Make sure you know what you're dealing with!

Analysis of phenoxypropionic herbicides using LCMS

Newly developed components increase the sensitivity of the LCMS-2010

In recent years, pesticides have been used with much greater care and more restraint. Increasing scientific evidence as well as improved detection methods have played an important role. In agriculture, users have changed their general attitude towards herbicides, fungicides and pesticides. Continuous control and analysis of pesticides should be a matter of routine. As knowledge and detectability will further increase in the future, the old saying, „Make sure you know what you're dealing with!" will, as always, remain applicable in the positive sense.

The so-called phenoxy herbicides have been on the market since the 1940's. These, at the time new, types of pesticides proved to be fast-acting and very effective. Even today, phenoxypropionic herbicides (such as fluazifop, fluazifopbutyl and quizalofopethyl) are still being used in agriculture worldwide, as they possess strong herbicidal properties. The mode of action is based on the disruption of the biosynthesis of fatty acids via the inhibition of the acetyl-CoA carboxylase enzyme.

Some types of the phenoxy herbicides received a bad reputation through their use as a military defoliant (Agent Orange), during the Vietnam War. The welldocumented damaging after-effects for the population did not, however, originate from the herbicide itself. One of the components of Agent Orange was contaminated with a high concentration of dioxin. With each gram of the herbicide mixture sprayed, up to 50 micrograms of the highly toxic dioxin was being applied simultaneously.

Today, the use of modern phenoxy herbicides, such as fluazifop, is allowed in the cultivation of medicinal plants and herbs under very strict conditions for the control of weeds. In addition to their high effectiveness, these herbicides distinguish themselves by an extraordinarily low toxicity to mammals. Poisoning can only occur after exposure to very high levels of these compounds resulting from careless storage or negligent maintenance.

Recently, however, the potential hormonal action of biocides and pesticides is under critical discussion. As fluazifop-P belongs to the biocides that are suspected of hormonal action, an efficient control of the pollution levels of foods by herbicide residues is therefore imperative.

Residue analysis using LCMS

The phenoxy herbicides are normally used as a salt of the phenoxycarboxylic acid (for instance fluazifop) or an ester (fluazifop-butyl). Residue analysis for quizalofop is routinely carried

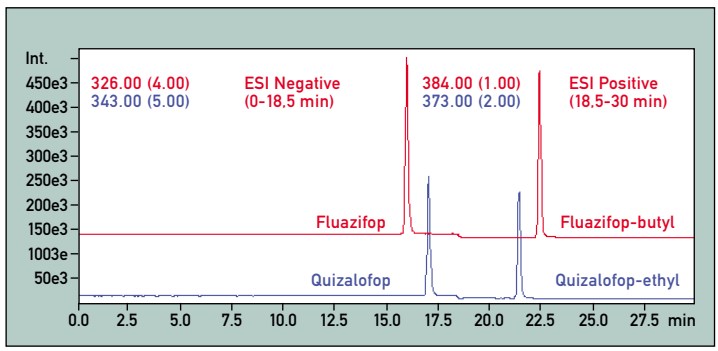

Figure 1: Simple LCMS analysis: allows the simultaneous determination of several phenoxy carboxylic acids

out using HPLC /LCMS and for fluazifop using GC/GCMS.

Figure 1 illustrates a simple LCMS method using the single quadrupole LCMS-2010 system, which allows the simultaneous determination of fluazifop, fluozifopbutyl and quizalofop and quizalofopethyl. Electrospray ionisation (ESI) at atmospheric pressure was used as the ionisation method. The carboxylic acid types are ionised in the negative ionisation mode, the ester types in the positive ionisation mode. In the separation of herbicides using reversed-phase liquid chromatography, the ester types elute much later then the free acids. When the MS detector is switched from the negative to the positive ionisation mode, after elution of the acids, all different herbicide species can be detected simultaneously with excellent sensitivity.

Figures 1 and 2 show the chromatograms of four herbicides detected in the SIM mode and the corresponding mass spectra with their characteristic masses. By using a semi-micro C18 HPLC column, the sensitivity of the method could be increased significantly, resulting in a calibration of 0.8 up to 500 ppb with excellent linearity for each compound. This is shown in Figure 3 for fluazifop (M/z 326).

The excellent separation of compounds using this method leaves room for further method optimisation in order to reduce the total analysis time. In terms of instrumentation, further development into a fast HPLC/MS method is certainly possible, making use of the fast switching times of the LCMS-2010 in multi-sequence mode and using the faster SIL-HT autosampler (15 s per standard injection).

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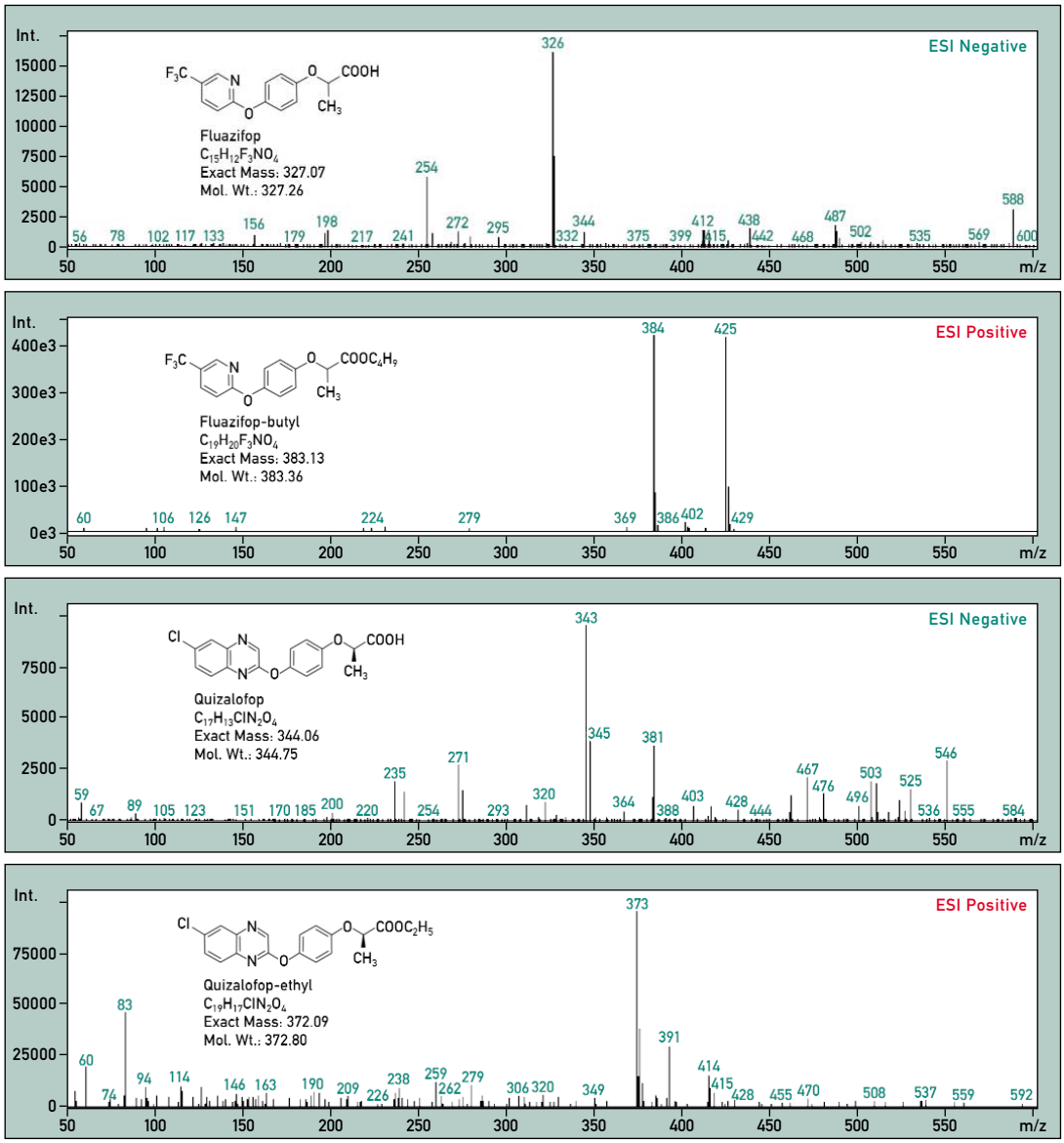

Figure 2: Chromatograms of four herbicides in the SIM-mode with their characteristic masses

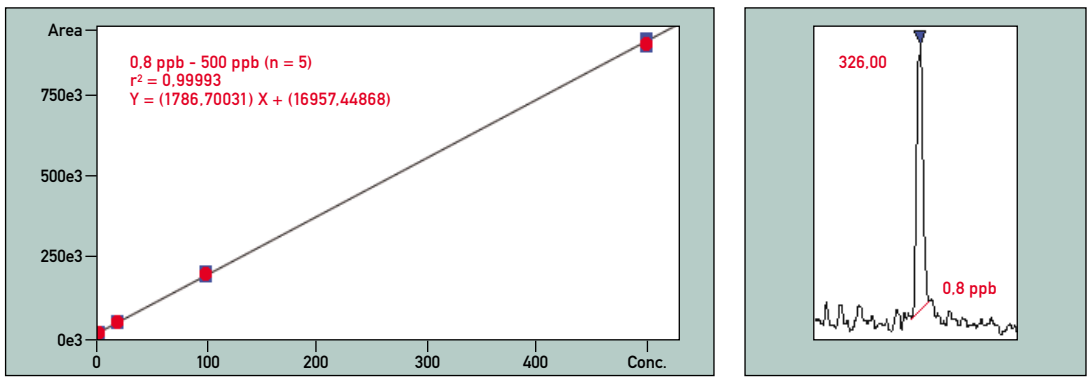

Figure 3: Linearity and sensitivity for the analysis of fluazifop