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Rapid and Sensitive Electrochemical, Spectroscopic and Spectroelectrochemical Detection of Glyphosate and Glufosinate and Their Copper Salts with Screen-printed Electrodes

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Abstract *N*-(Phosphonomethyl)glycine (glyphosate), known by the trade name Roundup®, is a broad-spectrum systemic herbicide used to kill various types of weeds. It was first synthesized in 1970 by John E. Franz, a chemist at the Monsanto agrochemical company. Glyphosate's mode of action is to inhibit a plant enzyme involved in the synthesis of some aromatic amino acids ("shikimate way"). The use of Roundup® is currently controversial, as its hazard potential has not been clarified. Glufosinate (2-Amino-4-[hydroxy(methylphosphonoyl)] butanoic acid) was discovered by German and Japanese scientists in a biological process: Species of *Streptomyces* bacteria produce a tripeptide that consists of two alanine residues and an amino acid that is an analogue of glutamate named phosphinothricin. Phosphinothricin was first synthesized by scientists at Hoechst (now Aventis) in the 1970s as a racemic mixture; this racemic mixture is called glufosinate. This article presents reliable and easily performed spectroscopic and (spectro)electrochemical measurements for identifying glyphosate and glufosinate.

Keywords: *electrogenerated chemiluminescence, screen-printed electrodes, nano-ZnO decorated screen-printed electrodes, derivatization*

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1. Introduction

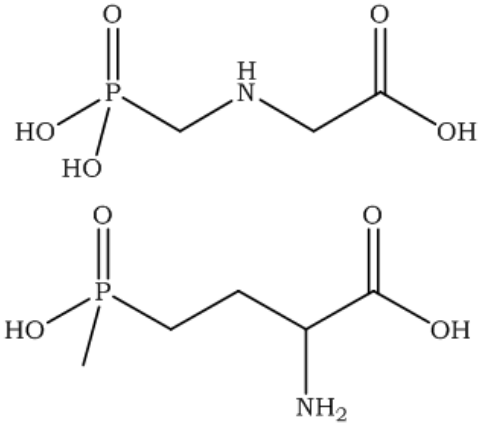


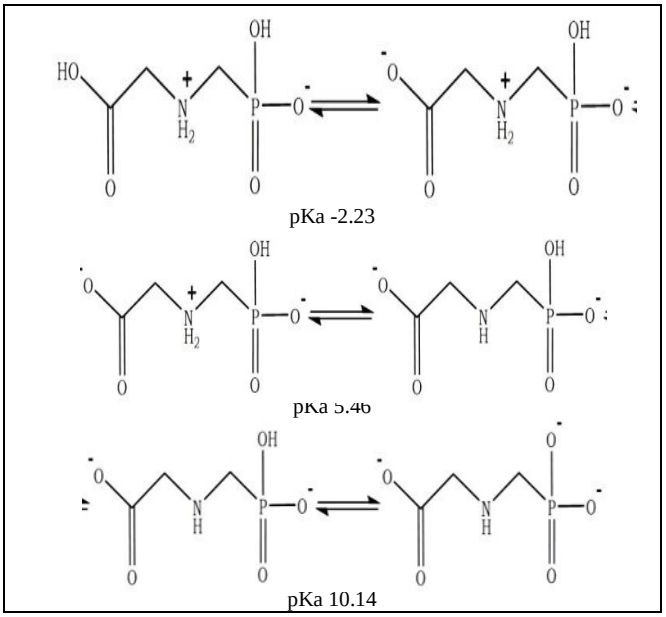
Figure 1. Structure of glyphosate (top) and glufosinate (bottom)

Glyphosate is one of the most common herbicides on current use. The list of arguments for and against the use of glyphosate exceeds the scope of this article. The number of publications about glyphosate is enormous: chemical studies on glyphosate alone yielded about 15,000 references in the SciFinder database. Here, ecological, biochemical, chemical, and physicochemical properties of glyphosate are most often found: i.e., the mode of action of glyphosate, the fate of glyphosate in soils and water [1,2,3], the (photocatalytic) degradation of glyphosate [4,5] and the chemical analytical detection of glyphosate. In addition to HPLC [6,7,8], a number of different spectroscopic, chromatographic, and electrochemical methods are available.

Glyphosate exists in different ionic forms, depending on pH (Table 1). At high pH glyphosate is present as Gly^{3-}, at low pH as (overall uncharged) zwitterion.

Roundup® formulations differ by counterion (ammonium or isopropylammonium ion), medium (solution in water or as granules), and glyphosate concentration. In addition, Roundup® contains so-called wetting agents to lower the surface tension of the water and to improve the penetration of plant cell walls. Most of these are tallow fatty amines, which account for about 15% of Roundup® [10]. Tallow fatty amines themselves are harmful, so it is reasonable to conclude that the commercial Roundup® mixture is more harmful to health than pure glyphosate itself.

Table 1. pH-dependent ionic forms of glyphosate [9]



In order to protect human health, various countries limit concentrations of glyphosate in water and crops: The US Environmental Protection Agency (EPA), Health Canada, and China's Ministry of Water Resources have set the maximum acceptable concentration (MAC) of glyphosate in drinking water at 0.7, 0.28, and 0.7 mg/L, respectively [11]. The current legal status of glyphosate in Germany is as follows: The German government, with the approval of Environment Minister Schulze and Agriculture Minister Klöckner, has passed a legislative package on insect protection. This regulates the use of pesticides to reduce insect mortality. The cabinet also approved a plant protection application ordinance, finalizing the phase-out of glyphosate use.

Schulze asserted that glyphosate kills every plant and thus deprives insects of their lives. The use of glyphosate is to be severely restricted initially and banned completely by the end of 2023. The German Farmers' Association, however, sharply criticized the proposed legislation. Rukwied, the president of the association, considers enforcing insect protection with bans "grotesquely wrong and even dangerous." He warned of significant effects on farmers. For example, if plant protection products were banned in protected areas, viticulture in the Kaiserstuhl region in Germany would be "completely history." Many farming families would lose their livelihoods, Rukwied continued: "We're not just talking about destroyed capital and lost jobs here, but about the end of a centuries-old part of our culture". [12]

Glufosinate-ammonium (2-Amino-4-[hydroxyl(methylphosphonoyl)] butanoic acid) was tested as a flexible post-emergence herbicide for control of cruciferous weeds in glufosinate-resistant winter oil seed rape [13].

Regardless of these political assessments, a persistent need exists for rapid, inexpensive, and sensitive detection of glyphosate and glufosinate.

Glyphosate and glufosinate often present an analytical challenge because of their high water solubility and the fact that both molecules have no chromophore or fluorophore in their chemical structure. Therefore, derivatization must be preceded by an analytical detection such as HPLC, GCMS, or optical spectroscopy.

HPLC requires the insertion of a chromophore into glyphosate molecules for absorption or fluorescence detection, while GCMS requires the polarity to be lowered, which increases volatility due to the insertion of a nonpolar moiety. This can be done by derivatization with dansyl chloride, FMOC, or other derivatization reagents. These additional preparation steps are labor intensive and can significantly reduce the detection limit.

Börjesson and Torstensson [14], following Deyrup et al. [15], developed new methods to determine the concentration of glyphosate with GCMS. These methods included derivatizing both molecules with a mixture of trifluoroacetic anhydride and trifluoroethanol. These experiments allowed the authors to quantify glyphosate near a railway line in Sweden more than a year after exposure. They estimated the limit of detection of glyphosate in soil to be approximately 3 mg/kg soil. Habekost described in detail the derivatization procedure of glyphosate by refluxing with trifluoroacetic anhydride and trifluoroethanol at 90°C [16].

Colombo and Masini [17] take a different derivatization route. They first oxidized glyphosate forming glycine. Glycine was then derivatized with a mixture of o-phthaldialdehyde and 2-mercaptoethanol at pH>9. After excitation at 340 nm the resulting product fluoresces at around 450 nm.

Kodama et al. [18] used capillary electrophoresis to investigate the contamination of various tea-based beverages with glyphosate. They created a complex of glyphosate and Cu(II) during the electrophoretic run and measured the retention time as a function of pH. Daniele et al. [19] published thermodynamic and spectrophotometric analyses of copper(II)-glyphosate complexes in an aqueous solution at different pH levels and temperatures. Unfortunately, all these methods are time consuming, expensive, and elaborate.

Even though glyphosate and glufosinate are not electroactive at accessible potentials, Pintado et al. [9] electrodeposited copper onto a carbon electrode to determine the concentration of glyphosate in drinking water. On adding the glyphosate solution, Pintado et al. saw an increase in current in the cyclic voltammogram, which was due to the formation of a copper-glyphosate complex. Their aim was to develop an electrochemical method to quantify glyphosate simply, quickly, and cheaply. The detection limit was 80 μmol/L, but preparing the electrode was quite tricky. Sierra et al. [20] studied the electrooxidation of glyphosate on nickel and copper surfaces. The anodic current peak in the cyclic voltammogram increased with glyphosate concentration. The authors suggested that the detection limit for glyphosate is much lower on copper (30 μmol/L) than on nickel.

Another method is to increase the electrochemical chemiluminescence (ECL) signal of $[Ru(bpy)_3]^{2+}$ in the presence of glyphosate or glufosinate as a coreagent.

To our knowledge, Bozorgzadeh et al. [21,22] were the first to observe an improved ECL signal after treating the electrode with ZnO nanopowder. They investigated peroxydisulfate and tripropylamine as coreactants of $[Ru(bpy)_3]^{2+}$ on multi-walled carbon nanotubes (MWCNTs) decorated with ZnO nanoparticles.

The main feature of the (spectro)electrochemical method employed here is screen-printed electrodes (SPEs) made from different materials. We used either gold (high- and low-temperature ink) or carbon nanotubes (CNTs), optionally decorated with nano-ZnO. Nano-ZnO can significantly enhance the electrochemical chemiluminescence (ECL) signal to produce a detection limit lower than 1 µmol/L for glyphosate. In addition, these methods are cheaper, faster, and more sensitive than, for example, spectroscopic tests.

A detailed overview of the different analytical detection methods can be found in [23].

2. Detection Methods

2.1. Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the most important methods in electrochemistry; it is the spectroscopy of the electrochemists. The main features of CV are described in several textbooks. One of the most detailed descriptions is in the book by Faulkner and Bard [24].

Figure 2 shows the CVs of copper without (dotted line) and with glyphosate (solid line). Before the CV was recorded, copper was deposited onto an Au-Bt-SPE ("Bt" means low temperature curing ink) at -0.8 V for 10 s. Note that the oxidation of copper is pH-dependent [25]. The two anodic peaks are clearly resolved at 0.1 V and 0.4 V. At higher pH, two reduction peaks can be measured ($Cu^{2+} \rightarrow Cu^{+} + e^{-}$ and $Cu^{+} \rightarrow Cu + e^{-}$) The first reduction peak is less intense than the second because the six-fold coordinated Cu^{2+} is more stable than the four-fold coordinated Cu^{+} [25].

With glyphosate, however, only one oxidation peak results ($Cu \rightarrow Cu^{2+} + 2e^{-}$). This peak is more intense than the anodic peaks without glyphosate. This can be explained by the higher stability and solubility of the $[Cu(glyphosato)_2]^{2+}$-complex [26].

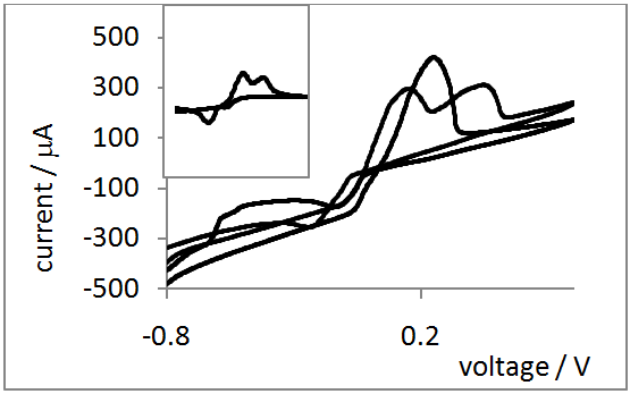


Figure 2. CV of copper sulfate (dotted line) and copper sulfate with glyphosate (solid line) on an Au-Bt SPE (Bt means low-temperature curing ink). Insert: pH = 10.

2.2. Electrogenerated Chemiluminescence Detection

Since the 1960s, ECL techniques have become increasingly attractive in analytical chemistry [27,28,29,30]. ECL involves generating an excited state in the commonly used and extensively investigated tris(2,2′-bipyridyl)ruthenium(II) $[Ru(bpy)_3]^{2+}$ on an electrode surface. $[Ru(bpy)_3]^{2+}$ is first oxidized before undergoing an electron transfer reaction with a coreactant. During this latter process, an excited state is reached that subsequently decays and emits light. $[Ru(bpy)_3]^{2+}$ luminesces strongly (Figure 3).

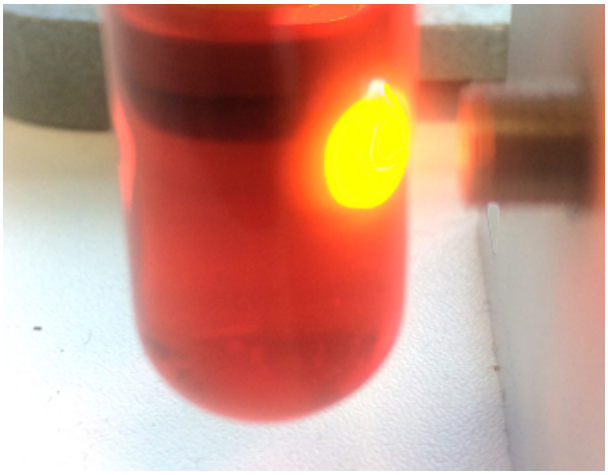


Figure 3. Luminescence of $[Ru(bpy)_3]^{2+}$ (left). Right: 460 nm LED

Finally, $[Ru(bpy)_3]^{2+}$ can be regenerated after the emission. ECL is a "marriage of electrochemical and spectroscopic methods" [30].

ECL is used to identify coreactants such as aliphatic amines [28], amino acids [31,32,33], derivatized amino acids [34,35], and pharmaceuticals [36,37,38,39]. Gerardi [40] and Fähnrich [41] have provided a comprehensive review of the analytical application of ECL of $[Ru(bpy)_3]^{2+}$.

Several investigations have been published concerning detection of glyphosate and related compounds using ECL: Ridlen [42] detected glyphosate and structurally related compounds via ion exchange chromatography (acid and alkaline as mobile phase, respectively) with post-column addition of $[Ru(bpy)_3]^{2+}$ and measured the ECL intensity as a function of pH. The glyphosate detection limit was 0.01 µmol. Adock [43] determined the mono-isopropylamine salt of glyphosate using flow injection analysis with ECL detection. They produced a detection limit of about 1 nmol. However, the experimental effort in both cases was extensive and time consuming, because it is not easy to mix the $[Ru(bpy)_3]^{2+}$ with the substance under investigation during the HPLC run in an appropriately small ECL detection cell with reproducible results. Thus, in our opinion this method is unsuitable for routine and high throughput analysis.

The current paper shows that (spectro)electrochemical methods are a promising way to quickly identify glyphosate and glufosinate in batch experiments using SPE with electrodes made from gold and CNT for ECL measurements. The detection limit with the ECL method can be improved by adding ZnO nanopowder to the electrode surface. The ECL with glufosinate, however, is significantly less pronounced.

2.3. Electrochemical Impedance Spectroscopy

Along with other electrochemical measurements such as cyclic voltammetry (CV), square wave voltammetry (SWV), or chronoamperometry (CA), electrochemical

impedance spectroscopy (EIS) plays an important role in measuring the characteristics of electrodes in electrolyte solutions [44].

If a potential is applied to an electrode-electrolyte interface, a flow of charge and matter occurs. Without going into details, in EIS the impedance (the resistance of the AC circuit) of the electrochemical system is measured as a function of the applied frequency. The processes at the electrode immersed in the solution can be described with different electrical compounds as resistors (solution resistor, R_s; charge transfer or polarization resistor, R_p), capacitor (Helmholtz double layer in front of the electrode, C_{dl}), and coil (inductance resulting from the current, which induces an electromotive force that opposes a change in current, L). One of the main purposes of EIS is to describe an electrochemical system through a combination of these passive electric compounds. In contrast to the ohmic resistor, capacitors and coils have a frequency-dependent resistance, which is inversely proportional to the frequency of the first and proportional to the frequency of the latter. EIS can be used to optimize electrodes by adding a more conductive material or a substance with a huge surface area. This will lower R_p.

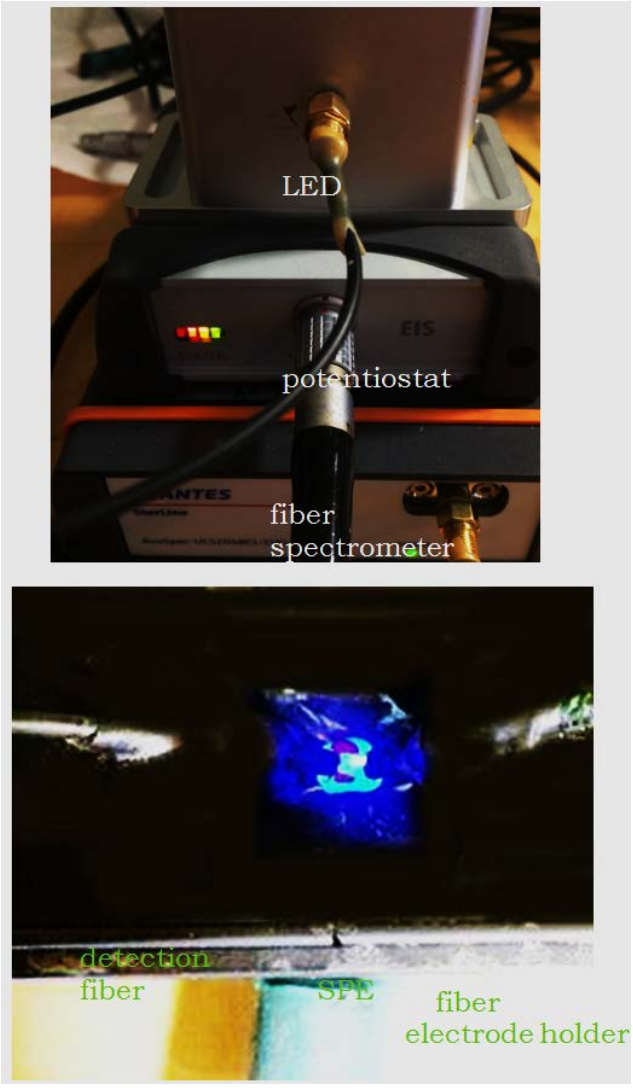


Figure 4. Top: Excitation LED, potentiostat and fiber spectrometer as detector. Bottom: homebuilt reflection-SPE cell

3. Experimental: Methods, Procedures and Results

Chemicals and instruments

Glyphosate (Sigma Aldrich, 54521), glufosinate (Sigma Aldrich, 45520), distilled water, $CuSO_4*5H_2O$ powder (Hedinger, Germany), ZnO nanopowder (Sigma Aldrich, 544906), NaH_2PO_4 powder Hedinger, Germany) (0.1 mol/L).

Fiber spectrometer (Avantes, ULS 2048, CL EVO, 340-800 nm), potentiostat (µ-STAT 400, DropSens / Metrohm), ECL-potentiostat (µ-STAT ECL, DropSens), screen-printed electrodes Au-AT- and Au-Bt-SPE (Au as working electrode, Pt as counter electrode, Ag as reference electrode), CNT-SPE, CNT as working electrode, C as counter electrode, Ag/AgCl as reference electrode), CNT-SPE with two CNTs as working electrodes, C as counter electrode, Ag/AgCl as reference electrode. All SPE from Metrohm / DropSens. A homebuilt reflection electrochemical cell with two fibers for excitation and detection, absorption spectrometer (Perkin Elmer) and an EIS-spectrometer µStat-400i (DropSens / Metrohm).

Figure 5. ECL-potentiostat (top) and ECL cell with the photodiode (bottom)

Figure 4 shows the experimental equipment for cyclic voltammetry and reflection measurement and the homebuilt electrochemical cell. Figure 5 shows the ECL apparatus employed.

3.1. Derivatization and GCMSD

Procedure

Trifluoroacetic anhydride (SigmaAldrich, No. 106232); trifluoroethanol (Sigma Aldrich, No. T 63002); GC-MSD with autosampler (GC: Hewlett Packard 5890, MSD: Hewlett Packard 5972, autosampler: Hewlett Packard 6890); column: RTX-35; carrier gas: He 5.0; 50-mL round-bottom flask; reflux condenser; capillary air bleed for solvent evaporation. Experimental procedure: 10 µg glyphosate was mixed with 200 µg trifluoroacetic anhydride (TFAA) and 100 µg trifluoroethanol (TFE) in a 50 mL round-bottom flask. The mixture was heated to 90°C with a controlled heater and refluxed for about one hour. Afterwards, the mixture was flushed with nitrogen for two minutes to evaporate the solvents. The residue was then mixed with 10 mL ethyl acetate and directly analyzed with GC-MSD. The temperature profile of the GC was 100°C in the first minute with a final temperature of 200°C. Temperature increased at a rate of 5°C/minute at an injection volume of 5 µL. The MS detector started after the solvent peak at 2.5 minutes. Figure 6 shows the derivatization of the different moieties and the complete derivatized glyphosate and glufosinate.

The GC-MS of glyphosate was published and interpreted in [45].

The GC of glufosinate is shown in Figure 7. The main peaks are labeled a - d.

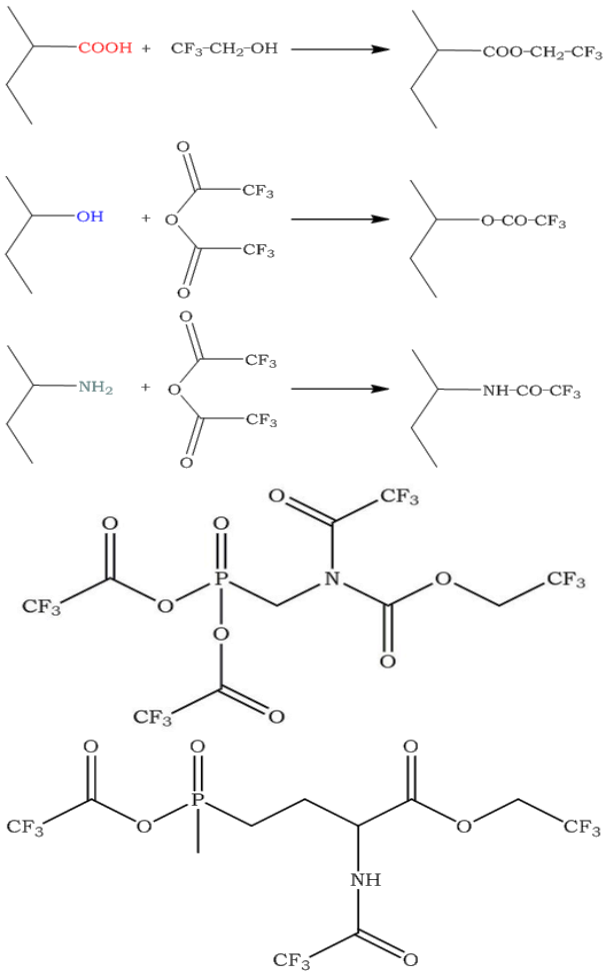


Figure 6. Derivatization of the COOH-, OH- and NH_2-moieties and the complete derivatized glyphosate and glufosinate (bottom)

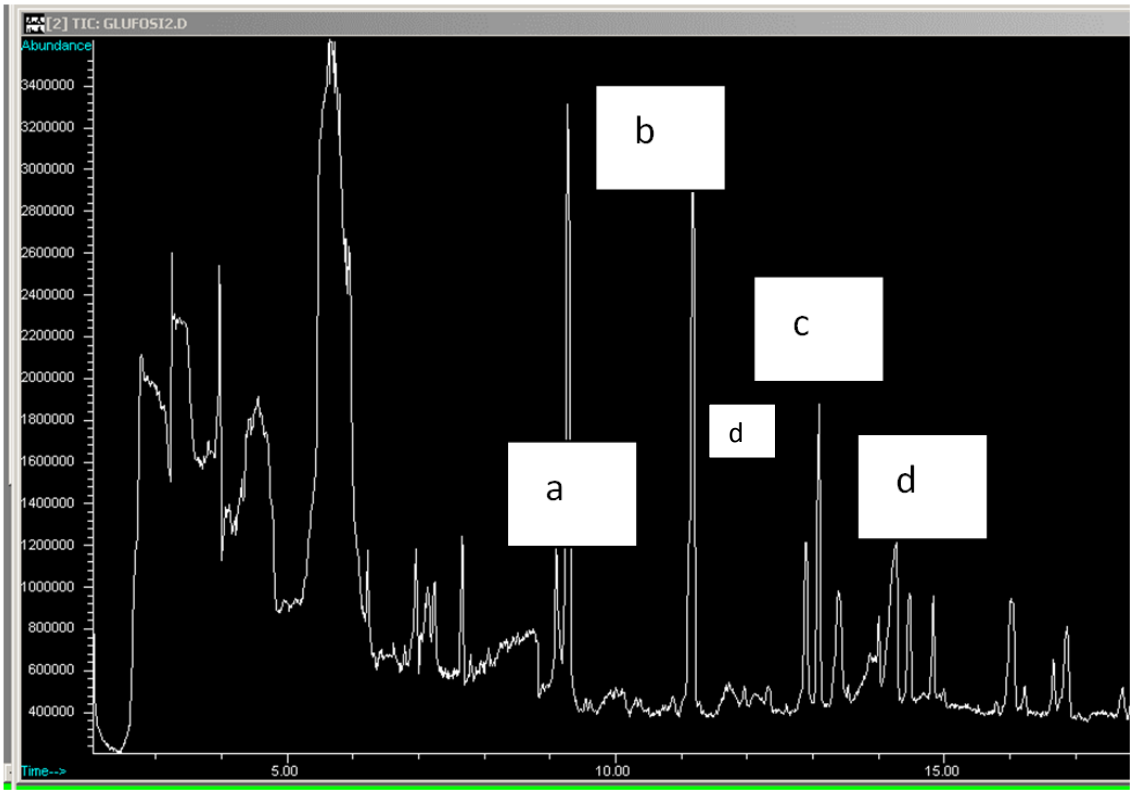


Figure 7. GC of derivatized glufosinate

Table 2 summarizes the main fragments of peaks a - d.

Table 2. Main EI (electron impact) peaks of the labeled GC peaks

	mass of the main EI fragments / amu
a	281
b	359, 267, 97, 69
c	429, 343, 325, 205, 147, 73
d	422, 314, 244, 192

Complete derivatization results in a molar mass of 455 amu. The main fragments are 359 amu (NH_2 not derivatized), 343 amu (without NH-CO-CF_3), 205 g/mol (without CF_3, CF_3, and NH-CO-CF_3), 192 amu (NH_2 not derivatized, without CF_3, without CH_2-CF_3, and without CH_3), 97 amu ($COCF_3$), 69 amu (CF_3).

Due to the manifold nature of the fragments it is not simple to completely interpret the EI-spectra.

3.2. EIS Spectrometry

Figure 8 shows the EIS of the $K_4[Fe(CN)_6]$ solution with Au-AT (blue line) and Au-AT decorated with graphene (red line).

Curve fitting shows that the charge-transfer resistance differs significantly from 118 (Au-AT) to 26.9 for Au-AT/graphene. Theoretical considerations must explain these results, but this goes beyond the scope of this paper.

Figure 9 shows the Bode plot of $K_4[Fe(CN)_6]$ with Au-AT and Au-AT / graphene.

The Bode plot, where the modulus of the impedance |Z| is plotted against the frequency, shows that |Z| is smaller for CNT with graphene (dashed curve) than without graphene (solid curve).

Therefore, the graphene-decorated Au-electrode is the electrode of choice for further measurements.

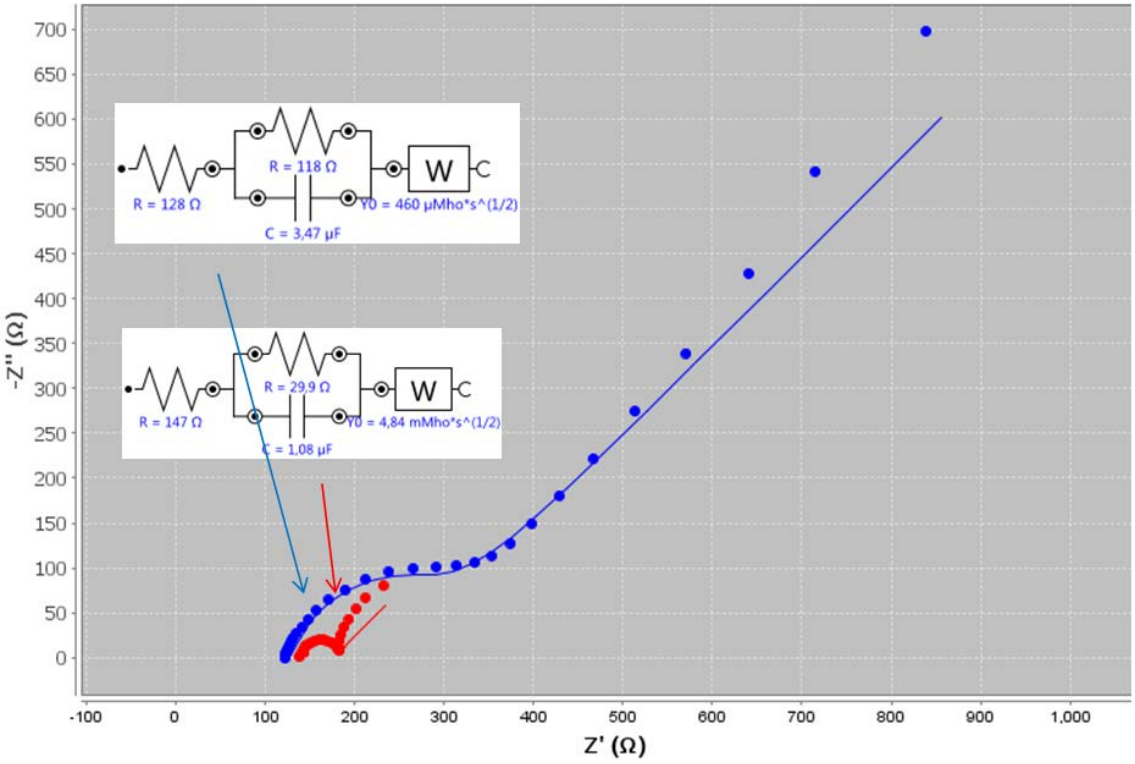


Figure 8. EIS of $K_4[Fe(CN)_6]$ solution with Au-AT (blue line) and Au-AT decorated with graphene (red line)

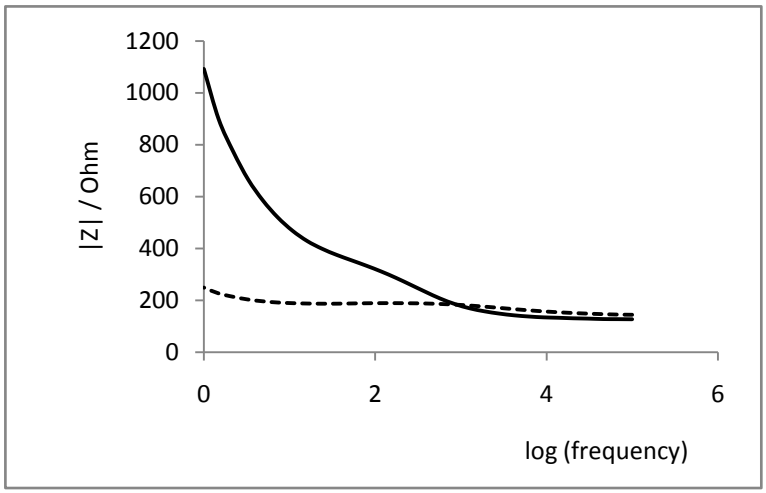


Figure 9. Bode plot. Solid line: CNT, dashed line: CNT with graphene

3.3. Production of Copper Glyphosate and Copper Glufosinate

Procedure

A mixture of 1 mmol copper sulfate and 1 mmol glyphosate (or glufosinate) in 10 mmol/L sodium sulfate were dissolved in 30 mL H_2O. The solution was dried in a furnace at about 60°C. The resulting product has a faint blue color (Figure 10). The color of Cu-glufosinate was quite similar.

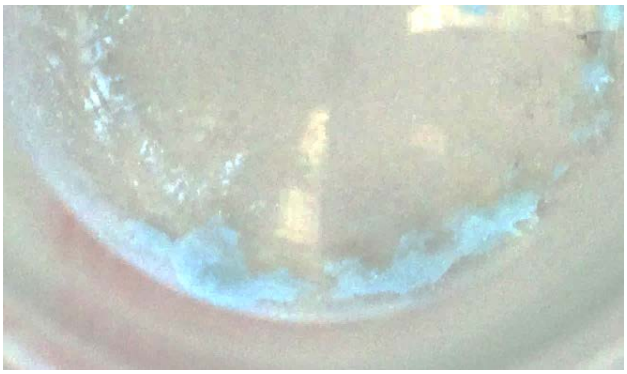


Figure 10. Cu-glyphosate

Figure 11 shows the UV-VIS spectra of copper glyphosate and copper glufosinate.

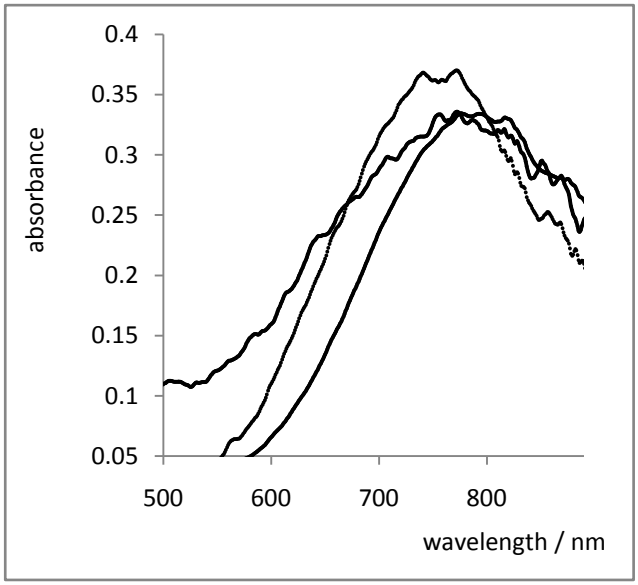


Figure 11. UV-VIS spectra of copper sulfate (solid line), copper glyphosate (dotted line), and copper glufosinate (dashed line)

Figure 11 shows that exchanging the ligands of copper (H_2O ↔ glyphosate ↔ glufosinate) results in minimal change to the spectrum. This is in line with the research of Daniele et al. [19].

3.4. Comparison between Cyclic Voltammogram and Reflection Measurement of Copper Glyphosate

60 L of copper glyphosate in a Na_2SO_4-solution (0.1 mol/L) was dropped onto the Au-AT-graphene electrode. The CV and the reflection spectrum (reflected light intensity at 460 nm as a function of the applied potential) were detected simultaneously. First, copper was deposited on the electrode at -1.0 V for 10 s. As Figure 12 shows, both the CV and the reflection correlate very well: Copper oxidation starts at about -0.2 V, resulting in an anodic peak. Simultaneously, the reflection changes (whether the light intensity increases or decreases depends on the angle of incidence of the light). In the reversed run Cu^{2+} was reduced to Cu and the reflection intensity returned to the initial state. The correspondence between CV and reflection becomes even clearer when the reflection spectrum is derived.

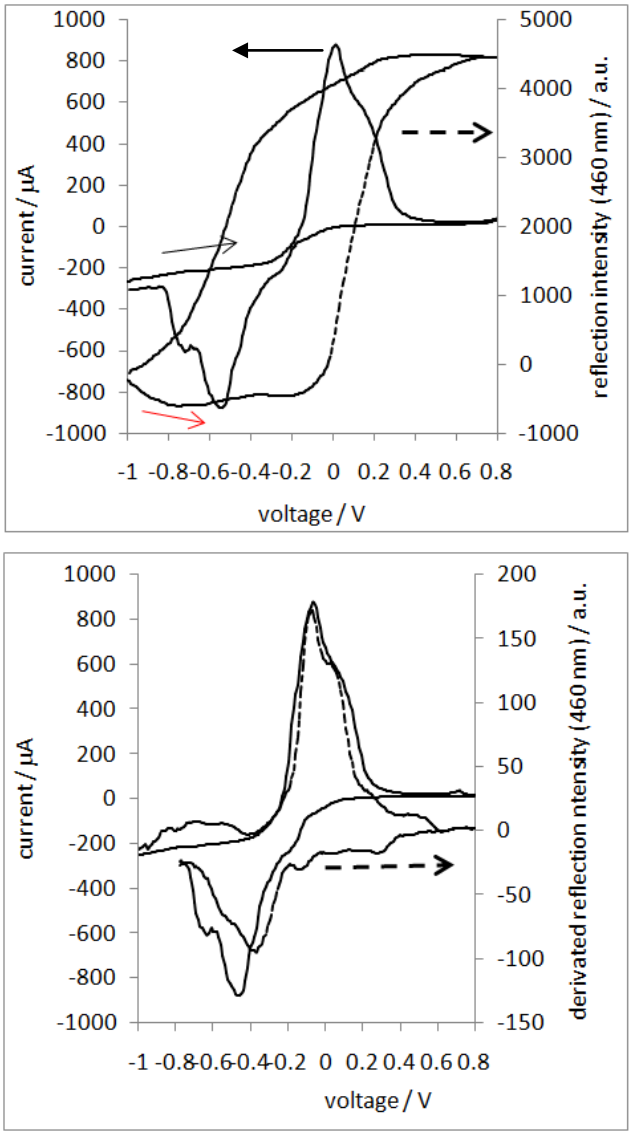


Figure 12. Top: Comparison of CV and reflection of 460 nm of copper-glyphosate (SPE: Au-AT). Bottom: derived reflection curve. pH about 6. Deposition voltage: -1.0 V, deposition time: 10 s.

3.5. Electrogenerated Chemiluminescence of Glyphosate, Glufosinate, and Their Copper Salts

A low-cost alternative to the photodiode presented above is a photomultiplier with a socket with integrated voltage amplifier (Figure 13).

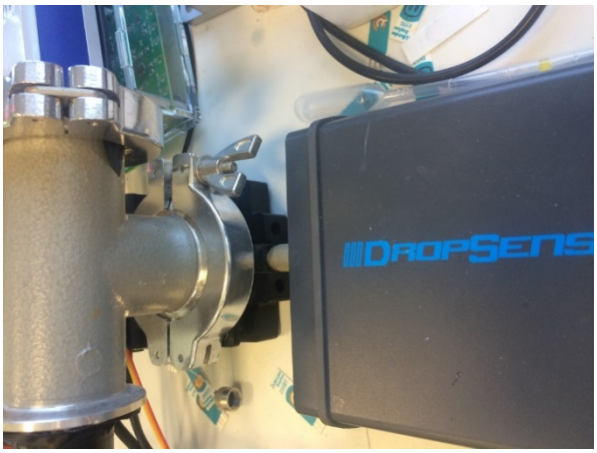


Figure 13. Left: Photomultiplier in a housing that protects against stray light directly above the SPE cell, right: potentiostat

The potentiostat employs the multipulse detection voltammetric method. A voltage pulse between 0 V and 1 V was applied several times to the working electrode covered with an aliquot mixture of $[Ru(bpy)_3]^{2+}$ and glyphosate (1 mmol/L). Current and ECL intensity were detected simultaneously. The duration of the pulses were 0.5 s, the repetition time was 2 s. Figure 14 shows the results. Over a long pulse sequence both current and ECL intensity changed only slightly. This means the ruthenium-glyphosate system is a very stable light source. The ECL intensity of ruthenium glufosinate is significantly lower, because the ECL of primary amines is usually lower than the ECL of secondary amines.

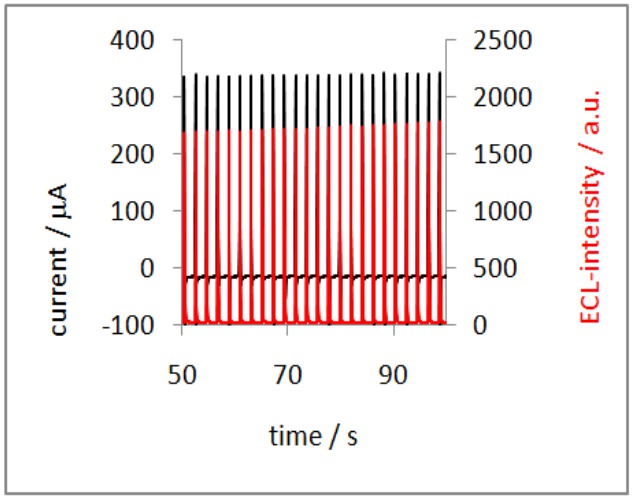


Figure 14. Current and ECL of $[Ru(bpy)_3]^{2+}$ / glyphosate with graphene decorated Au-AT-SPE

If the repetition time is short, the ECL intensity decreases within a few pulses, because the system does not have enough time to regenerate.

By adding ZnO to the electrode, the ECL increases by a factor of four, as Figure 16 shows.

The ECL intensity can be modulated by changing the start and end voltages. Increasing the start voltage up to about 1.2 V also increases the average ECL. Decreasing the end voltage also decreases the average voltage (Figure 17).

The ECL can also be recorded after spectral resolution. To do so, the entrance slit of a fiber spectrometer is placed directly above the SPE (Figure 18).

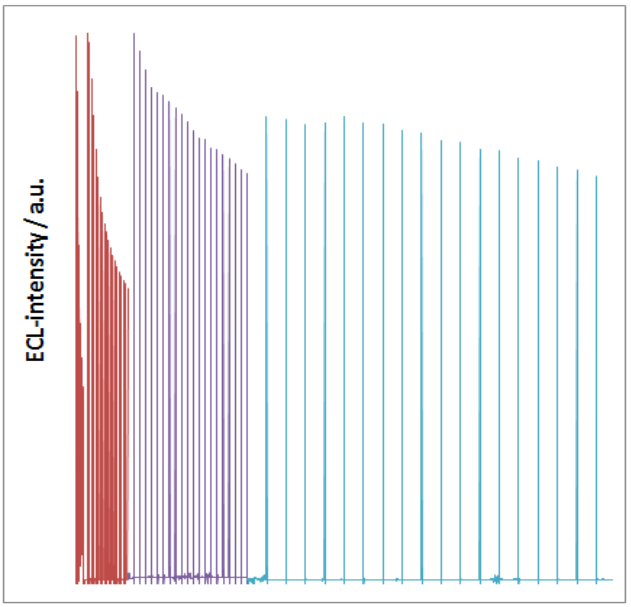


Figure 15. ECL at different repetition times. From left to right: 0.1 s, 2 s, 3.5 s, 10 s

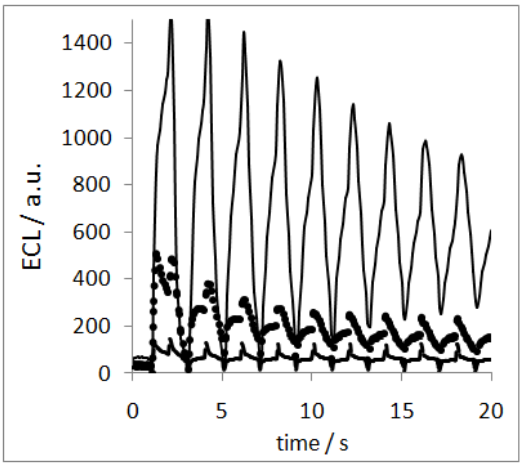


Figure 16. Multipulsing ECL with an Au-AT-graphene electrode with $[Ru(bpy)_3]^{2+}$ alone (dashed line), $[Ru(bpy)_3]^{2+}$ and glyphosate (dotted line) and $[Ru(bpy)_3]^{2+}$ / ZnO-decorated and glyphosate (solid line)

start	-0.5V →	-0.5V →	-0.5V →	-0.5V →	-0.5V →	1.2 V →	1.2V →
end	1.1V	1.0V	0.9V	0.8V	0.9V	1.0V	1.2V

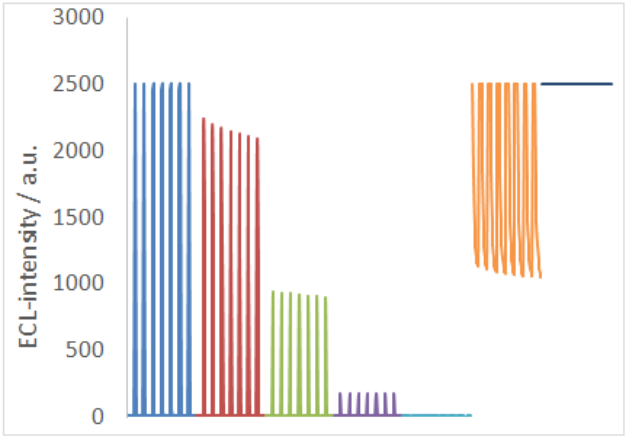


Figure 17. Modulation of the ECL by changing start and end voltage

Figure 18. Fiber spectrometer with entrance slit above the cell containing the SPE. Right: Potentiostat.

Figure 19 shows both the CV and the spectrum-resolved ECL.

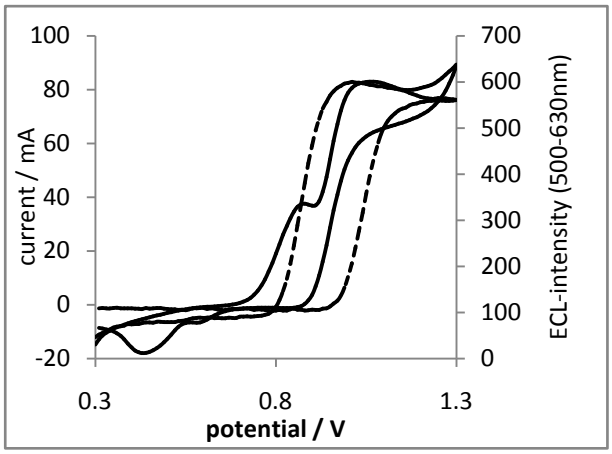


Figure 19. CV (solid line) and spectrum-resolved ECL (dashed line)

To extend the ECL spectrum Nile red was added to the $[Ru(bpy)_3]^{2+}$ solution. Figure 20 shows the fluorescence of Nile red alone and the total spectrum of the mixture. In addition, the spectrum of the mixture was mathematically unfolded because both spectra of [Ru(bpy)3]2+ and Nile red are easier to see.

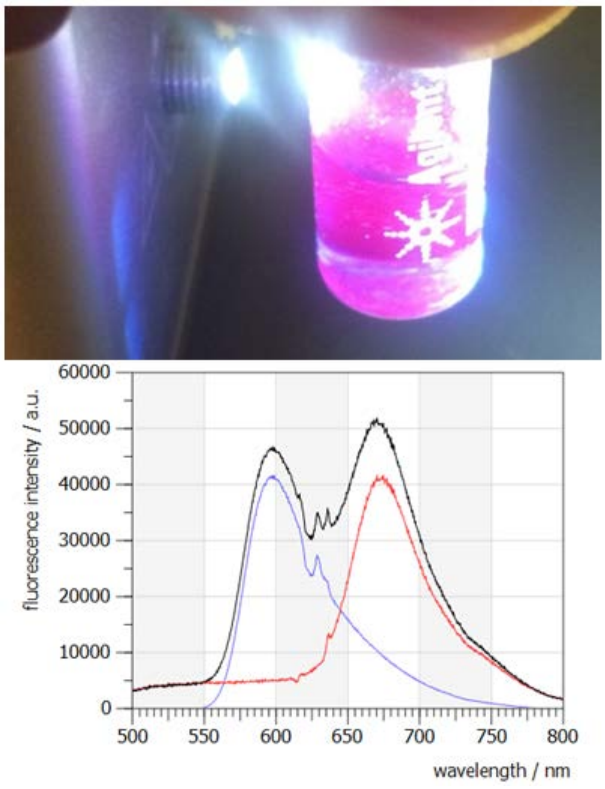


Figure 20. Top: Fluorescence $[Ru(bpy)_3]^{2+}$ with Nile red, excited by a 460 nm LED, Bottom: Fluorescence spectrum of the mixture: blue curve: fluorescence $[Ru(bpy)_3]^{2+}$, red curve: fluorescence of Nile red, black curve: fluorescence of the mixture

Several proposals for detecting glyphosate and glufosinate via color detection can be found in the literature [23]. A method has also been proposed using carbon disulfide to convert the GLY amine group into dithiocarbamic acid. The dithiocarbamate byproduct is then used as a copper-chelating group that results in a yellowish-colored complex used for measurements [46].

Chang and Liao indirectly detected glyphosate and glufosinate by quenching fluorescein [47].

Besagarahally et al. [48] oxidized a mixture of glyphosate and ninhydrin with Na_2MoO_4. After heating, water splits off and a purple colored product is formed (Ruhemann's purple) (Figure 21).

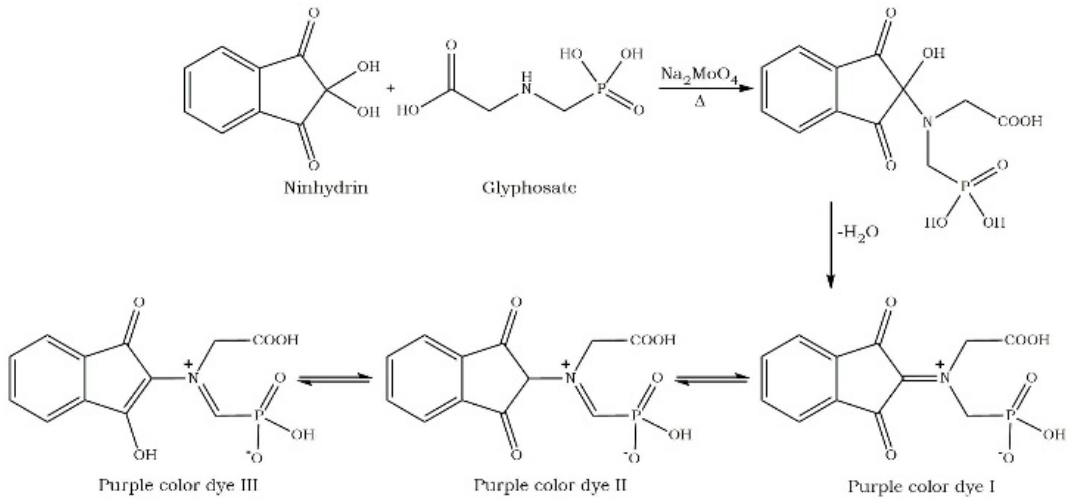


Figure 21. Reaction scheme of the reaction of ninhydrin and glyphosate in the presence of Na_2MoO_4 as oxidizing reagent: Formation of Ruhemann's purple

Although the reaction works well with glyphosate, it fails with glufosinate. This is perhaps due to the less reactive amino group of glufosinate. But heating alone results in a purple discoloration (Figure 22).

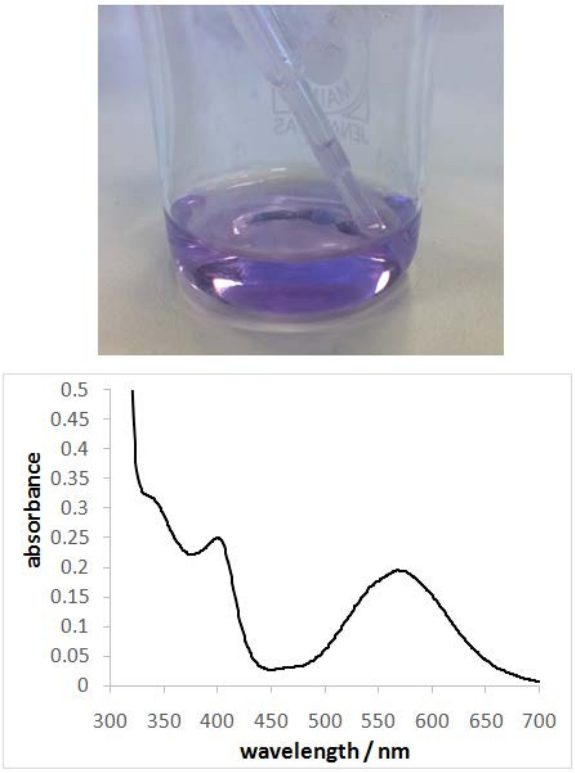


Figure 22. Top: Color of the reaction product of glufosinate with ninhydrin. Bottom: Absorption spectrum.

3.6. FTIR Spectra of Glyphosate, Cu-Glyphosate

In the glyphosate complex, several units may be involved in the binding with copper: the carboxylate group, the amino group, and the PO_3^{2-}-group. Undabeytia et al [49] analyzed the IR spectra at two different pH values and interpreted that the carboxylate and phosphonate groups interact with copper. The authors were unable to determine if the amino group was involved in the complexation. Following Undabeytia and Sheales [49,50], Figure 23 shows the change in COO^- and PO_3^{2-} vibrations of glyphosate by complexation with copper (see arrows in Figure 23).

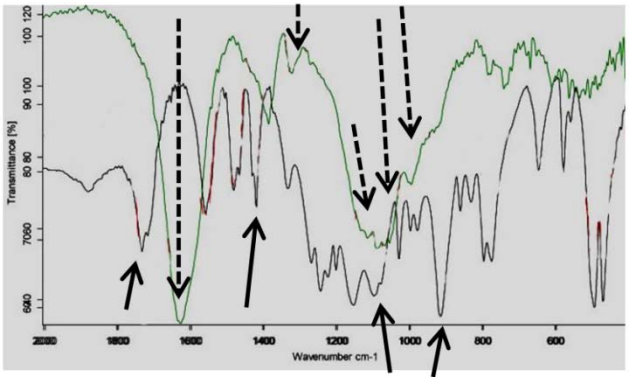


Figure 23. FTIR spectra of glyphosate (black line) and Cu-glyphosate (green line). Solid arrows: vibrational modes of glyphosate, dashed, inverted arrows: vibrational modes of the Cu-glyphosate complex

Table 3. Infrared band assignments (cm^{-1}) for glyphosate and Cu-glyphosate [49,50,51]

assignment	glyphosate (pH 7) solid arrows	Cu-glyphosate (pH 7) inverted, dashed arrows
ν_{asym} (COO^-)	1732	1625
ν_{sym} (COO^-)	1405	1385
ν_{asym} (P-O^-) PO_3^{3-}	1091	
ν_{sym} (P-O^-) PO_3^{3-}	979	
ν (P-O^-) PO_2(OCu)		1144, 1091, 1033, 994

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