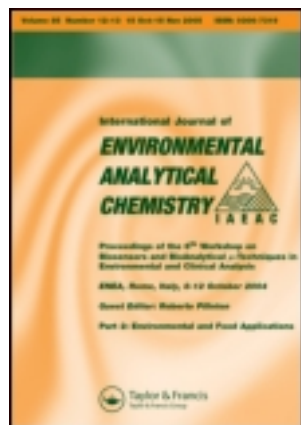


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DETERMINATION OF HERBICIDE RESIDUES BY LASER MICROPROBE MASS ANALYSIS (LAMMA)

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Diffusion of herbicide residues and derived substances in ecosystems can arise from agrochemical treatments, depending on environmental interactions and the chemical characteristics of the parent molecules and their degradation products. As adsorption phenomena affect both herbicide residues and their metabolites, a complete extraction and identification of them is very difficult with traditional methods. Laser ablation could be an effective system of analysis of herbicides on solid surfaces (soil, leaves) especially in the presence of degraded residues and several by-products. Acifluorfen, a diphenylether herbicide, and rimsulfuron, a sulfonylurea herbicide, were irradiated with a Nd:YAG laser at 266 nm. The decomposition fragments were detected by using a time-of-flight mass spectrometer. This technique allows the identification of stable ions useful for a better determination of the analytes. Fragments derived from a decarboxylation reaction and cleavage of the ether function of acifluorfen were obtained. In the case of rimsulfuron, fragments deriving from the pyrimidine ring, such as 2-amino-4,6-dimethoxypyrimidine, were detected.

Keywords: Herbicides; Acifluorfen; Rimsulfuron; Laser ablation; Time-of-flight mass spectrometry

INTRODUCTION

During herbicidal treatments, chemicals can be distributed both on the soil surface and plant leaves, forming a thin aqueous layer. With the evaporation of water, which happens particularly quickly in sunny areas and seasons, the crystallized substances remain exposed to solar irradiation. In these conditions hydrolysis and photolysis reactions can rapidly arise and compete with sorption of these chemicals onto either soil or waxy and fatty substances which cover the surface of leaves. It is foreseeable that the formation and distribution of unknown metabolites in the environment will depend on the reactions and chemical and physical characteristics (vapour pressure, light absorption, coefficients of repartition, solubility) of parent molecules and their derivative substances.

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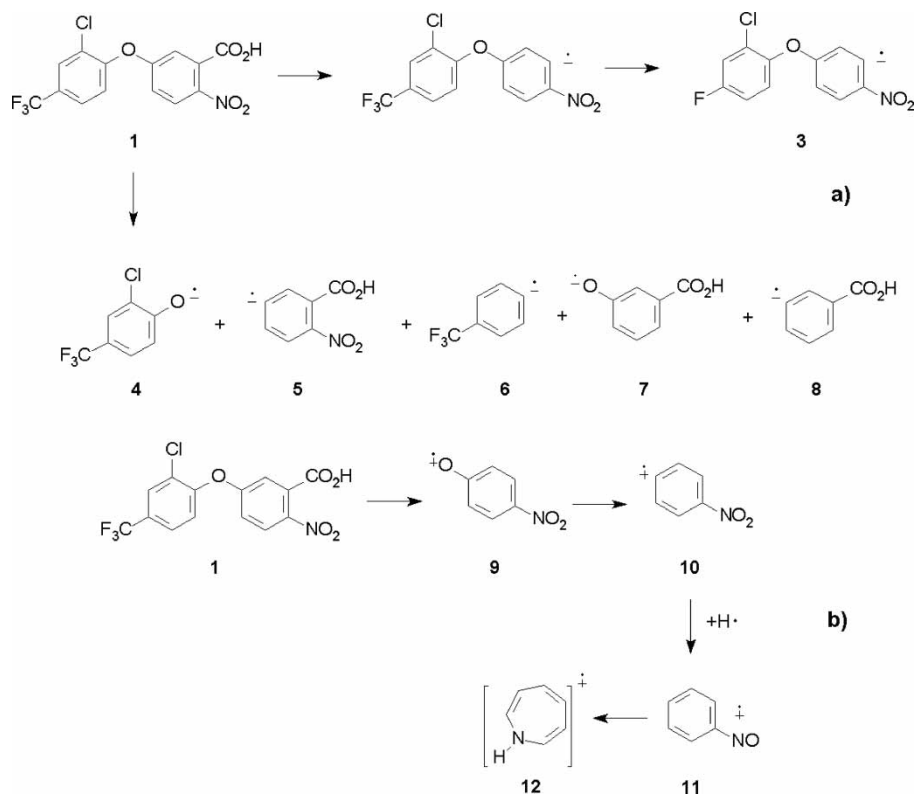
As sorption phenomena affect both herbicide residues and their metabolites, exhaustive extraction and identification of them could be very difficult with traditional methods. Laser ablation, avoiding classical extraction procedures, can offer a new system of herbicide analyses on solid surfaces (soil, leaves) especially in the presence of degraded residues and/or when several by-products are formed [1]. Moreover, mass spectrometry is particularly attractive for trace analysis as it allows the identification of stable fragments for better qualitative determination of target substances.

This article deals with the application of laser ablation and time-of-flight mass spectrometry to the identification of characteristic fragment ions of two widely used herbicides: acifluorfen and rimsulfuron.

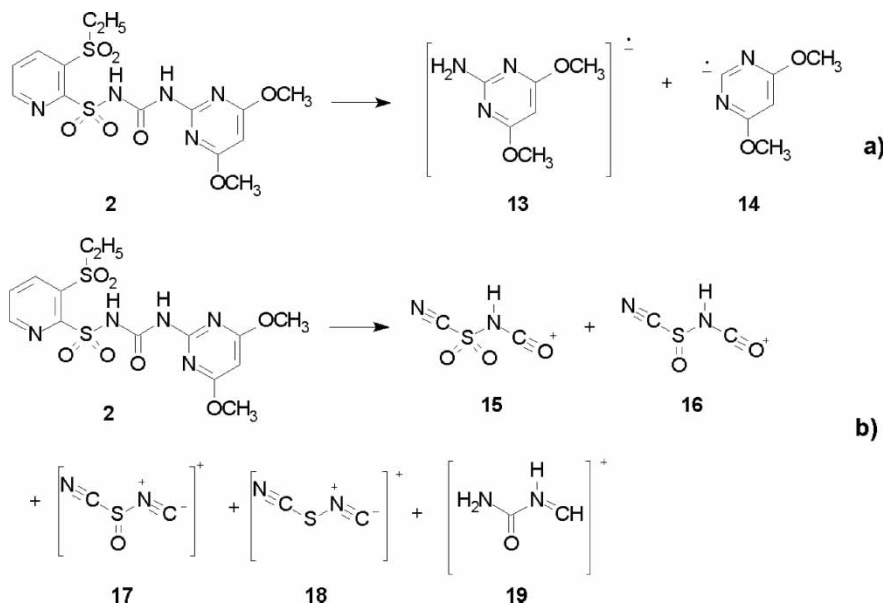
Acifluorfen **1** (Scheme 1), 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid, is a nitro-diphenylether herbicide that acts as a protoporphyrinogen oxidase inhibitor and is used at a rate of 0.38–0.6 kg of active ingredient per hectare to control monocotyledonous and broad-leaved weeds. The solubility in water is 120 mg L⁻¹. It has acute oral toxicological effects on mammals with oral LD₅₀ between 1370 and 2050 mg kg⁻¹ in rats, and moderate fish toxicity between 17 and 61 mg L⁻¹ [2].

This class of herbicides requires light to exhibit phytotoxic activity [3] and under irradiation can give rise to several photodegradation products [4].

Photolysis of acifluorfen has previously been studied in liquid phases [5–7], but data on its degradation and derivative formation in an adsorbed state are not available.



SCHEME 1 Proposed fragments arising from acifluorfen laser ablation – TOF mass spectrometry in (a) negative mode and (b) positive mode.



SCHEME 2 Proposed fragments arising from rimsulfuron laser ablation – TOF mass spectrometry in (a) negative mode and (b) positive mode.

Rimsulfuron **2** (Scheme 2), *N*-{[(4,6-dimethoxy-2-pyrimidinyl)amino] carbonyl}-3-(ethylsulfonyl)-2-pyridinesulfonamide, is a selective sulfonylurea herbicide for the post-emergence control of weeds in many crops [8]. The mode of action of this herbicide is related to the inhibition of acetolactate synthase, an enzyme involved in branched-chain amino acid biosynthesis in plants [9].

Recently, the degradation of rimsulfuron has been studied and some degradation products have been detected [10, 11].

Rimsulfuron is a white odourless solid, solubility $< 10 \text{ mg L}^{-1}$ in distilled water and 7300 mg L^{-1} in buffer solution at pH 7; $\text{p}K_a = 4.1$; $K_{ow} = 0.034$ at pH 7; vapour pressure $= 1.1 \times 10^{-8} \text{ Torr}$ at 25°C . It has little or no toxicological effects on mammals, with oral $\text{LD}_{50} > 5000 \text{ mg kg}^{-1}$ in rats and with dermal $\text{LD}_{50} > 2000 \text{ mg kg}^{-1}$ in rabbits [9, 10].

EXPERIMENTAL

Acifluorfen and rimsulfuron pure standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany). A commercial LAMMA (Laser Microprobe Mass Analyser) 500 instrument from Leybold-Heraeus (San José, CA) was employed. A very intense pulse from a Nd:YAG laser ($\tau = 6 \text{ ns}$) was frequency quadrupled ($\lambda = 266 \text{ nm}$) and tightly focussed on the sample. Powder samples (pure standards) of **1** and **2** were directly spread onto an electron microscope grid, covered with a quartz plate and inserted into the sample stage. Irradiation of the sample was performed in a vacuum chamber at a pressure of about 10^{-6} Pa and at a laser power between 10^8 and 10^9 W cm^{-2} . Data were averaged over several spectra.

RESULTS AND DISCUSSION

In laser ablation mass spectrometry (LAMS) a laser beam is focussed onto a solid target, and the ions produced are accelerated and detected by a time-of-flight (TOF) mass spectrometer. The high power density of the laser beam allows complete vaporisation of every kind of material, so this technique is very useful for qualitative analysis [12]. Nevertheless, a quantitative analysis requires a knowledge of the ionisation efficiency and detector response for each analyte present in the target [13]. A similar applications of LAMS can be found in the study of the photodissociation reactions of herbicides [14,15] leading to identification of the dissociation patterns and related products.

In our experiments we did not observe effects due to the laser intensity. The only particular feature of the mass spectra recorded at low fluence is the low peak intensity.

Figure 1 collects our results on acifluorfen. Figure 1(a) shows the negative-ion mass spectrum. The molecular peak of the parent compound ($m/z \sim 361$) was not observed. The highest recorded m/z value was 266; this ratio is attributable to the presence of ion **3** (Scheme 1a), which can be rationalised in terms of two dissociation steps. First the

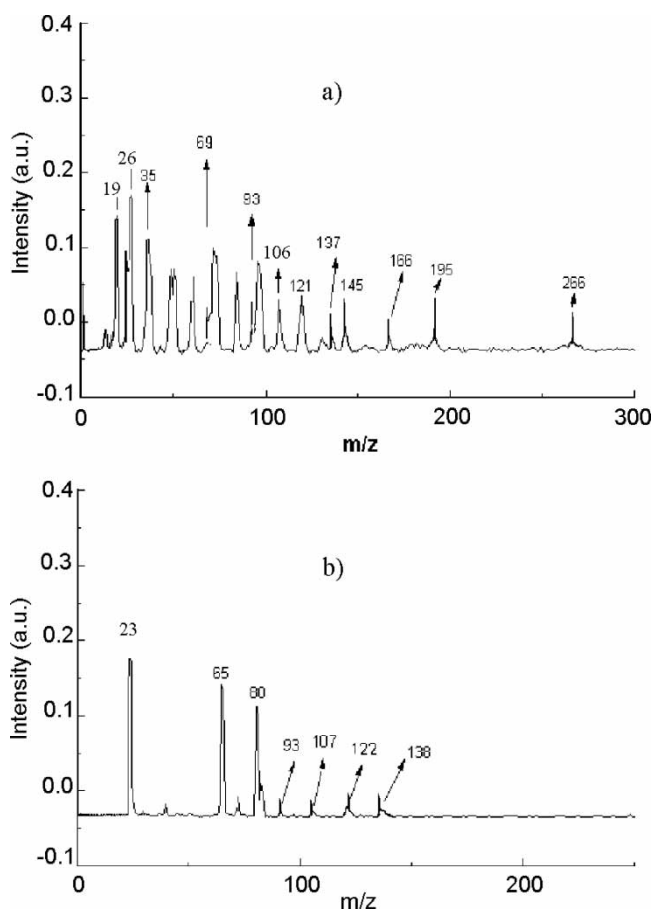


FIGURE 1 TOF mass spectra of acifluorfen laser ablation products in (a) negative mode and (b) positive mode.

molecule, or $[M-H]^-$ ion, loses the carboxylic group, as CO_2 , then a rearrangement on the trifluoromethyl group occurs to give the fluoroaryl derivative with the loss of CF_2 . The peak at m/z 195 (Fig. 1(a)) could correspond to the phenoxy derivative **4** (Scheme 1a). Other fragments were observed at: m/z 166, identifiable as the ionized *o*-nitrobenzoic acid **5**; m/z 145, the trifluoromethyl derivative **6**; m/z 137, the phenoxy derivative **7**; m/z 121, the phenyl derivative **8** (Scheme 1a). Smaller m/z values, which could be ascribed to other stable ionic fragments (high intensity peaks with $35 < m/z < 121$, in Fig. 1(a)), are not considered in this discussion because they can derive from several fragmentations of naturally occurring organic compounds and cannot be identified as characteristic acifluorfen derivatives or degradation products in the environment. Peaks at m/z values of 19, 26 and 35 can be ascribed to F^- , CN^- and Cl^- ions, respectively.

On the basis of these results, the main fragments obtained by laser ablation of acifluorfen can be rationalised as arising from two processes: loss of the carboxylic function and cleavage of the ether bridge.

This proposal is supported by analysis of the mass spectrum of positive ions (Fig. 1b). As in the negative mode, the spectrum of ionised positive fragments does not show the signal of the parent molecule; however, a peak at m/z 138 can be attributed to **9** (Scheme 1b). Peak assignments, together with a mechanism of formation of each fragment, are proposed as: loss of an oxygen atom from ion **9** leads to fragment **10**, observed at m/z 122; through a subsequent de-oxygenation and simultaneous addition of a hydrogen atom, ion **10** gives fragment **11** at m/z 107; finally, loss of another oxygen atom gives rise to ion **12** at m/z 93. The peak at m/z 80 could arise from **11** through loss of HCN; the same fragmentation could lead to the ion at m/z 65 starting from **12**. The intense signal at m/z 23 is due to Na^+ ions, which are often present as an impurity in positive-ion mass spectra. In this case also the observed ions derive from cleavage of the carboxylic group and from fragmentation of the ether bridge.

Laser ablation of rimsulfuron gave the mass spectra shown in Fig. 2. The mass spectrum in negative mode showed peaks at m/z 155 and 139 (Fig. 2a), but not the peak corresponding to the parent molecule ($m/z \sim 431$). We propose the formation of fragments as follows: the peak at m/z 155 can be attributed to ion **13** (Scheme 2a), and the signal at m/z 139 to ion **14** [$155 - NH_2$]. Other peaks shown in Fig. 2(a) are not relevant for the identification of characteristic fragments of rimsulfuron. It is noticeable that the pyridine fragment did not give stable negative signals.

Figure 2(b) shows the spectrum recorded in positive mode. The fragment at m/z 133 can be attributed to **15** (Scheme 2b). This assignment is consistent with the fragments observed at lower m/z values. Thus, ion **16**, at m/z 119, can arise through the expulsion of an oxygen atom from fragment **15**. Furthermore, by losing an oxygen atom, ion **16** can transform into fragment **17**, at m/z 103, which, *via* elimination of an oxygen atom, can be converted into ion **18** at m/z 87. Finally, the signal at m/z 72 can be attributed to ion **19**. Other intense peaks in Fig. 2(b) are due to smaller ions of minor concern.

The results described above allow us to consider application of the laser ablation method to the detection of herbicides. Literature data on acifluorfen degradation in aqueous solution show the formation of several derived compounds [6,7]. Laser irradiation permitted the identification of two characteristic fragments at m/z 195 (**4** in Scheme 1a) in negative mode, and m/z 138 (**9** in Scheme 1b) in positive mode, which are always present in mass spectra of environmental samples of this herbicide [7].

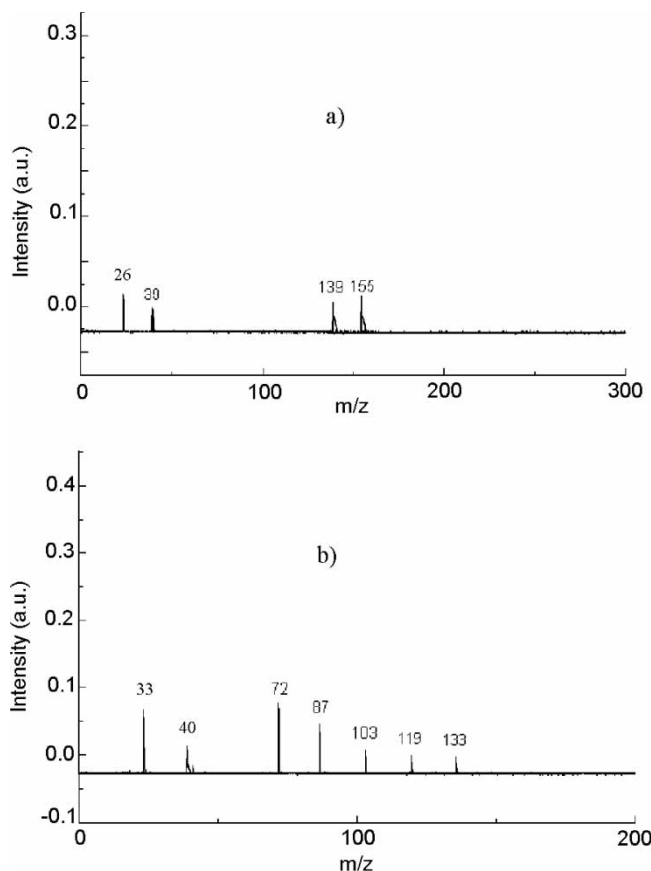


FIGURE 2 TOF mass spectra of rimsulfuron laser ablation products in (a) negative mode and (b) positive mode.

In relation to rimsulfuron detection, a characteristic stable fragment (**13** in Scheme 2a) was identified. It is the smallest among the degradation products previously found by Schneiders *et al.* [10] and Scrano *et al.* [11]. This fragment, observed in negative mode, was always found in spectra obtained from different samples of environmental concern in both the liquid phase and in the adsorbed state [10,11]. On the contrary, fragments among those revealed in positive mode (Scheme 2b) were never indicated in the literature as useful for the identification of rimsulfuron residues or metabolites in real samples. Equally, fragments shown in Scheme 2b cannot be considered as characteristic for rimsulfuron detection as they can also arise from many substances commonly present on soil and leaf surfaces.

CONCLUSIONS

The laser ablation technique allowed the identification of stable ions useful for the determination of herbicide residues in solid samples. Detection of 2-chloro-4-(trifluoromethyl)phenoxy and 4-nitrophenoxy ions for acifluorfen, and the 2-amino-4,6-dimethoxypyrimidinyl derivative for rimsulfuron, was shown to indicate the presence

of these two herbicides. The detection method offered in this paper avoids the classical time-consuming and environmentally appropriate extraction procedures, and gives good analytical results in qualitative determinations of herbicide residues and metabolites.

We think that the use of laser ablation technique can usefully contribute to data collection for enhancing the level of knowledge on the behaviour of chemicals of ecological concern. For this reason we are running two sets of samples for qualitative determination of several herbicides: the first has been obtained from cropping fields in which herbicidal treatments were carried out; the second has been prepared in the laboratory by sorbing herbicides on either soil constituents (siliceous materials, clay minerals, humic substances) or plant tissues (leaves).

Acknowledgement

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