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# Photo-Induced Luminescence

Mónica Catalá-Icardo[a], José Martínez Calatayud[b]
[a] Department of Chemistry, Polytechnic University of Valencia, Valencia, Spain
[b] Department of Analytical Chemistry, University of Valencia, Valencia, Spain
Address correspondence to J. Martíınez Calatayud, Department of Analytical Chemistry, University of Valencia, Valencia, Spain. E-mail: jose.martinez@uv.es

## Abstract

The present paper is a critical review dealing with the characteristics, reaction mechanisms and photoproducts, instrumentation and analytical applications of the photo-induced either chemiluminescence or fluorescence. Special attention is paid to the determination of pesticides by continuous-flow methodologies. The paper is divided into several sections covering the most relevant published papers.

**Keywords:** Luminescence, fluorescence, chemiluminescence, pesticide analysis, continuous-flow methodologies, PIF, PICL.

## GENERAL INTRODUCTION

The intensive use of pesticides to protect crops, cattle and households has increased and is an increasingly serious environmental problem. In fact, the toxicity, persistence and bioaccumulability of pesticides can lead to poisoning in living beings; short-, mid- and long-term pollution of water and edaphic resources; and the presence of undesirable residues of toxic substances in foods.

Both legal restrictions in many countries and society at large are becoming increasingly demanding regarding the production of pesticides and control of the end-products, and also in relation to the impact of various human activities on the environment. The need to extend control activities on pesticides to their environmental metabolites has led to a growing demand for analyses of increasing sensitivity and selectivity. This need has been addressed by developing a vast number of new analytical procedures based on various methodologies that combine automatability, expeditiousness and cost-effectiveness with a high reproducibility, sensitivity and selectivity.

Chromatographies are highly sensitive and selective. However, the high simplicity, robustness, precision and economy of continuous-flow techniques—not all of which are nonseparation techniques as widely assumed by the analytical community—in addition to their high throughput and ready automation make them highly attractive alternatives. Such techniques include flow injection analysis (FIA), sequential injection analysis (SIA), multisyringe (MS) and multicommutation (MC). The selectivity and sensitivity required can in principle be achieved by using an appropriate detection technique. Photochemically induced fluorescence (PIF) or chemiluminescence (PICL) detection constitute two very promising choices in this respect; both involve irradiating an analyte with UV light in order to convert it into a photoproduct differing in luminescent properties from the partner substance. Usually, the target is a luminescent (fluorescent or chemiluminescent) product or one with enhanced luminescence if the starting substance already possesses any. In some cases,

however, the target is a photofragment exhibiting little or no fluorescence or chemiluminescence relative to the parent compound and the purpose to examine some inhibitory effect on its fluorescence or luminescence. In fact, a number of analytical procedures are based on total or partial inhibition of luminescence. However, the most interesting reported methods are those where the photoproduct exhibits substantially increased emission with respect to the starting substance.

This paper reviews recent advances and available knowledge of batch and continuous PIF-and PICL-based methodologies as applied to pesticide analysis. Also, it discusses PIF and PICL methods used in combination with continuous-flow techniques.

## MOLECULAR PHOTOCHEMISTRY AND PIF/PICL APPLICATIONS

The discussion that follows can be better understood by previously evoking some essential concepts. Thus, irradiating a molecule can break it into fragments of a smaller molecular weight (photolysis) or induce a photocyclization, photoisomerization and photooxidation or photoreduction reaction.

Pesticides usually undergo photolysis upon irradiation. This is a general natural mechanism for destroying a number of contaminants, among other substances. Photodegradation can occur in a direct or indirect manner. Direct photolysis involves the absorption of photons by the molecule to be transformed. On the other hand, indirect photolysis involves the absorption of energy from another molecule which has previously absorbed photons; the two steps are connected and constitute a first-order kinetic process. The rate of the photolysis reaction depends on the amount of energy required to break bonds, that of luminous energy supplied and the presence of appropriate intermediates. In nature, the amount of luminous energy available depends on depth and time (viz. time of day and day of year), as well as on the amount of particles present in the water column. The variables influencing the photolytic degradation of pesticides generally include light intensity, exposure time, location and, obviously, the chemical properties of the pesticide (1).

Turro (2) has defined molecular photochemistry as "a science concerned with the description of physical and chemical processes induced by the absorption of photons, in terms of a concrete mechanistic model based on molecular structures and their implied properties." Every photoprocess involves some excited electronic state which is usually reached by absorbing a photon. The electron distribution in a photochemically activated molecule is different from that in a thermally excited molecule as the photon provides excess energy. Also, light is a more selective activator than heat.

The outcome of the excitation varies as a function of the particular molecule and conditions. As a rule, a photoreaction involves the following three steps: (1) absorption of light to generate an electronically excited molecule; (2) photochemical processes involving the excited molecule; and (3) side processes involving the reaction intermediates produced in the previous step.

This review focuses on photoreactions involving a pesticide and yielding a molecule with luminescent properties that depart from those of the parent molecule (the analyte). Such luminescent properties can be PIF or PICL. The analytical techniques based on these two properties are highly sensitive and selective. However, the number of substances that can be determined in a direct manner from their fluorescence or chemiluminescence is relatively small. This has fostered the use of derivatization reactions in order to expand the body of substances that can be determined with

adequate sensitivity in this way. The methods that use light as described above are known as PIF and PICL methods.

In this context, light is an ideal reagent (3) for reasons such as the following:

(a) It has a minimal environmental impact as it minimizes or avoids the use of potentially toxic reagents and hence the release of hazardous waste.
(b) It avoids the need to dilute samples, which is unavoidable in using dissolved chemical reagents.
(c) The use of lamps with different spectral characteristics is equivalent to using reagents of variable nature and results in increased selectivity. In fact, light can induce
a variety of reactions including oxidation, reduction and hydrolysis.
(d) Very often, it expedites analysis times as photochemical reactions usually involve intermediate radicals and are thus fast.
(e) It allows reaction times to be shortened by altering the irradiation conditions (e.g. lamp power, reactor configuration). Lamp power (viz. irradiation intensity) can be compared to the concentration of a chemical reagent.
(f) A wide range of inexpensive lamps is commercially available.
(g) The typically high stability of the light source allows a high reproducibility to be achieved by carefully controlling the operating conditions.
(h) It usually affords operation at room temperature.
(i) It also affords on-line coupling to continuous-flow manifolds, thereby facilitating automation of the process and simplifying the analytical procedure by dispensing with the need for reagent propulsion and mixing systems (e.g. merging points, mixing chambers).

As a rule, a photochemical reaction can be analytically useful if the following requirements are met:

(a) The light used to induce the formation of the photoproduct is strongly absorbed by the analyte, but not by the products.
(b) The photochemical yield is high.
(c) The photoproducts obtained are stable for as along as needed to complete the analysis. This is rarely a problem with continuous-flow techniques as the manifolds are closed systems—and hence protected from the atmosphere—and the photoreaction can take place in the vicinity of the fluorimeter flow-cell or the point of merging with the reagent of the chemiluminescent reaction, so usually a few seconds of stability is long enough.
(d) The products are more structurally rigid or aromatic than the reactants, so an adequate fluorescence quantum yield—and the obtainment of a chemiluminescent product in some cases—is ensured.
(e) The photoreactor is appropriately designed in regards to building material and spatial configuration.


**Advantages of PIF and PICL, and of Their Joint Use With Continuous-Flow Techniques**

The theoretical aspects of PIF have been studied by several authors (4–6) who have shown that, if irradiating a non fluorescence or weekly fluorescence compound produces a single, strongly fluorescent photoproduct, then its fluorescence intensity is proportional to the initial analyte concentration.

However, if irradiation produces more than one photoproduct, the previous two quantities may not be linearly related. Although PICL has been studied to a lesser extent, it also exhibits a linear relationship over wide concentration ranges.

In addition to the advantages gained in using light as a reagent, PIF- and PICL-based methods provide the following (7):

(a) They expand the body of samples that can be detected with fluorescence- or chemiluminescence-based methods.
(b) They provide improved sensitivity and selectivity.
(c) They afford greater simplicity and shorter analysis times by effect of using light as a reagent.
(d) They dispense with the need to identify the photoproduct provided the luminescence signal is reproducible and proportional to the analyte concentration.
(e) They also dispense with the need to separate reaction products.
(f) They can be readily implemented in continuous-flow systems.

A number of batch and continuous-flow PIF- and PICL-based methods for determining pesticides are now available. In PIF-, based methods, the sample is usually held in a quartz cell that is placed at a given distance from the light source and supplied with the required reagents—if needed—after a preset irradiation time prior to transfer to the detector for measurement of the analytical signal. In PICL-based methods, the sample is readily irradiated on-line and subsequently merged with appropriate reagents prior to reaching the flow-cell, which is placed in front of the detector. Although some PIF-based methods for pesticides such as aromatics, chlorophenoxy acids, and sulphonylurea and phenylurea herbicides, are implemented in a stationary medium (8), the equivalent PICL methods are confronted with problems arising from the usually very fast kinetics of chemiluminescent reactions. Flow methods are especially attractive for this type of determination as they allow the irradiation time to be easily controlled and the resulting photoproducts measured. Because such products are often unstable, the use of flowmethods provides improved reproducibility; also, it substantially increases throughput and automatability, while minimizing reagent consumption (especially if an SIA or multicommutated system is used) (9).

**Instrumentation**

The only difference between classical fluorimeters or luminometers and those used in PIF or PICL determinations lies in the photoreactor. A number of customized reactors have been developed in the absence of appropriate commercially available choices. Such reactors comprise two essential elements, namely: the light source and the container holding the solution to be irradiated.

The irradiation source (a lamp) should be chosen in terms of power and spectrum. Lamps can emit light spanning a continuous or discrete spectrum. The former span a wide zone in the UVvis region. Especially prominent among them is the Xe-Hg arc lamp, which features a high power; however, it releases a large amount of heat, which requires the use of some refrigerating device. This lamp is usually employed when the photoreaction concerned requires a large amount of energy.

Discrete-spectrum lamps provide a series of individual spectral lines that span a narrow wavelength range. One typical example is the low-pressure Hg lamp, which emits over the range 200–320 nm and maximally (roughly 85% of all light) at 254 nm.

Also, it exhibits minor lines between 300 and 600 nm. The second strongest line is at 184.9 nm. This lamp is very useful in many cases as most compounds absorb in this spectral zone. Monochromatic lamps are usually avoided as they require frequent replacement, 95 are monochromators, which can reduce the light intensity by absorption and reflection. Rather, the most common choice is broad-spectrum lamps encompassing the most useful zone for excitation and bond breaking purposes.

Lamp power is also crucial as the kinetics and mechanism of a photoreaction depend on the intensity of the light impinging on the reactants. Xe-Hg arc and high-pressure Hg lamps are the most widely used among high-power light sources. As noted earlier, however, these lamps release much heat, so they are usually employed in batch methods; by contrast, continuous-flow methods usually employ low-pressure Hg lamps with a power of 2–80 W. This type of source exhibits an appropriate spectrum, releases little heat, is inexpensive and can be purchased in a variety of shapes, sizes and power levels. The material of the photoreactor should be transparent to the
UV light emitted by most lamps in use.

The preferred material for batch methods is quartz. Thus, a quartz cell placed at a fixed distance from the light source can be an appropriate sample container, as shown in the determination of various sulphonylurea herbicides (10) by using a high-pressure Hg lamp of 200 W to photolyse the analytes, which are held in a magnetically stirred quartz cuvette accommodated in an opaque box furnished with a fan and located 30 cm from the lamp.

The earliest photoreactors used in continuous-flow systems consisted of water-cooled medium- or high-pressure Hg lamps, or air-cooled Xe or Xe-Hg lamps, which were wrapped in a quartz capillary through which the analyte solution was circulated. This design ensures efficient irradiation of the sample thanks to the high transparency of quartz to UV light; however, it is difficult to handle owing to its fragility and difficult adaptation to the variable geometry of photoreactors and hence to continuous-flow systems. Also, it is expensive. Therefore, its use is restricted to high-pressure lamps with powers above 200 W. The earliest joint use of PIF and liquid chromatography in the determination of pesticides was for the photolysis and detection of chlorophenols (11) in water and biological fluids.

In 1980, Scholten et al. (12) proposed using Teflon (polytetrafluoroethylene, PTFE) as a substitute for quartz. Teflon is currently the most widely used material in this context. Although the amount of light passing through the polymer micropores is small, the light undergoes many reflections inside the capillary before escaping to the outside. This phenomenon is known as "tunneling". Teflon is particularly effective in the zone from 200 to 300 nm, especially when combined with a low-pressure Hg lamp. This material avoids the fragility problems of quartz, is more flexible and adaptable to variable geometries and can be purchased at a low cost in different sizes. In addition, it provides narrower, more symmetric peaks in HPLC and FIA. However, Teflon also has some disadvantages associated to its high oxygen permeability, which can have an adverse effect on sensitivity, and limited heat resistance—it releases substantial amounts of F$^-$ and H+ ions above 50ºC, which can alter the fluorescence of the target compound and its photoreaction pathway (13).

The earliest designs consisted of a cooled high-pressure lamp accommodated in a quartz tube around which a Teflon tube was wrapped. Subsequent designs used no quartz tube, the PTFE tube being directly wrapped around the low-pressure lamp and placed in front of the light source; alternatively, a knotted open tubular mesh was used to reduce dispersion. Engelhardt and Neue (14) reported a more complex configuration where the Teflon tube was used to form a figure of four or six sides in order to increase

the exposed area. In any case, a Teflon tube wrapped around the lamp continues to be the preferred choice for most work of this kind.

In summary, low-pressure Hg lamps are useful in most PIF and PICL-based pesticide determinations and afford the use of simple, convenient reactors as they cause virtually no temperature changes and avoid adverse effects on Teflon as a result. Their most common use in continuous-flow methods is with the Teflon tube helically coiled around them and a piece of aluminium foil intended to maximize lighting.


## Variables Affecting the Photoreaction and PIF/PICL

The photochemical reaction is primarily affected by the following factors:
(a) Lamp spectrum;
(b) Irradiation time;
(c) Irradiation intensity (viz. lamp power and distance to the irradiated solution);
(d) The constituent material of the photoreactor and its configuration; and
(e) Properties of the medium containing the analyte (viz. acidity, polarity, temperature).

The lamp emission spectrum can affect the detection selectivity as, ultimately, the emission spectrum of the lamp will overlap with the absorption spectrum of the analyte, as confirmed by replacing the usual Hg lamp with a Cd or Zn lamp (15).

As a rule, the emission intensity, whether PIF or PICL, increases with increasing irradiation time up to a maximum corresponding to the optimum value, beyond which the trend is reversed. The first step produces the fluorescent or chemiluminescent photoproduct, which is degraded to non-fluorescent or non-chemiluminescent products in the second (16, 17). Some substances, however, depart from this behavior. Thus, the fluorescence of the insecticides fenvalerate and diflubenzuron (16) increases in a sustained manner with increasing irradiation time and exhibits no well defined maximum. This can be ascribed to the photolysis reaction taking place in a single step where the fluorescent products form slowly. Chlorpyriphos in the presence of β-cyclodextrine exhibits yet another behavior (18); thus, its PIF signal initially rises and then levels off. This suggests that an equilibrium between the pesticide photoproduct — which has been identified as dechlorinated chlorphyriphos by GC-MS— and its degradation product(s) is reached.

Unless the flow is stopped during irradiation, strict control of the irradiation time in continuous-flow systems can be accomplished by adjusting the reactor length and flow-rate. These variables additionally affect dispersion and result in broadened bands or peaks, thereby decreasing resolution in chromatographic systems and throughput in FIA—and also potentially degrading detection limits with both types of techniques. Gandelman and Birks (19) studied the relationship between irradiation time and dispersion in HPLC systems with post-column detection and concluded that long tubes of a small diameter were the best choice; however, the tubing most commonly used in this context is 0.2–2.0 mm in inner diameter as it is the most inexpensive and convenient to use.

Whenever a long irradiation time (more than 1 minute) is required, dispersion can be reduced by using a segmented-flow system. To this end, air bubbles or portions of an immiscible liquid are inserted into the system in order to fragment the eluent stream and then removed after irradiation but before they reach the detector. One other

approach involves stopping the flowing during irradiation in order to ensure near-zero dispersion
(20). This is especially convenient when using solenoid valves in multicommutated systems (9).

About the constituent material of the photoreactor and its configuration it has been noted in the above paragraphs the fragility of quartz and the operator's inability to alter the tube size and arrangement at will led Scholten to propose Teflon as a replacement material for the capillaries based on its efficiency as a photoreactor material. Teflon tubes are commercially available in variable diameters, wall thicknesses and pore sizes, and are quite inexpensive. These advantages have led to Teflon gradually replacing quartz since 1983, when Lang developed the first Teflon-based photoreactor. As reported, disadvantages of Teflon is that it releases substantial amounts of $F^-$ and $H^+$ ions being the released amount of $F^-$ released a function of the analyte residence time in the capillary and can be large enough to raise the background signal and alter the luminescence signal of the analyte. The effect of temperature can be lessened and construction of the experimental assembly simplified by using low-pressure Hg lamps, which have generated a large amount of analytical literature (21–26).

The properties of the photoreaction medium can be highly influential as they affect the stability of excited electronic states. The medium of choice in each case will be that resulting in the strongest possible signal with the shortest possible irradiation time.

The polarity of the reaction medium and its protic or nonprotic nature are two potentially influential variables. Thus, the PIF signals for deltamethrin and diflubenzuron are higher in protic solvents than in acetonitrile; on the other hand, the emission signals for fenitrothion and fenvalerate are higher in acetonitrile or dimethyl sulphoxide than they are in protic solvents (16). Also, pyrethroid herbicides (27) exhibit stronger PIF signals in protic solvents such as binary mixtures of water and organic solvents (e.g. methanol, ethanol, acetonitrile).

Aarón and Coly (8, 18) have shown that the use of micellar media or cyclodextrine solutions often increases the sensitivity and selectivity while reducing the need for organic solvents. Thus, cetyltrimethylammonium chloride (CTAC) increases the PIF signal for the herbicide 2,4-dichlorophenoxyacetic acid in water by a factor of 30.9(26). The signal rises with increasing CTAC concentration up to a roughly constant level above the critical micelle concentration (cmc) of the surfactant. This suggests that the photoreaction can take place within the micelles and that these prevent deactivation of the singlet excited state(s) of the photoproduct(s). Usually, the PIF signal increases as the cmc is approached. The outcome is "micellar-enhanced photochemically induced fluorescence" (MEPIF). Pyrethroid insecticides (28) also exhibit enhanced PIF signals in the presence of a cationic surfactant such as CTAC or an anionic one such as sodium dodecylsulphate (SDS), and so do sulphonylurea herbicides (10). The effect of cyclodextrines (CDs) (18, 29) varies among individual members of this chemical family. The absorption spectrum is usually altered by the presence of a CD; usually,
the outcome is increased UV-Vis absorption and a bathochromic shift. Similar changes can be induced in the emission spectrum (18). The effect of cyclodextrines has been ascribed to various factors (30) including increased radiative rate constants, decreased numbers of degrees of freedom and molecular motion, reduced collisional deactivation, increased availability of a micro-environment of favorable polarity and viscosity, and effective protection of the excited singlets of water, oxygen or other species present in solution. Thus, molecules containing OH or NH groups are quenched by water

molecules and CD chelation efficiently reduces exposure to water. Usually, CDs not only enhance PIF signals, but also alter the kinetics of the photolysis reaction, which requires a longer irradiation time as a result.

The content in dissolved oxygen can be a major influential variable as the paramagnetic nature of oxygen increases the quenching effect on the emission intensity. Also, the presence or absence of oxygen has been found to affect both the type of photolysis reaction undergone by some pesticides and the nature of the products it yields (31).

And last but not least, temperature rises due to the lamp pose an arduous problem in practice as they cause the formation of gas bubbles which can alter the flow-rate and lead to spurious signals, thereby seriously detracting from reproducibility (32).


## Reaction Mechanisms and Photoproducts

Although the PIF or PICL analytical determination of pesticides does not require a knowledge of the mechanism behind the photoreaction or the nature of the resulting products, such a knowledge can be very useful—and not only for academic purposes. A number of studies have focused on the use of light as a tool for removing or degrading pesticides in water and soil, whether in the natural environment or at processing plants. However, one should always bear in mind that both the reaction mechanism and the products can differ depending on the light wavelength and intensity used, as well as on the presence of certain species in solution.

Basically, the reactions triggered by light can be of the following five types: photolysis, photocyclization, photoisomerization, photooxidation and photoreduction. Photolysis reactions are no doubt the most common among pesticides.

For a direct photoreaction to occur, the emission spectrum of the lamp used should overlap with the absorption spectrum of the analyte, which absorbs light to form an unstable substance that subsequently undergoes some transformation.

These reactions are important in the environment when the UV spectrum for the target compound does not overlap with that of the light source. The unselective hydroxyl radical, OH, has proved the agent restricting the persistence of many compounds that are slowly degraded by direct photolysis. This photo-oxidant is produced at concentrations from $10^{-18}$ to $10^{-14}$ mol/l by photolysis of nitrate ion and some organic substances commonly present in surface waters. In indirect photolysis processes, another substance present in solution absorbs light that is then transferred to the pesticide, or some reactive species such as hydroxyl radicals are formed that subsequently react with the pesticide (33). Such species, which can be either organic or inorganic in nature, accelerate the process. Thus, nitrites and some calcium and magnesium chelates produce hydroxyl radicals upon irradiation (34); also, some $Fe^{3+}$ and $Cu^{2+}$ complexes catalyze the photoreaction.

The PIF-based determination of organophosphorus compounds (16) with a low-pressure Hg lamp involves the photolysis of the pesticide to orthophosphate in the presence of peroxydisulphate, possibly as a result of the presence of hydroxyl radicals resulting from the photolysis of the peroxydisulphate (35), in accordance with the following reaction scheme:

$$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^-$$

$$SO_4^- + H_2O \Rightarrow OH + SO_4^{2-} + H^+$$
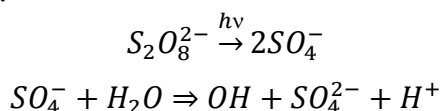
Subsequently, the orthophosphate produced reacts with molybdate to form molybdophosphoric acid, which in turn reacts with thiamine to give the fluorescent thiochrome. This methodology has been used to determine methamodophos (36) and malathion (37), and also arsanilic acid (38) and dimethylarsinic acid (39). In the presence of peroxydisulphate, the latter two are oxidized to As (V); this reacts with molybdate to form arsenomolybdic acid, which can oxidize thiamine to thiochrome.

Other species that are also effective photocatalysts for the degradation of pesticides (40) on account of their ability to form hydroxyl radicals subsequently reacting with pesticide molecules include NaOH and $Fe(II)/H_2O_2$, which are used in the photo-Fenton reaction (41, 42), and Fe(II) aqua complexes, which have been employed in the PICL-based determination of aldicarb with a low-pressure Hg lamp of 20W(21), among others. Iron (III) aquo-complexes act as highly effective catalysts in the photodegradation and mineralization of asulam (22) in water under natural or artificial light (43). The process is directed by hydroxyl radicals produced by excitation of $Fe(OH)^{2+}$. Once all Fe (III) has been reduced to Fe (II), asulam continues to be degraded in the presence of oxygen; however, the herbicide requires the continuous presence of Fe (III), Fe (II) and molecular oxygen to be completely mineralized.

Titanium dioxide has been proposed for decomposing a number of organochlorine and organophosphorus compounds in addition to triazine, thiocarbamate and various carbamates including asulam (43) in water purification processes. In fact, $TiO_2$ is used in many continuous-flow analytical procedures.

The organic compounds affording the indirect photolysis of pesticides include fulvic acids and humic acid, which absorb light from a triplet state and transfer it to the analyte (44), and also acetone (45).

In fact, acetone is a strong sensitizer for the photoreaction of carbaryl to methylamine (45). Of all hypotheses put forward to explain the phenomenon, the most plausible is that ascribing the sensitizing effect of acetone to a triplet state. The photochemical reaction starts with the absorption of light by acetone, which produces a triplet state, and is followed by a triplet-triplet energy transfer. Based on this principle, carbaryl was determined via its PICL. Interestingly, the reagent used to generate the chemiluminescence was obtained by photoreaction. Thus, tris (2, 2N-bipyridine)ruthenium (II) $[Ru(bpy)_3^{2+}]$ was photooxidized to tris(2,2N-bipyridine) ruthenium (III) $[Ru(bpy)_3^{3+}]$ and this was reduced to $[Ru(bpy)_3^{2+}]^*$ (i.e., an excited state), which emitted light upon falling to the ground electronic state, by reaction with the analyte. A similar approach was used to determine carbofuran and promecarb (46) and could in theory be applied to any N-methylcarbamate. Carbamoyl oxime, dithiocarbamate, phenylurea and carbamothioic acid pesticides can also be determined in this way as the alkylamines they produce upon irradiation can generate fluorescence with o-Phthaldehyde (OPA) (47).

Once methylamine has been obtained by irradiation as described above, its derivatization with OPA produces a fluorescent compound that takes part as an energy acceptor fluorophore in the peroxyoxalate chemiluminescent system (48). An irradiation time of 25 seconds ensures near 100% photolytic efficiency. Anthraquinone (49) has been used as a sensitizer in the production of PIF from four dinitraniline herbicides. The mechanism behind the photosensitizing effect of this aromatic ketone is similar to that described above for acetone.

Other substances have also been used as sensitizers in this context. Thus, riboflavin, Rodamine Band Methylene Blue have been proposed for the photodecomposition of ethylenethiourea (32). Acetone/acetonitrile mixtures and Triton

X-100 solutions have been used in the photodegradation of dinoseb and trifluralin (32). Also, ethanol has been used to sensitize the PICL signal of bromoxynil (23).

As noted earlier, the use of light sources can be combined with that of other chemical species which can act as:

(a) Reagents proper;

(b) Sensitizers capable of yielding a photochemically active compound by reaction with a non-photoactive analyte; and

(c) Catalysts for the photochemical process.

The use of photolysis reactions to obtain amine groups has expanded the range of substances that can be detected by reaction with o-phthaldialdehyde-2-mercaptoethanol (OPA/2-ME). Moye et al. (11, 47, 50, 51) have used this approach to determine a number of nitrogen-containing pesticides including triazines, dinitrophenols, amides, acetamides, carbamates, carbamoyloximes, carbamothioic acids, dithiocarbamates, sulphonylureas, thioureas, organophosphorus compounds and bipyridiniums. The use of a surfactant as a photosensitizer for this reaction increases the PIF signal in many cases (9).

The principal reactions induced by irradiation include dehalogenation, hydroxylation, dealkylation, deamination and molecular fragmentation. The resulting photoproducts are usually mixtures of various compounds, which prevail depending on operating conditions such as irradiation time, lamp type and photoreaction medium.

According to García-Campaña et al. (26), the absence of native fluorescence in pesticides containing chloride or some other halogen (e.g. chlorophenoxyacid herbicides) may be partly due to an intramolecular effect of the heavy atom (the halogen), which raises the intersystem crossing probability from an excited singlet state to a triplet state. The fact that irradiation with UV light increases the fluorescence suggests the potential loss of the halogen in the resulting photoproduct. Photolysis of the side chain in phenoxyacids can also produce phenol derivatives, the photoproducts probably consisting of a mixture of chlorinated phenols, dihydroxylated compounds and phenol.

As a rule, halogen-containing aromatic pesticides can lose their halogen atom (52). Thus, phenylurea pesticides undergo dechlorination by effect of sunlight or light of wavelength above 290 nm; this is the primary degradation mechanism for pesticides such as diuron (53), linuron (54), buturon and monolinuron (55). The other photodegradation products include OH, CHO and H derivatives. Some authors (29) have found one of the photoproducts formed by fragmentation of the parent molecule in the photolysis of phenylureas by irradiation with a high-pressure Hg lamp of 200 W to be methylamine or dimethylamine. Aniline and substituted anilines are also probably formed as their fluorescence spectra are similar to those of phenylurea photoproducts. Other studies (56) have revealed the formation of halogenated biphenyls upon irradiation of monuron, diuron, linuron, metobromuron or propanil with sunlight or a UV lamp.

Irradiating the phenoxyacids 2,4,5-T and 2,4-DT (57) with a xenon lamp produces chlorophenols, hydroxylated derivatives such as 2-hydroxy-4,5-dichlorophenoxyacetic acid, anisoles, phenols and chlorophenols. On the other hand, phenylureas can lose chloride atoms and form biphenyls and dehydroxylated products (57).

Chlorotriazine atrazine (58) gives hydroxyazine as the main product of its photodegradation by sunlight; however, additional products including 2H,2H-deisopropylhydroxyatrazine and 2-methoxydeisopropyl analogues have been detected in

solution when using $TiO_2$ as a photocatalyst for the reaction. On the other hand, atrazine (53) gives hydroxyatrazine when irradiated with light of wavelength greater than 290 nm.

Organophosphorus compounds (59) produce oxo derivatives and various phenols under both natural and UV light. Also, irradiation of a solution in fenitrothion in distilled water with a high-pressure Hg lamp causes the formation of fenitrooxon (60).

The carbamate group in N-methylcarbamates is rarely affected by irradiation with UV light; by exception, carbaryl gives 1-naphthol under these conditions. (61, 62) The fluorescence produced by sulphonylurea herbicides (10) under the influence of UV light from a high-pressure Hg lamp of 200 W is very likely due to an arylsulphonamide fragment.

Light induces the photoreduction of dinitraniline herbicides (49), which exhibit PIF.

Irradiating a solution of the herbicide propanil containing $O_2$ and $TiO_2$ as photocatalysts with 290 nm light from a Xe lamp gives various organic intermediates and inorganic end-products (63).

According to several authors (64–66), the photolysis of the nitrile herbicide bromoxynil in a phosphate buffer at pH 7 after 10 minutes of irradiation with a low-pressure Hg lamp produces hydroxylated compounds such as 3,4-dihydroxy-5-bromobenzonitrile and 3,4,5-trihydroxybenzonitrile in addition to hydrogenated compounds such as 3,4-dihydroxybenzonitrile and 4-hydroxybenzonitrile, which result from substitution of a bromine atom by an OH group and a proton, respectively, and have been identified by GC-MS (64).


**Resolution of Mixtures**

PIF has also been used in combination with various methodologies in order to resolve binary mixtures of pesticides. Thus, mixtures of chlorophenoxyacids such as that of mecoprop and 2,4-dichlorophenoxyacetic acid (67) in a micellar medium was resolved by using multivariate calibration (viz. the partial least-squares algorithm PLS-1). Also, a time-resolved photoactivation method was developed in order to resolve the same herbicide mixture and two other binary mixtures of pesticides from the same family (68) from differences in photodegradation kinetics between the mixture components; this entailed using a different irradiation time to obtain the optimum MEPIF for each compound. Properly resolving the mixtures therefore required constructing calibration curves at different irradiation times.

Binary mixtures of four sulphonylurea herbicides were resolved by using the first derivative of their PIF spectra, using the zero-crossing technique (69).

The method of standard additions has proved useful in the resolution of binary mixtures of fenitrothion and fenvalerate in synthetic samples (16).


**ANALYTICAL USES OF CONTINUOUS-FLOW METHODOLOGY FOR THE DETERMINATION OF PESTICIDES**

The earliest FIA-PIF determination of pesticides was reported by Aaron et al. (70, 71) in 1996 and involved fenitrothion, fenvalerate and diflubenzuron.

The applications discussed in this section are summarized in two tables for chemiluminescence and fluorescence based methods, respectively. As can be seen from both tables, the number of such methods is quite small, especially in relation to other analytical fields. Thus, the number of chemiluminescence based determinations of drugs with continuous-flow methods reported over the past five years amounts to nearly 300. Therefore, the potential of such methodologies for determining pesticides remains largely unexplored. Thus, as can be seen from Table 1, there are only 15 references to PICL-based methods for this purpose; only 13 if those concerned with the same pesticide are excluded. Also, unsegmented continuous-flow methods have only recently gained widespread acceptance. PIF-based methods are somewhat more common, albeit only in absolute terms; in fact, if one considers the massive use of fluorimetry for the analysis of organic products ever since its inception in the early 1950s, the spread of PIF methods has been no more extensive than that of PICL methods.

The advantages of flow methods (e.g. increased reproducibility, simplicity, economy, expeditiousness and automatability) are enhanced by those of photodegradation methodologies, which are described at length above. This leads to the obvious conclusion that an enormous effort remains to be done on the part of analysts to fully exploit a strategy of already proven advantages.

As can also be seen from Tables 1 and 2, FIA applications prevail over all others. In fact, only in recent years have uses of an emerging methodology such as multicommutation been reported. Also worth noting is the absence of applications of SIA despite its substantial degree of development. Other continuous flow methodologies such as multisyringe FIA have not been used in this context either.

The number of fluorescence- and chemiluminescence-based determinations conducted by FIA and other flow methods is enormous. Few methods, however, use on-line photodegradation as an advantageous auxiliary tool in such determinations. Based on molecular topology computations which have been confirmed by experimental means (viz. screening tests), a vast number of potential applications in this context remain unexplored.

Topology is a branch of mathematical analysis which correlates the positions and connections between different elements in a set. When applied to chemical structures, it can identify the positions and connections between atoms (elements) in a molecule (set). This is known as molecular topology and can used to characterize a molecule in a unique way via preset indices based on its structure, number of atoms and their connections, among other factors. Each molecule is thus depicted as a graph where its atoms are plotted as points (vertices) and their connecting bonds as lines (edges between vertices). Such graphs can be expressed in numerical form via matrices containing one or several topological descriptors. An appropriate selection of such descriptors can provide a unique description of the structure of the molecule and hence of many of its physical, chemical or biological properties.

The application of molecular topology to a group of compounds with a specific property (positives group) provides a topological profile where molecules lacking such a property do fit (negatives group). This allows one to anticipate whether a given compound will possess the property in question.

The earliest attempt in this context was the prediction of chemiluminescence production upon direct oxidation of organic compounds (pesticides and drugs) by inorganic species, which was accurate in 92.7% of cases (72) and later on successfully extended to polyphenols (73), ergot alkaloids (74) and other substances. Current research in this field is focusing on the prediction of PICL (75) and both native and photo-induced fluorescence.

The selectivity of these processes must be increased in order to simplify procedures and avoid the need for complicated separations by HPLC, GC or capillary electrophoresis. This can be accomplished in various ways including the development of less general photodegradation methods or more selective chemiluminescent reactions involving chelating agents. While such methods become available, the only effective alternative is to use flow manifolds affording the use of post-column devices or the integration of mini-solid-liquid columns for on-line separation.

Regarding chemical analytical methods, the needs echo those in other fields such as chemiluminescence induction without photodegradation or direct oxidation of the analyte with a strong oxidant—where potassium permanganate in a strongly acidic medium is the most common choice. The advantages are obvious as the oxidant itself produces the chemiluminescence emission. Systems based on the oxidation of Ru (II) to Ru (III) have become fairly common in this context in recent years. The ensuing determinations are also of the direct chemiluminescence product type as Ru (III) is the oxidant for the analyte; such a species, which is probably the most selective oxidant, can be obtained by oxidizing Ru (II) to Ru (III) with an auxiliary oxidant such as Ce (IV), ferricyanide or permanganate ion.

Derivatization of the analyte in fluorescence-based methods is usually affected by the light source itself. Rarely is the help of another chemical (oxidant) other than a surfactant needed, which testifies to the cleanliness of light as an "analytical reagent". In fact, the reaction medium only requires pH adjustment, the addition of a surfactant in order to protect excited species from interactions with their environment or the use of an organic solvent to adjust the polarity at most.

As noted earlier, one way of obtaining a high selectivity is by using post-column devices, which are commonplace in flow assemblies. Thus, in recent work, phosphates and two organophosphorus pesticides (viz. methamidophos and acephate) were determined following HPLC separation, which was connected to a flow manifold delivering the reagent (peroxydisulphate) needed to photodegrade the analytes by irradiation with a low-pressure Hg lamp. Orthophosphate ion thus formed reacted with molybdate ion to form phosphomolybdic acid, which then reacted with thiamine to form the fluorescent product (thiochrome). This analytical procedure can be improved by using a multicommutated system.

Reproducibility in these determinations is usually good, as expected from flow methods, and so is throughput. Regarding sensitivity, the comments made above in relation to chemiluminescence-based determinations also apply here. In fact, the most salient feature is the analytical and environmental gains in integrating on-line photodegradation with the new continuous-flow analytical methodologies.

Finally, it should be noted that reported methods have largely been applied to water samples and also, to a much lesser extent, to biological fluids and soil.


## TRENDS AND CONCLUSIONS

Both fluorescence- and chemiluminescence-based methods are deemed unselective (especially when the analyte is contained in a complex matrix such as an environmental or physiological sample). In fact, some methods of both types, but particularly those based on PICL, are highly selective and require no preliminary separation. In any case, incorporating a separation device such as a mini-column packed with an ion-exchange resin (to remove interferents) or a sorbent (to retain the analyte for subsequent elution) on-line into a flow manifold without appreciably altering its

throughput is a relatively easy task. Also, a procedure optimized for a specific pesticide can be readily adapted for implementation on a post-column system (particularly one of the multicommutated type) without the need to physically alter the original assembly.

This review reveals a strong preference of researchers for flow methods over classical batch alternatives. This is logical if one considers the increased throughput, automatability and cost effectiveness, and decreased sample consumption of samples and reagents of the former.

Applications have focused on the parent pesticides rather than their environmental degradation products (photodegradation products in many cases) which are comparably hazardous. Also, most analyses have been performed on water samples.

Finally, we should emphasize the analytical significance of being able to predict in theoretical terms the behavior of a given analyte in a specific analytical process. This can help reduce the need for screening tests and increase the reliability of these trial-and-error procedures. The ability to obtain solid predictions is real; in fact, the earliest attempts at introducing predictive mathematical functions in analytical chemistry involved chemiluminescence-based methods.

The selectivity of both PIF and PICL processes should be improved in order to simplify existing methods and avoid cumbersome separations by HPLC, GC or capillary electrophoresis. This can be accomplished by developing less general photodegradation methods or boosting the selectivity of chemiluminescent reactions by using chelating agents, among others. The only choice at hand while such alternatives are realized is using manifolds affording post-column separation or the on-line integration of specific mini-solid-liquid separation columns for specific purposes.

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**Table 1.** Photo-induced chemiluminescence flow analysis.

| Analyte | Flow method | Medium and reagents for the photodegradation | Oxidation system | Photodegradation interval | LOD (µg/l) | Sample throughput ( $h^{-1}$ ) (R.S.D.) | Sample type | References |
|---|---|---|---|---|---|---|---|---|
| Carbofuran, promecarb | FIA | Phosphate buffer pH 6.5 | tris(2,2´-bipyridine) ruthenium(II)/ peroxydisulphate | 85 s | 53 85 | 200 (1.6%) | Water, soil, corn | 46 |
| Carbaryl | FIA | Phosphate buffer pH 6.5 | tris(2,2´-bipyridine) ruthenium(II)/ peroxydisulphate | 85 s | 12 | 200 (1.2%) | Water, soil, corn, serum | 45 |
| Carbaryl | FIA | Imidazol/SDS | bis(2,4,6 trichlorophenyloxalate)/ ophtaldehide/$H_2O_2$ | 25 s | 31 | 114 (2.8%) | Water, plants | 48 |
| Asulam | Multicommutation | Glycine buffer pH 8.3 | $KMnO_4/H_2SO_4$ | 90 s | 40 | 30 (4.1%) | Water | 22 |
| Aldicarb | Multicommutation | Fe (III)/quinine | $KMnO_4/H_2SO_4$ | 150 s | 0.069 | 17 (3.7%) | Water, formulations | 21 |
| Chlorsulfuron | Multicommutation | Glycine buffer pH 9.5 | $KMnO_4/H_2SO_4$ | 100 s | 60 | 25 (3.8%) | Water | 24 |
| Propanil | Multicommutation | Acetic/acetate buffer pH 5 | $KMnO_4/H_2SO_4$ | 120 s | 8.5 | 20 (2.9%) | Water, formulations | 17 |
| Alachlor | Multicommutation | Acetic/acetate buffer pH 5 | $KMnO_4/H_2SO_4$ | 120 s | 41 | 20 (2.8%) | Water | 17 |
| Flumetsulam | Multicommutation | Acetic/acetate buffer pH 5 | $KMnO_4/H_2SO_4$ | 120 s | 25 | 20 (1.9%) | Water | 17 |
| Furalaxyl | Multicommutation | Acetic/acetate buffer pH 5 | $KMnO_4/H_2SO_4$ | 120 s | 34 | 20 (3.4%) | Water | 17 |
| Ofurace | Multicommutation | Acetic/acetate buffer pH 5 | $KMnO_4/H_2SO_4$ | 120 s | 58 | 20 (2.3%) | Water | 17 |
| Bromoxynil | FIA | KOH/ethanol | $KMnO_4$/plyphosphoric acid | 12 s | 5 | 134 (2.3%) | Water, formulations | 23 |
| Ferbam | FIA | $Fe^{3+}$ | Oxalate | 1.5 min | 200 | 45 (1.23%) | Water, corn | 76 |
| Paraoxon | FIA | Luminol/Peroxidase | Coline oxidase/ $H_2O_2$ | 60 min | 0.75 | 1 (3.7%) | Soil, plants | 77 |
| Aldicarb | FIA | Luminol/Peroxidase | Coline oxidase/ $H_2O_2$ | 60 min | 4 | 1 (3.7%) | Soil, plants | 77 |

**Table 2.** Photo-induced fluorescence flow analysis.

| Analyte | Flow method | Medium and reagents for the photo-degradation | $\lambda_{exc}$ (nm) | $\lambda_{em}$ (nm) | Photo-degradation interval | LOD ($\mu$g/l) | Sample throughput ( $h^{-1}$) (R.S.D.) | Sample type | References |
|---|---|---|---|---|---|---|---|---|---|
| Fenitrothion | FIA | Water | 366 | 422 | 50 s | 3 | 61 (2.5%) | Water, formulations | 71 |
| Fenvalerate | FIA | Acetonitrile | 293 | 333 | 95 s | 10 | 61 (1.4%) | Water, formulations | 71 |
| Deltamethrin | FIA | Ethanol | 291 | 317 | 95 s | 18 | 61 (3.2%) | Water, formulations | 71 |
| Diflubenzuron | FIA | 2-Propanol | 343 | 407 | 90 s | 19 | 61 (4.7%) | Water, formulations | 71 |
| Sumicombi | FIA | Methanol | 295 | 338 | 95 s | 4 | 61 (3.6 %) | Water, formulations | 71 |
| MCPA | FIA | Methanol/pH 5 | | | 90 s | 26 | | Water | 70 |
| Mecoprop | FIA | Methanol/pH 5 | | | 90 s | 23 | | Water | 70 |
| MCPB | FIA | Methanol/pH 5 | | | 90 s | 30 | | Water | 70 |
| 2,4-D | FIA | Methanol/pH 5 | | | 720 s | 98 | | Water | 70 |
| 2,4-DP | FIA | Methanol/pH 5 | | | 600 s | 82 | | Water | 70 |
| Fenvalerate | FIA | SDS | 277 | 329 | 60 s | 210 | 30 | Water | 78 |
| Chlorsulfuron | FIA | CTAC/NaOH | 314 | 380 | 150 s | 0.2 | 56 (1.5%) | Water | 25 |
| Metsulfuron-methyl | FIA | SDS/NaOH | 322 | 378 | 60 s | 0.1 | 80 (3.7%) | Water | 25 |
| 3-Rimsulfuron | FIA | CTAC pH 7 | 317 | 365 | 150 s | 0.1 | 56 (1.8%) | Water | 25 |
| Sulfometuron-methyl | FIA | CTAC pH 9 | 290 | 341 | 150 s | 0.1 | 56 (2.4%) | Water | 25 |
| Mecoprop | FIA | CTAC | 270 | 298 | 10 min | 33.5 | - (3.7%) | Water | 26 |
| 2,4-D | FIA | CTAC | 270 | 298 | 15 min | 73.2 | - (3.1%) | Water | 26 |
| Imidacloprid | FIA | pH 11.8 | 334 | 377 | 30 s | 0.3 | 60 (2.1%) | Water | 79 |
| Linuron | FIA | SDS pH 7 | - | - | 4 min | 330 | (11%) | Water | 29 |
| Diuron | FIA | SDS pH 7 | - | - | 8 min | 920 | (1.3%) | Water | 29 |
| Isoproturon | FIA | CTAC pH 7 | - | - | 6 min | 450 | (1.4%) | Water | 29 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Isoproturon | FIA | CTAC pH 7 | - | - | 12 min | 740 | (3.4%) | Water | 29 |
| Methamidophos | FIA | Peroxydisulphate/ molibdato/ HNO$_3$/tiamina | 375 | 440 | 11 s | 1.7 | 70 (3.0%) | Water, plants | 36 |
| Dimethylarsinic acid | FIA | Peroxydisulphate/ molibdato/ HNO$_3$/tiamina | 375 | 440 | 20 s | 14 | 60 (0.5%) | Water, plants | 39 |
| Mecoprop | FIA | CTAC pH 3 | 270 | 298 | - | 73.2 | 10 (3.1%) | - | 80 |
| 2,4-D | FIA | CTAC pH 3 | 270 | 298 | - | 33.5 | 10 (3.7%) | - | 80 |
| Malathion | FIA | Peroxydisulphate/ molibdate/ HNO$_3$/tiamina | 375 | 440 | - | - | 70 | Water, corn, plants | 37 |
| Arsanilic acid | FIA | Peroxydisulphate/ molibdate/ HNO$_3$/tiamina | 375 | 440 | 20 s | 10 | 55 (1.3%) | Water, animal food | 38 |