.0nM and 3.0nM respectively.[12]

Determination of Methyl Parathion by Raman Spectroscopy

Lee, D. *et al*. proposed an ultra-sensitive and fast trace analysis of MeP pesticides in a polydimethylsiloxane (PDMS) microfluidic channel that uses confocal surface-enhanced Raman spectroscopy (SERS). A 3D PDMS-based passive micromixer was synthesized for this purpose which showed a high mixing efficiency because the simultaneous vertical and transverse dispersion of the confluent streams causes a strong chaotic advection. Once MeP effectively adsorbs onto silver nanoparticles whilst flowing along the upper and lower alligator-teeth-shaped PDMS channel, the confocal SERS signal was measured. A quantitative analysis of the Methyl Parathion pesticides was performed based on the measured peak height at 1246 cm^{-1} characteristic of C─O stretching. The method was found to have a detection limit of 0.1 ppm.[13]

Sato-Berru, R. Y. *et al*, reported NIR-Raman Quantitative analysis of methyl-parathion pesticide microdroplets on aluminum substrates. The Near-Infrared Raman spectroscopy coupled with an alternative mathematical model was used to determine the concentration of a MeP in given liquid sample at parts per million level. Aliquots of ~2µL were placed on the aluminium foil; the solvent was allowed to evaporate from the aliquots at room temperature. Later, Raman spectra of five representative microdroplets (from 10 to 180µm) which were of the biggest size and uniform were recorded for all samples for them to be averaged. Two characteristic peaks were chosen for the analysis, i.e. the most intense peak (1345 cm^{-1}) and one more peak (1110 cm^{-1}) for analysis. The Raman intensity of each peak was measured from the base line at varying concentration and concentration ranges viz., 1000 ppm, 10000 – 40 ppm, 1000 – 10 ppm, and 100 – 10 ppm. The intensity of the Raman peaks were analyzed and taken in the respective graph from which respective RSD was calculated in all cases. For both the peaks, i.e., 1345 cm^{-1} and 1110 cm^{-1} linear regression analysis of the experimental data obtained was performed and the correlation coefficient, r^2 was found to be 0.996[14].

CONCLUSION

Various analytical methods have been reported to determine Methyl parathion in environmental samples. The most commonly used analytical technique is Mass Spectrometry coupled with Gas/Liquid Chromatography with selective sample treatment and extraction procedures. A range of electrochemical, fluorescent, piezoelectric and optical biosensors have been developed which are based on the enzymatic reaction of Acetylcholinesterase with OP pesticides. These biosensors avail simple approaches for OPs detection and have several advantages such as low cost, fast response, high sensitivity, and on-site operation. However, quantitative analysis of methyl parathion by Raman Spectroscopy is rapidly gaining interest. Additional research includes residual analysis of MeP, analysis of degradation products of MeP, immunochemical assays in biological and environmental samples.

REFERENCES

1. National Center for Biotechnology Information. PubChem Compound Summary for CID 4130, Methyl parathion. https://pubchem.ncbi.nlm.nih.gov/compound/Methyl-parathion.
2. Howard, P.H. (ed.). Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Vol. III: Pesticides. Lewis Publishers, Chelsea, MI, 1989.
3. Nielsen, P. G. Quantitative analysis of parathion and parathion-methyl by combined capillary column gas chromatography negative ion chemical ionization mass spectrometry. Biological Mass Spectrometry, 1985; 12(12): 695–698.
4. Pimenta, G., de Queiroz, M., Victor, R., Noronha, L., Neves, A., de Oliveira, A., & Heleno, F DLLME-GC/ECD Method for the Residual Analysis of Parathion-Methyl and its Application in the Study of the UV-Photodegradation Process. Journal of the Brazilian Chemical Society, 2017.
5. Da Silva, D. F., Paiva Silva, F. E., Silva, F. G. S., Nunes, G. S., & Badea, M. Direct determination of methyl parathion insecticide in rice samples by headspace solid-phase microextraction-gas chromatography-mass spectrometry. Pest Management Science, 2014; 71(11): 1497–1502.
6. Fernández, M., Picó, Y., Girotti, S., & Mañes, J. Analysis of Organophosphorus Pesticides in Honeybee by Liquid Chromatography−Atmospheric Pressure Chemical Ionization−Mass Spectrometry. Journal of Agricultural and Food Chemistry, 2001; 49(8): 3540–3547.
7. Rao, Ch. Ramamohana and L. Cyril Arun Kumar Qualitative and Quantitative Analysis of

Fenvalerate, and Methyl Parathion Pesticides in Mango and Grapes collected by Hplc Method, 2012.
8. Mishra, S., Thakur, L. K., & Richhariya, N. Gas Chromatographic Determination of 23 Organophosphorus Pesticides Residue in Bottle Guard Matrix. International Journal of Pharmacy and Pharmaceutical Sciences, 2018; 10(1): 53-59.
9. Arjmand, M., Aray, A., Saghafifar, H., & Alijanianzadeh, M. Quantitative Analysis of Methyl-Parathion Pesticide in Presence of Enzyme Substrate Using Tapered Fiber Optic Biosensor. IEEE Sensors Journal, 2020; 1–1.
10. Li, Y., Wan, M., Yan, G., Qiu, P., & Wang, X. A dual-signal sensor for the analysis of parathion-methyl using silver nanoparticles modified with graphitic carbon nitride. Journal of Pharmaceutical Analysis, 2020; 04.
11. Tan, X., Liu, Y., Zhang, T., Luo, S., Liu, X., Tian, H., Chen, C. Ultrasensitive electrochemical detection of methyl parathion pesticide based on cationic water-soluble pillar[5]arene and reduced graphene nanocomposite. RSC Advances, 2019; 9(1): 345–353.
12. Govindasamy, M. *et al*. Methyl parathion detection in vegetables and fruits using silver@graphene nanoribbons nanocomposite modified screen printed electrode. Sci. Rep., 2017; 7: 46471.
13. Lee, D., Lee, S., Seong, G. H., Choo, J., Lee, E. K., Gweon, D.-G., & Lee, S. Quantitative Analysis of Methyl Parathion Pesticides in a Polydimethylsiloxane Microfluidic Channel Using Confocal Surface-Enhanced Raman Spectroscopy. Applied Spectroscopy, 2006; 60(4): 373–377.
14. Sato-Berrú, R. Y., Medina-Valtierra, J., Medina-Gutiérrez, C., & Frausto-Reyes, C. Quantitative NIR–Raman analysis of methyl-parathion pesticide microdroplets on aluminum substrates. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2004; 60(10): 2231–2234.