**Supplementary information**

**A comprehensive review of liquid chromatography hyphenated to post-column photoinduced fluorescence detection system for determination of analytes**

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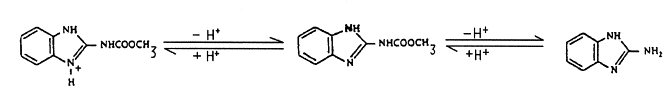
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**Figure S1** carbendazim photo-dissociation behavior in alkaline and acidic pH.

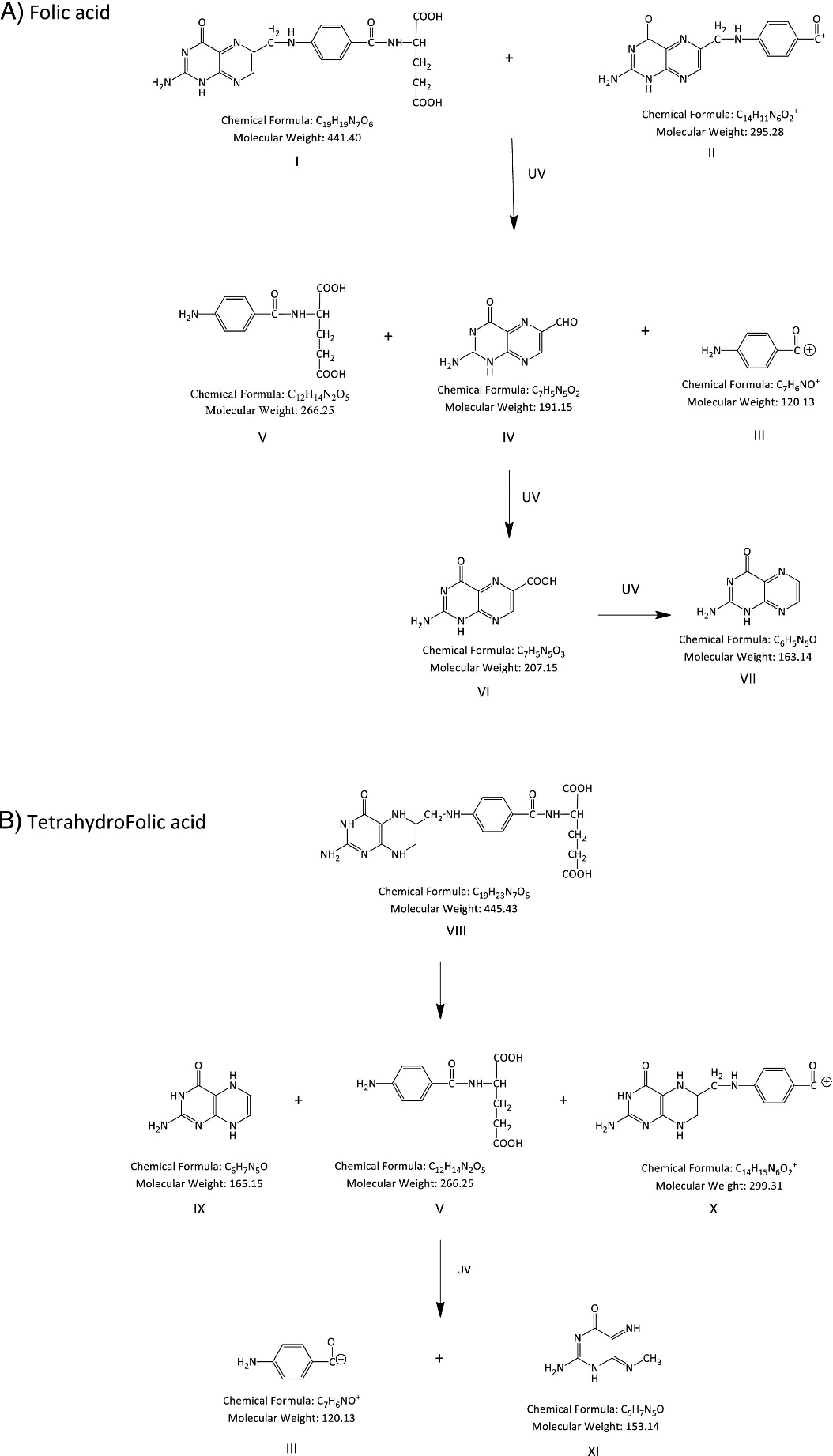
**Table S1** Comparison between pre-column and post-column photo derivatization techniques.

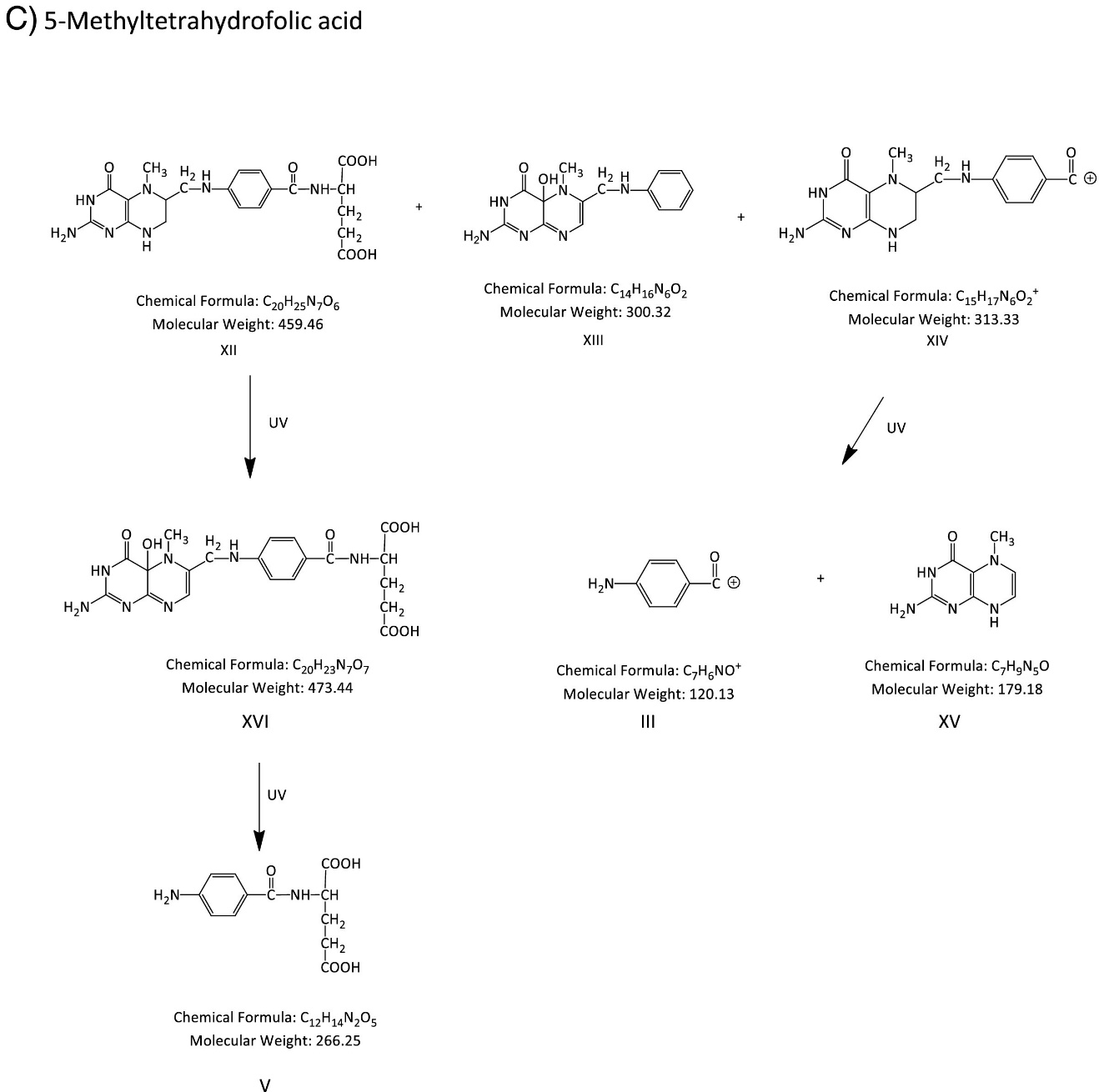
|  |  |  |
| --- | --- | --- |
| **Pre-column derivatization** | **Post-column derivatization** | **Ref.** |
| Analytes aren’t separated in their original form, and separation condition need to optimize considering each analytes and their photoproducts. | Analytes are separated in their original form, which allow to adopt the optimized and published separation conditions. | ([Brinkman 198](#_ENREF_3" \o "Brinkman, 1987 #4)7)**Error! Hyperlink reference not valid.** |
| Derivatization might be complete, but derivatives limited time stability, and generation of interfering species from target analytes can cause various quantification problems such as background signal, decrease in the signal intensity of the derivatives. | Derivatization reaction doesn’t need to complete, and derivatized products also don’t need to be stable as long as the reaction is deemed reproducible. | ([Brinkman 1987](#_ENREF_3), [Ibrahim et al., 2010](#_ENREF_14), [Rigas 2012](#_ENREF_34)) |
| Time consuming, poor reproducibility, and formation of many interfering species and side products. | Efficient, highly reproducible formation of fluorescent active product, minimum formation of side-product. | ([Shen and Tomellini 2007](#_ENREF_36)) |
| Generally, photoderivatives are less stable as a result entail poor reproducibility, because the product is normally formed (sample storage & chromatographic separation time) long before its detection. | This provide excellent reproducibility, because photoproducts are formed just before the detection. | ([Jones et al., 2015](#_ENREF_15)) |
| These reactions are normally slow and complete in minutes to hours. | These reactions are generally rapid and finish in seconds. | ([Parlar and Surmann 2000](#_ENREF_28)) |
| Pre-column derivatization most of the time is carried out offline in batch mode. | It is performed only in on-line and automated mode for the efficient conversion of the target analytes into fluorescent form. | ([Rigas 2012](#_ENREF_34)) |
| Separation conditions have minimum or no effect on the photoderivatization reactions and PIF signals of target analytes. | The optimized chromatographic separation conditions may be not very suitable for the detection step. For instance, various parameters such as solvent composition, pH, oxygen, presence of buffers, ion-paring reagents, temperature, residence time, intensity and wavelength of the light source may have critical effects on the reaction and PIF signals of target analytes. | ([Lores et al., 1999](#_ENREF_18)) |
| More than one photoproducts are formed for a compound can be easily separated in pre-column mode, and it helps to understand the extent to which the photochemical reaction took place. | Sometime more than one photoproduct formed for a compound can’t be separated in post-column mode, and are often difficult to understand to the extent the photochemical reaction took place. | ([Lores et al., 1999](#_ENREF_18), [Fedorowski and LaCourse 2010](#_ENREF_8)) |
| This mode of derivatization can assist to understand the degradation rate constants and characterize the photoproducts of target analytes. | This mode of derivatization is comparatively less informative to understand the degradation rate constants and characterization of the photoproducts of target analytes. | ([Parlar and Surmann 2000](#_ENREF_28)) |

**Table S2** Application of LC-*uv*-FLD for determination of wide range of analytes in various matrice.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Analytes** | **Application** | **Extraction** | **Technique** | **Characteristics** | **Recoveries (%)** | **LODs (µg/kg)** | **Ref.** |
| **Pharmacetical drugs** | | | | | | | |
| Tamoxifen-DNA adduct | HL-60 cells | Mannheim Boehringer DNA isolation kit | HPLC-*hv*-UV/FLD | Column: Radial-Pak 8MBC18 L (10 mm, 8 mm ID, 10 cm); photochemical reactor: a PTEF knitted reactor coil (0.25 mm ID, 5-m) mounted around UV lamp (254-nm); fluorescence detector: λex/ λem = 260/375 nm; | -------- | ------ | ([Sharma 2000](#_ENREF_35)) |
| Cyclooxygenase inhibitor: 5-chloro-3-(4-methanesulfonylphenyl)-69-methyl-bipyridinyl |  | Plasma and urine | HPLC-*hv*-FLD | Column: Keystone Prism® RP analytical column (15 cm × 4.6 mm, 5 µm); photochemical reactor: a PTFE reaction coil (5.0-m x 0.3-mm ID) mounted around UV lamp (254-nm); fluorescence detector: λex/ λem = 260/375 nm. | 66.9 – 108.2 | ≤ 5 | ([Matthews et al., 2001](#_ENREF_22)) |
| Efavirenz | LLE | Human plasma | HPLC-*hv*-FLD | Column: Dinitrobenzoyl leucine column (4.6 × 250 mm); photochemical reactor: a KOTR PTFE coil (10 m × 0.3 mm ID) mounted around 254 nm UV lamp, fluorescence detector: λex/ λem = 310/390 nm | 95.0 – 104.0 | ------- | ([Matthews et al., 2002](#_ENREF_23)) |
| Carbamazepine, dihydrocarbamazepine, diazepam, ketoprofen, ibuprofen, aspirin, nap roxen, bezafibrate, diclofenac | SPE | Waste water | HPLC-*hv*-FLD | Column: Nova-Pak C18 (150 × 3.9 mm) ; photochemical reactor: a homemade photo reactor was made of 40 W xenon lamp providing 254 nm wavelength of radiations. | ----------- | --------------- | ([González-Barreiro et al., 2003](#_ENREF_11" \o "González-Barreiro, 2003 #73)) |
|  |  |  |  |  |  |  |  |
| **Pesticides** | | | | | | | |
| Insecticides: iflubenzuron, ufenuron, triflumuron, hexaflumuron, flufenoxuron | Tomato | SPE | HPLC-*hv*-FLD | Column: Silica-based column (150 × 3.9 mm); photochemical reactor: a knitted open tube reactor (KOTR) with PTFE coil (5 m × 1.6 mm OD × 0.3 mm ID) mounted around 4 W Xe lamp; fluorescence detector: λex/λem = 330/410 nm. | 79 - 102 | 5 - 21 | ([Martı́nez-Galera et al., 2001](#_ENREF_20)) |
| Pyrethroids insecticides: cyfluthrin,  tau-fluvalinate,  fenpropathrin, acrinathrin, bifenthrin  fenvalerate, deltamethrin, |  | Cucumber | HPLC*-hv*-FLD | Column: Bondapack C18 (300 × 3.9 mm); photochemical reactor: a KOTR PTFE coil (5 m × 1.6 mm OD × 0.3 mm ID) mounted around 4 W Xe lamp; fluorescence detector: λex/λem = 283/300 nm. | 95 - 116 | 0.24 – 2.70 | ([López-López et al., 2001](#_ENREF_17)) |
| 2,4-dichlorophenoxyacetic acid, mecoprop |  | water | FIA-*hv*-FLD | photochemical reactor: a PTFE tubing (0.5 mm ID) mounted around a germicide UV-lamp (254 nm, 8 W); fluorescence detector: λex/ λem = 270/298 nm. | 97.0 - 107.8 | 33.5 - 73.2 | ([Garcı́a-Campaña et al., 2001](#_ENREF_9)) |
| Acetamiprid | SPE | Vegetables | HPLC-*hv*-FLD | Column: Silica-based column (15 cm × 3.9 mm); photochemical reactor: a KOTR PTFE coil (5 m × 1.6 mm OD × 0.3 mm ID) mounted around a 4 W xenon lampl; fluorescence detector: λex/ λem = 283/300 nm. | 65.0 – 75.0 | 6.0 | ([Martínez Vidal et al., 2002](#_ENREF_21)) |
| Diuron, isoproturon  ,linuron, neburon | ------- | ------- | HPLC-*hv*-FLD | Column: Nova-Pak C18 (150 × 3.9 mm); photochemical reactor: a KOTR PTFE coil (5 m × 1.6 mm OD × 0.3 mm ID) mounted around a 4 W Xe lamp; fluorescence detector: λex/ λem = 324/403; 301/433; and 326/385 335/411; nm for diuron, isoproturon, neburon, and linuron, respectively. | ------- | 0.07 - 0.46 | ([Muñoz de la Peña et al., 2002](#_ENREF_27)) |
| Propanil, diuron, isoproturon, linuron, neburon | SPE | River water | HPLC-*hv*-FLD | Column: Nova-Pak C18 (150 × 3.9 mm); photochemical reactor: a KOTR PTFE coil (5 m × 1.6 mm OD × 0.3 mm ID) knitted around 4 W xenon lamp; fluorescence detector: λex/ λem 368/455 nm for propanil, λex/ λem = 275/ 333 nm for diuron; λex/ λem = 295/428 or 274/331 for isoproturon, λex/ λem = 335/411 nm for linuron and 326/385 nm for neburon. | -------------- | 0.08 – 0.80 | ([de la Peña et al., 2003](#_ENREF_5)) |
|  |  |  |  |  |  |  | **Error! Hyperlink reference not valid.** |
| Triflumuron, flufenoxuron, diflubenzuron, lufenuron, hexaflumuron | LLE | vegetables | LC-LC-*hv*-FLD | Column: C18 (30 × 4.6 mm) were used as the first dimension separation column; whereas, lmChrompack C18 (50 × 4.6 mm) was used as second dimension column; photochemical reactor: a KOTR PTFE coil (5 m × 1.6 mm OD × 0.3 mm ID) knitted around 4 W Xe lamp; fluorescence detector: λex/ λem = 344/4148 nm. | 80.0 – 119.2 | 0.14 – 0.98 | ([Gil García et al., 2004](#_ENREF_10)) |
| Diuron, monolinuron, neburon, linuron, and propanil | SPME | Groundwater | HPLC–PIF–FLD | Column: AQUASIL C18 (150 × 4.6 mm ID, 5 µm); photochemical reactor: a KOTR PTFE coil (5 m × 1.66 mm OD × 0.3 mm ID) knitted around 4 W xenon lamp; fluorescence detector: λex/ λem = 300/400 nm. | 86.0 – 105.0 | 0.019 – 034 | ([Mughari et al., 2007](#_ENREF_25)) |
| Fenpropathrin, *λ*- permethrin, fenvalerate, deltamethrin, cyhalothrin, bifenthrin and *π*- fluvalinate | SPME | Groundwater | HPLC–PIF–FLD | Column: C18 (250 × 4.6 mm ID, 3.5 µm); photochemical reactor: a KOTR PTFE coil (5 m × 1.66 mm O.D. × 0.3 mm ID) knitted around 4 W xenon lamp, fluorescence detector: λex/ λem =283/330 nm. | 92 – 109 | 0.03 – 0.075 | ([Vázquez et al., 2008](#_ENREF_40)) |
| cis-combretastatins | ---------- | ---------- | HPLC–PIF–FLD | Column: C18 (15 cm × 3 mm ID, 3 µm); photochemical reactor: a PTFE tubing (75 cm × 1/16 in. O.D × 0.006 in. ID) wound around mercury lamp (19 mm × 7 mm); fluorescence detector: λex/ λem = 320/390 nm. | ---------- | ---------- | ([Stratford 2008](#_ENREF_38)) |
|  |  |  |  |  |  |  |  |
| Bifenthrin, *π*-fluvalinate, fenvalerate, deltamethrin,  λ-cyhalothrin,  permethrin, fenpropathrin | SPME | Cucumber& watermelon | HPLC–PIF–FLD | Column: C18 (250 × 4.6 mm ID, 3.5 µm) ; photochemical reactor: a KOTR PTFE coil (5 m × 1.66 mm OD × 0.3 mm ID) knitted around 4 W Xenon lamp, fluorescence detector: λex/ λem = 283/330 nm. | 91 – 110 | 1.3 – 5 | ([Vázquez et al., 2008](#_ENREF_41)) |
| Flufenoxuron teflubenzuron, hexaflumuron, triflumuron, lufenuron, diflubenzuron, and | SPME | Orange juice | HPLC–PIF–FLD | Column: C18 (350 × 3 mm ID, 3 µm); photochemical reactor: a KOTR PTFE coil (5 m × 1.66 mm OD × 0.3 mm ID) knitted around 4 W Xenon lamp, fluorescence detector: λex/ λem = 330/410 nm. | 85 – 110 | 0.05 -0.15 | ([Parrilla Vázquez et al., 2008](#_ENREF_29)) |
| Thiacloprid | Simple filtration | Water | IC–PIF–FLD | Column: Ion Pac® AS 11 (250 × 4 mm ID, 3.5 µm, 13 µm p.s); photochemical reactor: a KOTR PTFE coil (2 m × 1.5 mm OD × 0.5 mm ID) knitted around germicide UV-lamp (254 nm), fluorescence detector: λex/ λem = 236/353. | 95.5 - 114.0 | 9.9 | ([Subhani et al., 2014](#_ENREF_39)) |
| Isoproturon,  rimsulfuron, monuron, MCPA,  thiabendazole, fuberidazole, carbaryl | Filtration | Water samples | HPLC-PIF-FLD & second-order  chemometric algorithms. | Column: C18 (15 cm × 4.6 mm ID, 5 µm); photochemical reactor: a KOTR PTFE coil (3 m × 0.8 mm OD × 0.3 mm ID) knitted around 8 W mercury lamp; fluorescence detector: λex/λem= 272/288-460 nm. | 79 – 110 | 19 - 280 | ([Arancibia and Escandar 2014](#_ENREF_1)) |
| Carboxin, monalide, propanil | SPE | Water samples | DL-PIF–HPLC | Column: C18 (15 cm × 3.9 mm ID, 5 µm; photochemical reactor: 450 µL flow cell irradiated by Nd: YAG tunable laser: fluorescence detector λex/λem= 245/370 nm for carboxin; λex/λem= 245/354 nm for monalide and λex/λem= 255/464 nm for propanil. | 89.5 - 115.9 | 0.53 – 3.64 | ([Mbaye et al., 2015](#_ENREF_24)) |
| **Miscellaneous analytes** | | | | | | | |
| Pteridins, biopterin,  Tetrahydrobiopterin, dihydrobiopterin | ---------- | Urine | HPLC–DAD–PIF–FLD | Column: C18 (250 × 4.6 mm ID, 5 µm) and (150 × 4.6 mm ID, 5 µm); photochemical reactor: a KOTR PTFE coil (4.5 m × 1.66 mm OD × 0.3 mm ID) knitted around 8 W Xenon lamp; fluorescence detector: λex/λem= 272/445 nm. | ---------- | ---------- | ([Cañada-Cañada et al., 2009](#_ENREF_4)) |
| Resveratrol  & piceid isomers | Simple dilution | wine | HPLC–PIF–FLD | Column: C18 (150 × 3.9 mm ID, 4 µm); photochemical reactor: a KOTR PTFE coil (3 m × 1.66 mm OD × 0.3 mm ID) knitted around 4 W Xenon lamp; fluorescence detector: λex/ λem = 260/364 nm.. | ---------- | 0.001 - 0.01 mg/L | ([Durán-Merás et al., 2008](#_ENREF_7)) |
| Aflatoxin B1 | LLE and Immunoaffinity column clean-up | Eggs | HPLC–PIF–FLD | Column: Phenomenex Prodigy column C18 (25 cm × 4.6 mm ID, 5 µm) for lab 1 and Phenomenex Kinetex C18 (150 × 4.6 mm ID, 2.6 µm) for lab 2; photochemical reactor: Kobra cell; fluorescence detector:λex/λem=362/425 nm. | 70 | 0.001 – 0.005 | ([Pavšič-Vrtač et al., 2014](#_ENREF_30)) |
| Aflatoxins ( G1,G2, B1, B2), zearalenone, ochratoxin A | SPE | Cereals | HPLC–PIF–FLD | Column: C18 (150 × 4.6 mm ID, 3.5 µm); photochemical reactor: a KOTR PTFE coil (4.5 m × 1.66 mm OD × 0.3 mm ID) knitted around 8 W Xenon lamp; fluorescence detector: λex/λem= 60/455 nm for 0 – 18 min for Aflatoxins, λex/ λem = 276/460 nm for 18 – 29 min for zearalenone and λex/ λem = 335 /460 nm for 29 – 35 min for ochratoxin. | 77.31– 104.1 | 0.004 – 0.5 | ([Rahmani et al., 2013](#_ENREF_32)) |
| Aflatoxin B1, B2, G1, G2 | SPE | Grains and Cereals | HPLC–PIF–FLD | Column: C18 (250 × 4.0 mm ID, 5 µm) photochemical reactor: Kobra cell™; fluorescence detector: λex/λem=365/435 nm | 89.2 – 97.8 | 0.062 - 0.080 | ([Asghar et al., 2016](#_ENREF_2)) |
| Saxitoxin, neosaxitoxin, decarbamoylsaxitoxin, gonyautoxins 1 and 4, gonyautoxins (GTX )2 and 3, decarbamoylgonyautoxins 2, 3,  GTX5 (B1), C1, C2 | LLE | Mussels, clams, scallops, razor clam | HPLC–PIF–FLD | Column: C8 column (25 × 4.6 mm, 5 µm p.s) for C toxins, Zorbax Bonus-RP column (15 cm × 4.6 mm ID, 3.5 μm) for STX and GTX toxins; photochemical reactor: homemade; fluorescence detector : λex/ λem = 330/395. | ------ | 0.1 - 0.1464 | ([Rey et al., 2015](#_ENREF_33)) |
| Aminosulfide and nitrosulfide impurities | Simple extraction | Vortioxetine  Manufacturing Process | HPLC–PIF–FLD | Column: XSELECT Charged Surface Hybrid Phenyl-Hexyl column (100 × 4.6 mm ID, 2.5 µm);photochemical reactor: a KOTR PTFE coil (7.5 m × 1.66 mm OD × 0.3 mm ID) knitted around UV lamp (254 nm);fluorescence detector: λex/λem = 272/300 nm. | ----------------- | 0.026 – 0.015 | ([Douša et al., 2016](#_ENREF_6)) |
| Aflatoxins AFB1, AFB2, AFG1, AFG2, AFM1 | DLLE | Yogurt | HPLC–PIF–FLD | Column: C18 Kinetex (150 × 4.6 mm ID, 2.6 µm); photochemical reactor: homemade; fluorescence detector: λex/λem = 360/430 nm | 76.5 - 99.7 | 0.0015 – 0.0055 | ([Hamed et al., 2017](#_ENREF_12)) |
| Aflatoxins G1, G2, B1, B2, and Ochratoxin A | LLE | Animal  feed | HPLC–PIF–FLD | Column: C18 UG120 (25 cm × 4.6 mm ID, 5 µm); photochemical reactor: homemade; fluorescence detector: λex/λem = 360/450 nm for all aflatoxins except λex/λem = 330/460 for Ochratoxin A, | 78.1 - 94.4 | 0.20 – 1.01 | ([Kim et al., 2017](#_ENREF_16)) |
| Aflatoxin M1 | LLE & immunoaffinity AFLATEST column clean-up | Milk and dairy products | HPLC–PIF–FLD | Column: C18 (250 × 4.6 mm ID, 5 µm); photochemical reactor: a KOTR PTFE coil (5 m × 0.25 mm OD × 0.3 mm ID) knitted around mercury lamp (k = 254 nm), fluorescence detector: λex/λem = 360/440 nm | 85.2 – 107.0 | 0.0085 - 0.025 | ([Shuib et al., 2017](#_ENREF_37)) |
| Aflatoxins AFB1, AFB2, AFG1, AFG2 | Solid-liquid extraction | Rice | HPLC–PIF–FLD | Column: C18 (50 × 2.1 mm ID, 1.8 µm); photochemical reactor: a KOTR PTFE coil (5 m × 0.25 mm OD × 0.3 mm ID) knitted around mercury lamp (k = 254 nm): fluorescence detector: λex/ λem = 365/46 nm. | 84.5 – 105.3 | 0.07 – 0.28 | ([Huertas-Pérez et al., 2018](#_ENREF_13)) |
| Rimsulfuron, fuberidazole, carbaryl, naproxen, albendazole, carbamate,tamoxifen | SPE | Environmental Water | Third-order LC–PIF–FLD | Column: C8 (30 mm × 4.6 mm, 5 µm p.s); photochemical reactor: a PTFE coil (5 m × 0.3 mm OD × 0.5 mm ID) knitted around tubular 8 W mercury lamp (k = 254 nm), fluorescence detector: λex/λem = 227-277 (4 nm increment) /310-400 nm (2 nm. increment for all aflatoxins | ----------- | 0.02 – 0.27 | ([Pellegrino Vidal et al., 2018](#_ENREF_31)) |
| Aflatoxins AFB1, AFB2 | Fe3O4/rGO Magnetic SPE | Vegetable oils | HPLC–PIF–FLD | Column:Kromasil C18 column (150 mm × 4.6 mm, 5 µm p.s); photochemical reactor: Pribolab Pte. Ltd., Singapore: fluorescence detector: λex/λem = 360/440 | 80.4 - 106.0 | 0.01- 0.02 | ([Yu et al., 2019](#_ENREF_42)) |
| Aflatoxins B1, B2, G1, G2, zearalenone Ochratoxin A, Ochratoxin B | OASIS PRIME HLB SPE cartridge & DLLME | Poultry and meat | HPLC–PIF–FLD | Column: C18 (150 mm × 4.6 mm ×2.7 µm); photochemical reactor: UV lamp (254 nm), fluorescence detector: λex/λem = 365/440 nm for all aflatoxins, except λex/λem = 234/469 nm for Ochratoxin A, Ochratoxin B, zearalenone. | 73.6 - 88.0 | 0.64 - 42 | ([Muñoz-Solano and González-Peñas 2020](#_ENREF_26)) |
| Aflatoxins AFB1, AFB2, AFG1, AFG2 | Fe3O4 nanoparticles based extraction | Vegetable  Oils | HPLC–PIF–FLD | Column: Insert ODS-3 (250 × 4.6 mm, 5 µm); photochemical reactor: a ethylene tetrafluoroethylene tube (2.5 m × 500 µm ID) knitted around 8 W Hg lamp (30 cm × 3 cm × 3 cm); fluorescence detector: λex/λem = 384/406 nm. | 82.6 - 106.2 | 0.01 - 0.16 | ([Zhang et al., 2020](#_ENREF_43)) |

D-PF:First-derivative photochemically induced fluorescence; FIA–MEPIF: Flow injection analysis micellar-enhanced photochemically induced fluorescence; SPME: solid-phase microextraction; HPLC–PIF–FD: High performance liquid chromatography combined with post-column photochemically induced fluorimetric derivatization and fluorescence detection.





**Fig. S2 (A-C)** Schematic mass-spectrometric data based photo-degradation pathway of AF, THF and MTHF. From ([Martín Tornero et al., 2017](#_ENREF_19))**Error! Hyperlink reference not valid.***with permission from Elsevier.*

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