

Flow Injection Analysis Coupled with Chemiluminescence for Pesticide Determination in Water: A Review

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Abstract

In this review the determination of pesticides in water by flow injection analysis coupled with chemiluminescence. Several sensitive and rapid FI-CL reported method from the recent years has been discussed. FI-CL are the most sensitive and precise technique for the determination of pesticides in surface water samples. The methods includes in the present article are advanced and economic methods. These methods were applied for the quantitative measurements of unknown concentration of different classes of fungicides, herbicides, insecticides and rodenticides in various water samples. Following the detection limits ranges from 0.1 -3.0 mg per liters. The calibration curves and relative standard deviations are described with their recoveries. The FI-CL methods are discussed here with the cited references. The specific CL reactions are also discussed with their produced CL ranges and wavelengths of the CL reaction. Some new advancement are developed in CL methods for future research aims.

Keywords: Pesticides, Flow injection, Chemiluminescence, Water

INTRODUCTION:

Pesticides are the most hazardous compound which are merely known for the harmful environmental pollutant. The exhaustive nature of pesticides is due to their stability and long term effect on living species [1]. Pesticides are widely used compound in agriculture to give productive amounts of fruits. The long and persistence use of pesticides makes their alarming concentrations in fruits, vegetables and specially the water [2]. Due to the extreme toxic behavior of pesticides are consider as a hazardous aquatic pollutant, bioaccumulation and environmental persistent[3]. Pesticides Mojiri are the class of organic compound which is a worldly used compound used for the prime aim of controlling pests and their preventions. Only a minute portion of pesticides active ingredient reaches to crops rest of the portion spreads in environmental component [4]. The over and constant use of pesticides in agricultural fields makes greater the contaminated concentration of pesticide in fruits, vegetables, cereal crops, soil, air and water which severely affects the human health through drinking water and food chain [5].

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The different types of pesticides having different nature and structures. The different types of pesticides are used to kill, control or repel.

- Herbicides use to control, repel and to kill the herbs
- Insecticides use to control, kill or repel the harmful insects
- Fungicides use to control, repel and to kill the fungus.
- Rodenticides use to kill, control and to repel the rodents

The application of these pesticides on crops lets a remarkable effects on the yield and quality of crops. Formers achieves more than target yield. Besides positive aspects there are many hazardous effects of pesticides [6].

Types of pesticide pollutants in surface drinking water:

Pesticides have been classified on the basis of their targeted species to which they are introduced for specific function of controlling the growth of pests in crops. Usually used in urban and rural farmland. The pesticides such as insecticides herbicides and fungicides are widely used product on commercial and subsistence farming. Fungicides secure plants from fungal infection herbicides are known to kill and controlling of weeds insecticides are used to kill harmful insects in crops field.

Table 1: The given table categorize the pesticides on target species:

Pesticides	Guideline value (µg/L)
Alicarb	20
Altrazin	2
Bentazone	300
Carbofurane	7
DDT	2
Lindane	2
Hexachlorobenzene	1
Metachlore	10
Simazine	9
Propanil	20
Chlordane	0.2
2,4,5 T	7
Molinate	6
Pyridate	100

Flow injection analysis (FIA):

Flow injection analysis (FIA) is a easy, precise, economic and easy analytical technique. Which is a widely used analytical technique centered on the injection of sample (the sample contains analyte) into a non-segmented carrier stream which is carried forward in manifolds of specific diameter toward the detector to produce signals. Several modes and methods of has been developed for precise and accurate analysis since the late 1950,s. Among all flow modes of analysis the most important and unique one is sequential flow analysis and segmented injection analysis (SIA)[6]. Flow injection analysis earns most of its importance in analytical area of analysis. The development and progress in the development of completely novel concept for the analytical determinations and measurements. Of different automation degrees and integration, of several importance of measuring systems and physical sciences. The influential progress flow injection analysis determinations , the complete instrumentations for the biochemical analysis associated with variations of the interest in the use of the method in the diverse fields of practical of application [7].

Chemiluminescence:

Luminescent reaction are the reactions which emit light from excited electrons when it jumps back to its ground state from excited state. Namely they are too called as light reaction. Approximately there are three well known types of luminescent reaction which are widely in analytical research. chemiluminescence which emits light when two or more chemical reactant react to each other , bioluminescence in which biological species emits light after their exposure to any thermal source and defined as the generation of electro-magnetic radiation such as ultraviolet (UV) Visible (VIS) and infrared the third is the electroluminescence emits light electrochemical source . Chemiluminescence (CL) IS (IR) in the results of chemical reaction between reactive species. In the result of the reaction one specie of the following product must be excited that should emit light in UV, VIS and IR ranges when re jumps to its lower energy level. All the reactions cannot produce CL to produce CL the following requirements should be fulfill [8].

It must release energy in enough amount to produce an unstable energetic electronic state in the ultra violet region. The photon energy ranges from 44 to 71 kcal/mol.

The reaction path must support the excited electronic state.

The unstable energetic state should either be luminescence itself or capable of transferring energetic excitement to next molecule.

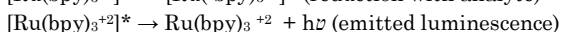
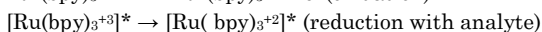
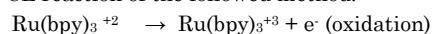
FIA coupled with CL is the most sensitive, precise and powerful technique and instrument , which not only display the exclusive feature involving mechanization, adaptability , and it is very inexpensive including the lower limit of detection (LOD) as well wide linear range . These all feature meet to all requirement of modern chemical analysis [9]. On the basis of all these features FIA-CL system becomes the center of attraction for research community. FIA-CL system is widely used in the following areas such pesticides, biochemical, trace metals, pharmaceuticals, forensics and green chemistry [10].

Most commonly used CL systems: there are some very commonly used CL system in the analytical community of research.

Tris, DPA CL system:

A very modest , sensitive and economic FI technique has been reports to diagnose the concentration of thiram fungicide and aminocarbs fungicides in surface water samples(river , lake , ponds) the developed method was based on the strong enhancing signal factors. The effect of these fungicides on tris (2, 2-bipyridyl) ruthenium, (11)-diperiodatargenate (111) (Ru (bipy) 3-DPA) chemiluminescence system follow optimized experimental conditions. The reagent used in this method are ethanol, tris, DPA, sulphuric acid. The produced chemiluminescent intensity were linear in the range of 1-1000 and 1-10000 ng^{-ml}. (n=7) ,and (n=11) for thiram and aminocarbs followed by relative standard deviation (RSD); n=3) in the range 1-2.6 percent. The lower limited detection (LOD) is in the range of 0.1 ng per ml for both aminocarbs and thiram with injection sample throughput was 150 injections per hour. This method was effectively applied to water samples [11].

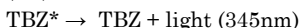
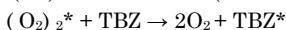
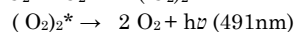
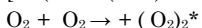
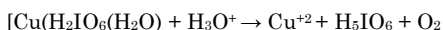
CL reaction of the followed method:



Diperiodatocuprate (III)- Sulphuric acid CL system:

FI –CL method was developed for the quantitative measurement of fungicides (TBZ) in water sample. The developed method based on the enhancer effect on diperiodatocuprate (III) (DPC), sulphuric acid chemiluminescence (CL) system. And obtained a linear calibration graph in the concentration range 1-2000 microgram per liter with the limit of detection of 0.3 microgram per liter. In this method the injection throughput was kept 60 per hour with the relative deviation RSD (n=4) of 1.1-2.9 percent in the concentration under all optimized experimental parameters. The reagent used in the method was potassium hydroxides (KOH), sulphuric acid (H₂SO₄), phosphoric acid (H₃PO₄), nitric acid (HNO₃). The method was successfully applied for the determination of TBZ in water samples [12].

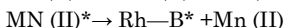
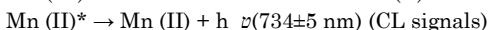
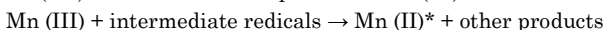
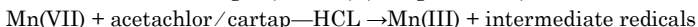
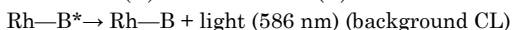
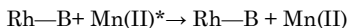
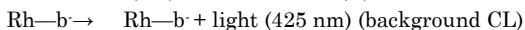
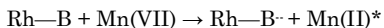
CL reaction of the followed method:



KMnO₄ –rhodamine-B CL system:

FI-CL method using the low PH (acidic) media of potassium permanganate(KMnO₄) – rhodamine-B reaction with chemiluminescent detection. This technique was recognized for the measureable analysis of acetachore and cartep –HCL pesticides in fresh aquatic samples. All the parameters for the established experiment were well optimized and the chelex 100 cationic exchanger mini column and solid phase extraction (SPE) were utilizes as a separation technique. The obtained calibration curve which was observe in this process was a linear one for the stock solution of acetachlore and caetep –HCL over the ranges of 0.005-2.0 mg/L (n=8). The limit of detection (LOD) and the limit of LOQ were 7.5 – 0.1 ×10⁻⁴ and 8.0 10⁻⁴ mg per liter 2.5× 10⁻³ mg / L .respectively. The injection throughput were kept 140 h⁻¹. The result obtained from these experiments were not significantly different at a 95% confidence level to those of other reported method . Recoveries for cartep-HCL and acetachlore were obtained over the limited ranges of 93-112% (RSD=1.7-3.8%) , The reagents used in the followed method were sulfuric acid , copper nitrate ,cobalt nitrate manganese nitrate ,ferroys ammonium sulfate , magnesium chloride , sodium chloCride , potassium dihydrogen phosphate ,sodium sulfate , sodium bicarbonate , absolute ethanol , humic acid ,phenol and ascorbic acid and seveal ranges solution of the followed pesticides. These methods were successfully applied for the estimation of cartep-HCL and acetachlore with or without SPE [13].

CL reaction of the followed method:



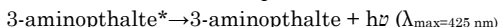
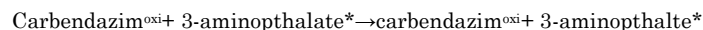
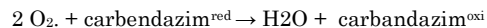
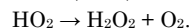
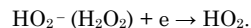
Cerum(IV) CL system:

In this fast and economic Flow injection chemluminescence (FI-CL) method for the quantitative determination of Fenamiphos pesticides in a very easy way. This method was proceed in a basic media. The fenamiphos was firstly photodegraded in the basic media. The cerum (IV) reacted with photofragments this reaction provided the chemiluminescence signals. The chemical and physical parameters for the proposed method were well optimized, for the sensitivity and accuracy. Before solid SPE C18 catridges were applied . By applying solid phase extraction (SPE) to 250 ml of the standard. For this method the dynamic linear range was kept between the ranges 3.4 and 60 microgram per liter. The limit of detection (LOD) was kept 1 microgram per liter which describes the sensitivity of the method. after this the SPE was applied to the 500 ml od the standard the LOD was fixed here to 0.5 microgram per liter (the final volume was 10 ml for bothe 250 and 500 ml standard) these 0.5 and 1 LODs were under the emission limit values established by Spanish Regulation of the Hydraulic public Domain for pesticides (50 microgram per liter) at European directive on the quality of water for Human consumption. The sample input was kept 126 per hour. Intraday and enterday coefficient of variation were below 10 % in all cases. No interferences have been observed in the usual concentration of anion, cation and other organophosphorus pesticides. The reagents used in the method were hydrochloric acid cerum sulfate , formic acid sodium salt of acetic acid , ammonium sulfate , potassium sulfate , sodium hydrogen phosphate , potassium per manganate , potassium ferri cynate , sodium hydroxide , sodium chloride . cations interferences were prepared from chlorides . This method was magnificently applied for the analysis of environmental water samples collected from diverse areas and the recoveries were from 96 to 107.5 % [14].

Luminol Hydrogen Peroxide CL System:

A sensitive flow injection chemiluminescence system established for the quantification of carbendazim in water samples. The method developed on the reaction based between luminol and H₂O₂ the reaction between luminol and H₂O₂ produce luminescence which is further used for the quantification of pesticides. The chemiluminescence intensity can further enhanced with sodium dihydrogen phosphate and sodium hydroxide basic Medias. (PH=12.6) under optimized condition. The linear range for the quantification of carbendazim is 2.00× 10⁻⁸ to 2.00 10×10⁻⁶ mg L⁻¹ with the LOD of 7.24×10⁻⁹ g ml⁻¹. The RSD IS 1.8% for 1.0 ×10⁻⁷ (n=8). The reagents used in the method were of best grade the reagents were luminol, hydrogen peroxide, distil water, sodium hydroxide, sulfuric acid. This method was successfully applied for the concentration of carbendazim in the tap water samples used for drinking bathing and washing purposes [15].

CL reaction for the followed method in an alkaline medium:

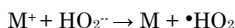
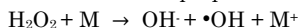


Copper(II) Hydrogen Peroxide CL system:

An easy, cheap, simple, rapid and sensitive FI-CL system developed for the quantification of benzimidazole fungicide, benomyl, furbidazole and carbendazim. This method is based on the improvement of the chemiluminescence (CL) signals. The CL

generated signal is produced through the reaction of BF_s with H₂O₂ and Cu (II) in basic media in the absence of luminescent reagents. The calibration graph was obtained linear in the concentration range of 5-2000, 25-2000, and 25-5000 ng ml⁻¹ for fuberidazole, Benomyl and carbendazim respectively. The RSD was in the range of 1.2-2.6% with the LOD 3 ml⁻¹ for the fuberidazole and 15 ng ml⁻¹ for benomyl and carbendazim. The sample throughput for the followed method was kept 120 injections per hour. The interferences were faced from cation, anions and some pesticides. The recoveries were in the range of 94±1 to 105 ± 1%. The reagents used in the proposed method were luminol, sodium hydroxide, sodium hydrogen phthalate, hydrogen peroxide and sulfuric acid. All the reagents are of analytical grade and prepared in their standard form of specific concentration. This method was fruitfully applied for the quantitative analysis of carbendazim and benomyl in the tap water samples [16].

CL reaction of the proposed method:



This reaction produces a weak CL

Photograde Ferricyanide CL system:

A very simple, sensitive and cheap and rapid flow injection chemiluminescence system has been developed for the quantification of MCPA in aqueous samples. The instrumentation for the followed method was very simple and rapid enough method for analysis. The chemiluminescent signal was generated by treating ferricyanide with photograde MCPA in an alkaline media. The chemical and physical parameters were optimized for the proper performance of experiment. To get an interference free setup SPE with SBD-1 cartridges and C₂H₅OH elution was performed. The generated signal of MCPA mass relation was direct in concentration intervals between 0.0015 and 0.6 microgram ml⁻¹ all the calibration lines obtained were linear statistically similar in various working conditions. Standard with C₂H₅OH and deprived of ethanol extractions allowing standards was to be excluded from extraction step which further simplifies the process. The lower limit of detection was kept 0.5 ng ml⁻¹. which is of the same order of Mmaximum limit of detection was established in the legislation pesticides limit in water used for human use. A DOL of 0.13 ng ml⁻¹ can be reached if a sample of 100 ml is preconcentrated. The interday variance coefficient is 3 % the sample input was kept 90 samples per hour. the reagents used in the followed process were all of analytical grade which are MCPA, sulfuric acid, hydrogen peroxide, acetonitrile and acetone, potassium permanganate, potassium ferri hexacyanate, phosphoric acid, nitric acid, potassium iodate, perchloric acid, sodium hydroxide, hydrochloric acid and cesium sulfate. Several salts such sodium, calcium and carbonate salts were used for the testing of interferences potential of cations and anion interferences. The method was effectively useful for the determination of MCPA in surface water samples [17].

Diperiodatnekelate(IV)- Sulfuric CL system:

An economic and precise flow injection chemiluminescent method was developed for the determination of thiram (fungicide) in the fresh water samples. The CL reaction for the process was based on the reaction between the sulfuric acid and the diperiodatnekelate (IV). Quinine was used as a sensitizer in this method. The possible CL mechanism for the reaction was describe by using ultraviolet, visible (UV—Vis), absorptions and the spectra of CL. All the experimental parameters were optimized by applying univariate approaches. The obtained calibration graph was

absolutely linear in the applied ranges of $1.0 \times 10^{-3} - 2.0 \text{ mg L}^{-1}$. With the smallest limit of detection (LOD) of 5.0×10^{-4} . The injection throughput was kept 200 samples h^{-1} . The reagents used in the method were potassium periodate (KIO_4) potassium sulfate ($\text{K}_2\text{S}_2\text{O}_8$), Nickel(II) sulfate heptahydrate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$), sulfuric acid (H_2SO_4), potassium nitrate (KNO_3), potassium dihydrogen phosphate (NaH_2PO_4), Sodium chloride (NaCl), calcium chloride (CaCl_2), potassium chloride (KCl), zinc nitrate ($\text{Zn}[(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$), Copper nitrate, cobalt nitrate ascorbic acid, humic acid and phenol. The method was successfully on the determination of concentration of thiram in fresh water samples by using solid SPE, and successfully attained the recovery rate of the 94%-110%. With the relative standard deviation (RSD) of 1.9-3.7%. The obtained results compared with the reported FI-CL and HPLC [18].

CL reaction of the followed method:

$\text{THI} + \text{DPA} \rightarrow \text{intermediate complex}$

$\text{Complex} \rightarrow \text{CS}_2^* + \text{side products}$

$\text{CS}_2^* + \text{DPN} \rightarrow \text{SO}_2^* + \text{other product.}$

$\text{SO}_2^* + \text{quinine} \rightarrow \text{quinine}^*$

$\text{Quinine}^* \rightarrow \text{quinine} + \text{hz} (450\text{nm})$

Diperiodatonikelate(IV)-Rhodamine 6-G-Brij CL system:

A rapid and sensitive flow injection chemiluminescence (FI-CL) method was developed to determine the concentration of maneb and mencozeb in natural surface water samples, which are fungicides overwhelming the ranges of 0.0025-0.25 parts per million (ppm) and 0.01-0.75 ppm. With the least limit of detection (LOD) of 0.001 and 0.005 ppm. The RSD of 1.75% and 1.8%. The sample throughput was kept 200 samples h^{-1} . The reaction was based on diperiodatonikelate(IV)–Rhodamine 6-G-brij-35 CL reaction in a basic medium of potassium hydroxide (KOH) which is further enhanced by maneb and mencozeb. Different oxidizing agent except the diperiodatonikelate (IV) are applied and checked and periodatoargenate (III) were appreciably enhanced the emission of CL intensity. The reagents were used in the method were of analytical grades. They were nabam, carbophenothion, fubridazole, feneramol, benomyl, propanil, other solutions of Mn^+ , Fe^{+2} , Zn^{+2} and Cr^{+3} were used other reagents ascorbic acid, humic acid, DPN, lactose and phenol.

Maneb and mencozeb were extracted from water samples by solid phase extraction (SPE) technique. The recoveries which were calculate in the range of 92-108%. The relative standard deviation (RSD) of 1.41-2.67%. The method was successfully developed for the quantification of maneb and mencozeb in water samples [19].

The chemiluminescent reaction of the followed method:

$\text{Rh6-G} + \text{DPN} + \text{OH}^- \rightarrow \text{Rh6-G}^*_{\text{ox}}$

$\text{Rh-G}^*_{\text{ox}} \rightarrow \text{Rh6-G}_{\text{oxidation}} + \text{light} (420\text{nm})$

$\text{Rh6-G}^*_{\text{oxidation}} + \text{Rh6-G} \rightarrow \text{Rh6-G}^*_{\text{oxidation}}$

$\text{Rh6-G}^* \rightarrow \text{Rh6-G} + \text{light} (550 \text{ nm})$ (background CL)

Maneb/ Mencozeb + $\text{OH}^- \rightarrow \text{Mn}^{+2} + \text{Nabam}$

$\text{Mn}^{+2} + \text{dissolved } (\text{O}_2) \rightarrow \text{Mn (oxidation state)} + \text{O}_2^*$

$\text{O}_2^* + \text{O}_2 + 2\text{H}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$

$\text{Mn}^{+2} + \text{H}_2\text{O}_2 \rightarrow \text{Mn (H.O.S)} + \text{OH}^* + \text{H}^*$

$\text{Rh6-G} + \text{DPN} + \text{O}_2^* / \text{OH}^* \rightarrow \text{Rh6-G}^*_{\text{ox}}$

$\text{Rh6-G}^*_{\text{oxidation}} \rightarrow \text{Rh6-G}_{\text{OXidation}} + \text{light} (420 \text{ nm})$ (emitted signal)

$\text{Rh6-G}^*_{\text{oxidation}} + \text{Rh6-G} \rightarrow \text{Rh6-G}_{\text{OXidation}} + \text{Rh6-G}^*$

Rh6-G* → Rh6_G + light (wavelength 550 nm) (Chemiluminescence)

DPA (III)- H₂SO₄ CL System:

An economic, easy and sensitive flow injection method (FI-CL) were proposed for the determination of carbofrane in fresh water samples. The method were based on the reaction of diperiodatocuprate (III) (DPA) and sulfuric acid (H₂SO₄) coupled with Flow injection. All the experimental parameters were optimized for appropriate results. The obtained calibration curve was linear in the range of 0.001-8.00 mg L⁻¹ (n=11) following the RSD of 1.4-3.7 % (n=4). The lower limit of LODs was kept in the range of 5.00× 10⁻⁴ mg L⁻¹. The S/N =3. The sampling rate was kept 180 injection h⁻¹. The reagents used in the method were of analytical grade sulfuric acid (H₂SO₄), nitric acid (HNO₃), hydrochloric acid (HCl), DPA, potassium hydroxide (KOH), acetic acid, luminol and deionized water. This sensitive and rapid method was successfully applied for determination of carbofurane (CF). CF is carbamate insecticide exhibit a systematic mode of contact against wide range of insect [20]. (S.L chopra etal 1991). The acute toxic nature of CF for mammals can be recognized from its low oral LD₅₀ value for rat [21].

The method was successfully applied for the determination of concentration of carbofurane in water samples using solid phase extraction (SPE) with the recoveries of 94-110 % [22].

CL reaction of the followed method:

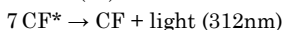
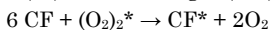
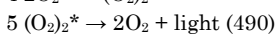
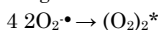
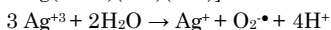
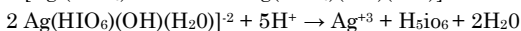
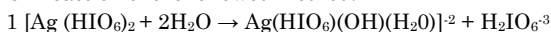


Table 2: Proposed FIA CL methods for different analytes in water samples.

S.No.	Analyte	Reagents	Calibration range (µg/L)	LOD (µg/L)	RSD (%)	Sample	Ref.
1	Thiram	Tris -DPA CL method	1.0-1000	100	1.3-2.6	water	11
2	aminocarb	Tris-DPA CL	1.0-10000	0.1	1.0-2.3	Fresh water	11
4	TBZ	Diperiodatocuprate -sulfuric acid cl system	2-242	0.7	1.1-2.9	Water	23
5	TBZ	Diperiodatocuprate -sulfuric acid cl system	8-120	2.8	1.1-2.9	Surface water	24
6	Cartep-HCl	KMnO ₄ -rhodamin -B CL system	0.05-1000	0.08	2.6	Irrigation water	13
7	Acetachlore	KMnO ₄ -rhodamin -B CL system	0.05-2000	0.75	2.4	Well water	13
8	Penamiphos	Cerum(IV) CL system	3.4-60	1	2.5	Environmental water	14
9	carbendazim	Luminol -hydrogen peroxide CL system	0.025-2.0	0.0074	1.8	Tap water	15
10	Fuberidazol	Copper-(Hydrogen peroxide II) CL system	0.025-2.0	0.003	1.3	Surface water	16
11	benomyl	Copper-(Hydrogen peroxide II) CL system	0.025-5.0	0.015	2.6	Natural water samples	16
12	carbendazim	Copper-(Hydrogen peroxide II) CL system	0.025-5.0	0.015	2.6	Surface water	16
13	MCPA	Photograded -ferriicyanide CL system	0.0015-0.6	5	0.5	Natural water	17
14	Thiram	Diperiodatoniccklete(IV) quinine CL system	0.5-2000	0.6	2.1	Natural water	22
15	Thiram	Diperiodatoniccklete(IV) quinine CL system	0.5-2000	0.5	1.9	Surface water	22
16	Thiram	Diperiodatoniccklete(IV) quinine	0.5-2000	0.5	3.2	Irrigation water	22

		CL system					
17	Thiram	Diperiodatoniclete(IV) quinine CL system	0.5-2000	0.5	3.7	Lake water	22
18	carbofurane	DPA(III)-H ₂ SO ₄ , CL	1-800	0.05	3.7	Tap water	18
19	carbofurane	DPA(III)-H ₂ SO ₄ , CL	1-800	0.05	1.4	Irrigation water	18
20	carbofurane	DPA(III)-H ₂ SO ₄ , CL	1-800	0.05	1.6	Lake water	18

CONCLUSION:

We have presented an up to date and considerable review article of flow injection chemiluminescence FI-CL determination of pesticides in surface drinking and irrigating water samples. Different precise, sensitive and rapid methods has been discussed that can come up with an alternativity in term of sensitivity, speed and simplicity. Moreover advancement is yet required to make it more improve the selectivity and reproducibility of these methods. the sensitivity and accuracies can further be enhanced by other powerful tools and techniques such as gas chromatography , high performance liquid chromatography etc. all these approaches has been widely used analytical research tools in analytical quantitative and quantitative findings of pesticides in various environmental samples which will bring more sensitivity in CL detection methods.

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