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ARTICLE

Data Processing Approach for the Screening and Quantification of Pesticide Residues in Food Matrices for Early-Generation Gas Chromatography Time-of-Flight Mass Spectrometry

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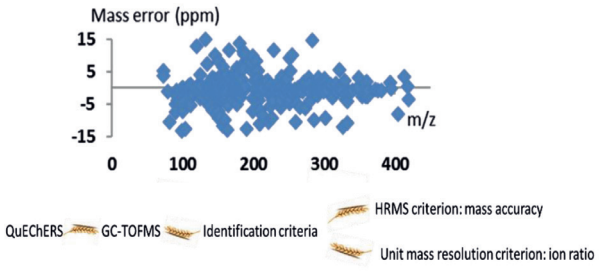

The application of high-resolution mass spectrometry (HRMS) in pesticide residue analysis is gaining popularity worldwide. Upgrading from early-generation gas chromatography time-of-flight mass spectrometry (GC-TOFMS) to higher resolution analysers is quite challenging, economically wise, for third countries' laboratories. Given the insufficient resolution of 12000 full width at half maximum (FWHM) or less offered by GC-TOFMS, meeting the HRMS identification requirements in some *Analytical Quality Control* guidelines may be challenging. This paper presents a useful approach for GC-TOFMS data processing for the screening and quantification of pesticide residues in cereals for laboratories disposing of that same equipment. The data obtained from spiking four types of cereals (wheat, rye, rice, and barley) at three different concentrations, 0.01, 0.02, and 0.1 mg kg^{-1} were evaluated with an "in-house" accurate-mass database of 102 pesticides, on the basis of two processing approaches. The data were first evaluated by considering the identification criteria in HRMS, which consists of the detection of two fragment ions of mass ≤5 ppm. The screening detection limits in that case were above 0.1 mg kg^{-1} for 25% of the compounds, owing to the high mass error (> 5ppm) obtained for some ions at low levels. The unsatisfactory results obtained were examined, and the data were re-evaluated by comparison with injected standards for identification (ion ratio). With this validated approach, the screening detection limit achieved for 85% of the compounds was 0.01 mg kg^{-1}. Therefore, given the insufficient resolving power of the instrument for some pesticide/commodity pairs, the HRMS requirement of 12000 FWHM in TOFMS was demonstrated to be inapplicable. Consequently, we recommend applying the requirements for identification of unit mass resolution for these specific mass spectrometers, to ensure accurate screening and quantification.

Keywords: Cereals, pesticide residues, mass accuracy, resolving power, screening detection limit, data processing.

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INTRODUCTION

The last true paradigm shift in the field of screening of pesticide residues in food was the shift from low-resolution mass spectrometry to high-resolution mass spectrometry (HRMS). HRMS enables broad-spectrum analysis and the collection of full scan spectra with excellent mass accuracy and mass resolution. Because of the variety and complexity of food matrices and the different matrix/pesticide combinations that may be present, accurate mass information by HRMS is required for good selectivity and identification capabilities. High-resolution analysers can resolve the ions of interest from most possible interferences originating from both matrix ions and the chemical background in complex samples. However, Balogh [1] has noted that the sensitivity decreases as the mass resolving power is increased in ToF analyzers, and the argument for higher mass resolution does not become persuasive until the molecular weights being measured become significant. A higher resolution is theoretically a better option in the presence of co-eluting isobaric compounds.

Numerous applications of HRMS in the literature indicate that this technique is highly suitable for screening pesticide residues in various food matrices [2,3]. Time-of-flight mass spectrometry (TOFMS) is a valuable approach that operates in full scan mode and can be combined with the development of an accurate-mass database for screening purposes; it has led to substantial improvements in food monitoring. GC-TOFMS is a powerful tool for screening pesticide residues in fruits and vegetables at a resolving power between 12500 and 18000 FWHM [4-7].

With the availability of GC-Orbitrap-MS, Mol *et al.* [8] have evaluated and demonstrated the efficiency of the full scan at a resolving power of 60000 FWHM in fruits and vegetables. The efficiency of a full scan with GC-Orbitrap-MS operated at a resolving power of 17500 FWHM for the analysis of pesticide residues in complex matrices, such as spices, has been described [9]. GC-Orbitrap-MS (resolving power: 100000 FWHM) is also effective in the analysis of pesticide residues in matrices that are difficult to analyse, such as wheat, maize and animal feed [10]. Thus, in the literature, a resolution ranging between 17500 and 100000 FWHM has been found to allow screening of pesticide residues in various matrices. However, generally, the more complex a sample extract is to analyse, the higher the resolution power is needed [11] to avoid false positive detection. If resolving power is a limitation, the sample preparation may be optimized for complex samples to decrease the complexity.

Cereals are known as difficult/dirty dry matrices with a fat content varying from 2% (e.g., wheat) to 6.5% (e.g., oats) [12]. Sample preparation aims to decrease potential chemical interference and consequently the resolution requirements. However, even with the latest extraction methods, because of the development of multiresidue methods aiming to cover as many compounds as possible, a certain resolving power is necessary to distinguish isobaric compounds in difficult matrices such as cereals. Maximum residue limits (MRLs) for cereals have been established by the European Union (EU) in Directive 32/ EC for 353 pesticides, at values between 0.01 and 0.1 mg kg^{-1} for 94% of the compounds [13]. Therefore, low screening detection limits (SDLs) and limits of quantification (LOQs) are essential to fulfil the MRL requirements.

In this paper, the use of high-resolution full scan GC-TOFMS as a screening and quantification platform for pesticide residue analysis in cereals is described and evaluated. Compound identification was performed with an in-house updated high-resolution accurate mass database covering 102 pesticides. The 102 pesticides selected are not among the most frequently found pesticides (only 15 compounds are included in the European Union multi-annual monitoring program), hence the relevance of their use in testing the screening method. The European Union monitoring program and the European Union member states focus on the control of pesticides and the commodities that contribute most to the dietary intake of pesticides. Though new pesticides are authorised and illegal uses occur and it is therefore relevant to supplement the control programmes with a wide scope screening programme. GC-TOFMS operating in full scan mode at a resolving power of 12000 FWHM was evaluated with respect to mass resolution, mass accuracy, ion ratio, precision, and sensitivity. The main research question was whether a resolution of 12000 FWHM might be sufficient for accurate qualitative and quantitative screening of pesticide residues in cereals, in accordance with the EU screening requirements. Therefore, with spiking of four types of cereals at 0.01, 0.02, and 0.1 mg kg^{-1} and a QuEChERS extraction method, the SDLs were assessed

according to SANTE guidelines, on the basis of accurate mass measurement of at least two representative ions [14]. The results were then re-evaluated by using additional requirements (standard and ion ratio). The validated method based on the second evaluation approach was finally applied in the screening of pesticide residues in 38 real samples of cereals and feeding stuffs.

MATERIALS AND METHODS

Chemical and reagents

Pesticide standards (purity > 96%) were purchased from Sigma-Aldrich or LGC Standards. Pesticide standard stock solutions of 1.000 mg mL^{-1} were prepared in toluene and stored at -18 ºC in ampoules under an argon atmosphere. A standard mixture of 10 mg mL^{-1} was prepared from these stock solutions. Working standard solutions were prepared with standard-matched calibrations with cereal blank extract. The blank extracts were obtained from the extraction procedure described in the 'Extraction method' section. Acetonitrile (HPLC Grade 5) was purchased from Rathburn Chemicals (Walkerburn, UK). The buffer salt mixture was purchased from Thermo Scientific, and the clean-up sorbent Supel™QuE (EN) tubes were purchased from Supelco (Belleffonte, PA, USA).

Extraction method

The extraction procedure was performed with an acetate-buffered version of the QuEChERS method. The adopted method was previously validated by Herrmann et al. [15] with 25 mg Primary Secondary Amine (PSA) per mL extract in the clean-up step for wheat, in accordance with EN 15662 [16]. Five grams of sample was weighed into a 50 mL centrifuge tube; 10 mL of cold deionized water and ceramic homogenizers were added; and the tubes were shaken vigorously so that the sample was soaked thoroughly. Afterward, 10 mL of acetonitrile was added, and the tubes were shaken vigorously by hand for 1 min. A buffer-salt mixture from Thermo Scientific™, consisting of 4 g magnesium sulfate ($MgSO_4$), 1 g sodium chloride (NaCl), 1 g trisodium citrate dehydrate, and 0.5 g disodium hydrogencitrate sesquihydrate was added. The tubes were shaken with an automatic shaker (SPEX SamplePrep 2010 Geno/Grinder®) for 1 min at 750 rpm and then centrifuged for 10 min at 4500 rpm with a Heraeus™ Multifuge™ X3 Centrifuge. Aliquots comprising 8 ml of the acetonitrile extracts were transferred to 15 mL centrifuge tubes and stored in a freezer for a minimum of 1 hour at -80 ºC. The still-cold extracts were centrifuged in a cool centrifuge (at 5 ºC) for 5 min to precipitate the low-soluble matrix co-extractives. Then 6 mL of acetonitrile extract was transferred to Supel™QuE tubes containing 150 mg of PSA and 900 mg of $MgSO_4$. PSA allows the removal of fatty acids from the extract. The tubes were shaken in an automatic shaker for 1 min at 750 rpm and then centrifuged for 5 min at room temperature (20 ºC) at 4500 rpm. Subsequently, 4 mL of the cleaned-up extracts was transferred into 15 ml centrifuge tubes, and 40 µl of 5% formic acid solution in acetonitrile was added to each extract to adjust the pH for storage stability. The extracts were later diluted by a factor of 2 with acetonitrile (0.25 g of sample/mL) to obtain the same matrix concentrations as those in the calibration standards, according to the in-house routine procedure for the quantitative methods.

Equipment

The samples were analysed with an Agilent 7200 Accurate-Mass Q-ToF-GC/MS, 7890A GC coupled to a PAL-GC automated Sampler 80.

For gas chromatographic separation, a 7890A gas chromatograph (Agilent Technologies) was used. The samples were injected in programmed temperature vaporizer (PTV) mode. The PTV enables the injection of solvents with high vapor expansion, in contrast to the split/splitless injection mode, thereby enabling the use of acetonitrile as injection solvent. Thus, solvent exchange involving exchanging the acetonitrile from the final QuEChERS extracts with, e.g., ethyl acetate was unnecessary. The injection volume was 5 µL, and the inlet temperature was 60 ºC. The analytes were separated in two fused silica HP-5MSUI capillary columns with 15 m x 250 µm inner diameter and a film thickness of 0.25 µm (Agilent). Helium (99.999% purity) was used as a carrier gas with a flow of 1.2 mL min^{-1} in the first column

and 1.4 mL min^{-1} in the second. The oven temperature program was as follows: 60 °C hold for 3 min, increase to 180 °C at 30 °C min^{-1}, and then increase to 300 °C at a rate of 5 °C min^{-1}. The total run time was 31.8 min, with four additional minutes for backflushing at 310 °C. The benefits of backflushing in capillary gas chromatography include better quality data and lower operating costs; it reduces the carryover of high boiling point compounds and it also helps to keep the electron ionization (EI) source clean resulting in less chemical background.

For the mass spectrometric analysis, a 7200 Accurate-Mass Q-ToF-GC/MS quadrupole time of flight (Q-ToF) mass spectrometer Agilent 7200 (Agilent Technologies) was used. The ion source operates in EI mode and spectra were collected at 70 eV. The EI emission value was set at 3.8 μA. The ion source temperature was set at 230 °C, and the transfer line temperature was set at 300 °C. The high-resolution mode of 4 GHz (12000 FWHM) at which the TOFMS operated in full scan enabled higher confidence in analyte identification. Internal mass calibration with perfluorotributylamine was performed before each injection for improved accurate mass operation. An automatic stop of the sequence occurred when the mass error exceeded 5 ppm. Data acquisition was performed with GC-Q-ToF MassHunter Data Analysis at a mass range of 69–500 Da with an acquisition rate of 5 spectra/s. MS data were collected in centroid mode.

Database

An exact mass database was created and optimized for 102 compounds (Supplementary Material). For each pesticide, the chemical formula and molecular weight, as well as the formulas and exact masses of at least three selective/sensitive fragment ions were added.

When a new compound was to be included in the database, the ion fragmentation was first predicted with ChemDraw (up to five fragments). The percentage of fragment probability (mass accuracy) and the assigned formula were verified in Agilent Qualitative Software (*Formula Calculator* Tool) and ChemCalc software (*Molecular Formula Finder* tool). The exact mass of the fragment ions was calculated in Agilent Qualitative MassHunter software with the *Mass calculator* tool and on the Scientific Instrument Services, INC (SIS) website. The mass-to-charge ratio (*m/z*) corresponding to the molecular ion (M^+) was obtained by subtraction of the electron´s mass from the neutral mass (M). Even though the electron mass was very low (0.00054858 Da), not subtracting it would have resulted in an initial theoretical mass error of 5 ppm for ion masses of $m/z \leq 100$.

Later, a standard mix of the 102 pesticides was injected in the GC-TOFMS at different concentrations to create the database. The retention times were collected, and the three most selective/sensitive fragment ions in the total ion chromatogram were selected.

The database also included isotope clusters. Isotopes are variations in chemical elements with different numbers of neutrons and thus different masses: they have the same number of protons and electrons but a different number of neutrons. Their occurrence increases with increasing molecular weight. Chlorine, e.g., exists as a pair of isotopes, ^{35}Cl and ^{37}Cl, in a near 3:1 ratio. M+2 (^{37}Cl) are elements with an isotope mass of 1.997050 Da above that of the most abundant isotope (^{35}Cl). In some cases, and in accordance with selecting the most abundant ions for optimizing the method sensitivity, isotope clusters were included in the database to provide the most intense peaks. Bixafen (formula: $C_{18}H_{12}Cl_2F_3N_3O$, exact mass: 413.030951) is one such example. One of the three selective and sensitive ions of bixafen is an isotope cluster (formula: $C_{18}H_{12}Cl(37Cl)F_3N_3O$; exact mass: 415.028001).

For sample screening, an automatic library search using the “Find compounds by formula option” in Agilent Qualitative Software is useful. The search can be filtered, selecting at least three fragment ions, a mass accuracy threshold of ± 5 ppm, a minimum peak intensity and a score of formula matching including isotopes (above 70%). However, with this approach, the number of false positive findings is high. To decrease the number of incorrect hits, the results must be assessed manually, thus making data review time consuming [17]. This approach is not recommended for sample screening on GC-QTOF. Therefore, the optimized database that was first maintained as a Microsoft Excel spreadsheet was imported into Agilent MassHunter Quantitative software for rapid data review and sample screening.

Spiking procedure

Four different types of cereals including blank samples of rice, rye, and barley, and two blanks of wheat were spiked at three concentrations of 0.01, 0.02, and 0.1 mg kg^{-1}. The spiking experiment was performed with five replicates for each matrix at each concentration level. A total of 75 samples were injected for the validation of the screening and quantification method. Another 75 non-diluted extracts were injected to study the effect of the increased sensitivity on mass accuracy.

Identification criteria

Mass accuracy is generally reported as a ppm error and is calculated by taking the difference between the theoretical mass and the measured experimental mass, dividing by the theoretical mass, and then multiplying by 10^6. According to SANTE guidelines [14], the requirements for identification with HRMS (>10000) include a mass accuracy ≤ 5 ppm for m/z > 200, whereas for m/z < 200, the mass accuracy must be < 1 mDa. For example, a fragment ion of m/z 141.06988 must have a mass error less than ± 7.1 ppm ($0.001/141.06988 \times 10^6$). Consequently, the mass error threshold is higher for lower m/z. However, for low mass range molecules and fragments, the probability of possible elemental composition is lower because there are fewer elements to combine. Consequently, a higher mass error can be accepted [18]. Moreover, regarding identification requirements, the signal to noise ratio must be ≥ 3, and the analyte peaks of the fragment ions in the extracted ion chromatogram (EIC) must fully overlap.

Method validation for screening

The qualitative screening method was validated according to SANTE guidelines. The validation involved at least 20 samples. The SDL was set at the lower concentration for which a certain analyte could be identified in at least 95% of the samples.

Method validation for quantification

The quantification method was validated according to SANTE guidelines [14]. The analytical performance of the method was determined by evaluation of the linearity, the recoveries and repeatability, the LOQ, the inter-day and intra-day precision, and estimation of the expanded uncertainty of the entire method. The matrix effect was also assessed.

Recovery and repeatability in terms of relative standard deviation (RSD) were calculated with each matrix at the three concentrations in the five replicates. The inter-day precision of the method was evaluated at the concentrations of 0.01, 0.02, and 0.1 mg kg^{-1} and was obtained by performing the same spiking process for five consecutive days. The intra-day precision was obtained by measuring the analytes five times on the same day and was also estimated at the three concentrations. The uncertainty (u') was estimated by the sum of the bias component results (u'bias) and the recovery's uncertainty u'(Rw) as follow:

$$u' = u'(bias) + u'(Rw) \quad \text{where } u' \text{ bias} = \sqrt{RMS'(bias)}$$

The u'(bias) was estimated by calculation of the root mean square of the bias (RMS'bias) derived from the inter-day reproducibility. The u'(Cref) contributions could be included in the bias component. The u'(Rw) was obtained from the standard deviation of recoveries obtained on the same day. The expanded uncertainty U' was expressed as 2u' and was required to be less than 50%. The uncertainty was also estimated at the three concentrations. The assessment of the matrix effect was performed by comparison of the slopes obtained with the calibration curves of wheat, rice, and barley to the slope of the calibration curve obtained with rye, the supposed easiest matrix, by calculating the slopes' relative standard deviation.

Real samples

The validated GC-TOFMS method was applied to 38 real samples of cereals and feeding stuffs sampled from the Danish market as part of the annual control program and corresponding to samples of wheat, barley, rye, basmati rice, jasmine rice, parboiled rice, white rice, red rice, pudding rice, rapeseed, linseed, sunflower seed, and hemp seed. Feeding stuffs have similar matrix profile than cereal samples, therefore it was relevant to analyse feeding stuff samples using the validated method of cereals.

RESULTS AND DISCUSSION

Evaluation of screening detection limits

First approach

First, the examination of the average mass accuracy of the 306 ions was conducted, after screening of 75 samples spiked at different concentrations. The average mass accuracy obtained from the 25 injections at the concentration of 0.1 mg kg^{-1} was below ± 5 ppm for 88% of the fragment ions. In addition, 78% of the ions showed an average mass accuracy below ± 5 ppm at 0.02 mg kg^{-1}, and 72% of the ions showed an average mass accuracy below ± 5 ppm at 0.01 mg kg^{-1}. Overall, the average mass accuracy obtained at different concentrations for all the compounds indicated that the probability of mass error was higher at low concentrations (0.01 mg kg^{-1}) and low *m/z* (<200).

However, according to SANTE guidelines, to calculate the SDL for accurate screening, the results must be evaluated for each compound, as described in the 'Identification criteria' section. Figure 1 shows the percentage of compounds that achieved an SDL of 0.01, 0.02, 0.1, and above 0.1 mg kg^{-1}. The SDL was 0.01 mg kg^{-1} for only 16% of the compounds, 0.02 mg kg^{-1} for 27% of the compounds, and 0.1 mg kg^{-1} for 37% of the compounds. No SDL could be established for 25% of the compounds. These compounds were not validated, but an SDL above 0.1 mg kg^{-1} was associated with those compounds.

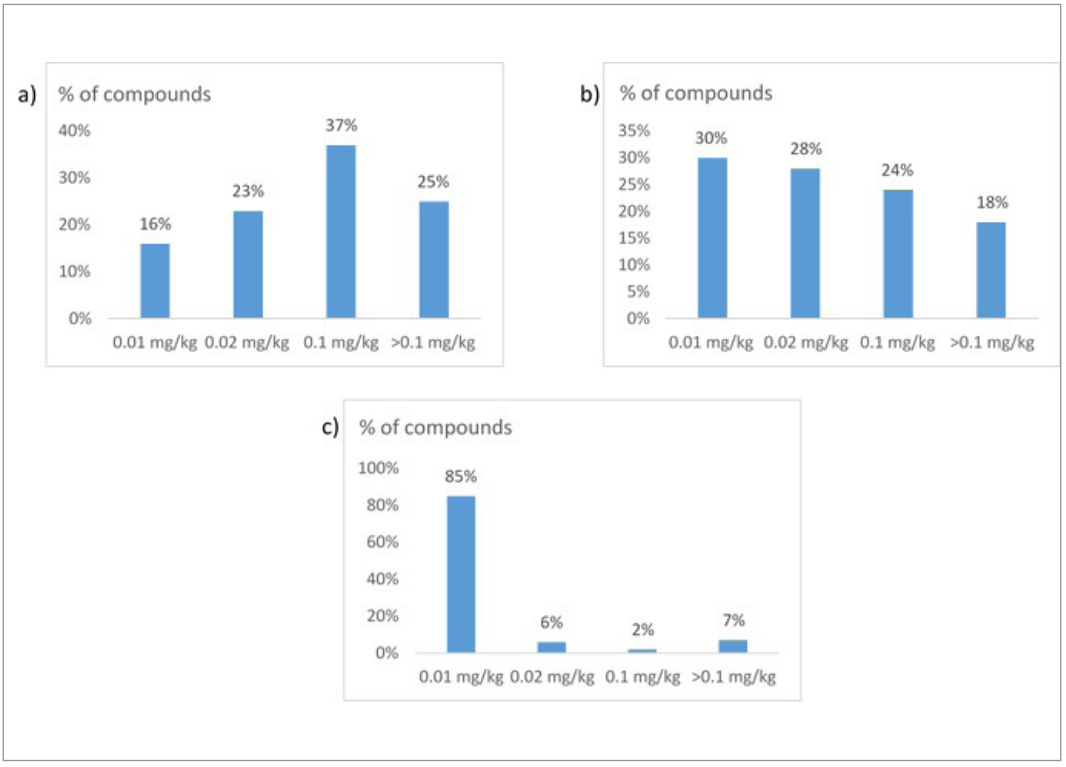

Figure 1. SDLs in mg kg^{-1} of the 102 compounds obtained with a) diluted extracts, b) non-diluted extracts, c) non-diluted extracts and considering the standards.

Some of the compounds were not well extracted with acetonitrile and required a single residue method to obtain satisfactory results; these compounds included cycloxidim (log P: 1.36), chloridazon (log P: 1.19), 8-hydroxyquinoline (log P: 1.915), and cyromazine (log P: 0.069). Dicrotofos (log P: -0.5) and amidosulfuron (log P: -1.56) were also not well extracted with acetonitrile. Other compounds showed poor extraction efficiency, such as dimoxystrobin (log P: 2.2), flumioxazin (log P: 2.55), and tralkoxydim (log P: 2.1). Ametoctradin (pKa: 2.78) is a strong acid and may be retrieved in its ionized form, and therefore is better extracted with water or other water-miscible solvents. The other compounds exhibited low sensitivity. The small molecules carvone ($C_{10}H_{14}O$, exact mass: 150.104465) and fuberidazole ($C_{11}H_8N_2O$, exact mass: 184.063663), having small fragments, showed very low sensitivity, in agreement with findings from Ramanathan *et al.* [19] who have shown that a mass resolution of 12000 FWHM is insufficient for detecting small molecules at low concentrations, owing to interference from endogenous compounds. The high SDL obtained for some compounds was associated with the four different matrices examined in this study. A major matrix peak was observed in the total ion chromatogram between 15 and 21 min with rice matrix. The matrix peak was generated by the high amounts of fatty acids in rice. In the 15–21 min time segment, a high number of pesticides also eluted.

In light of the data obtained, and given that low sensitivity was associated with the diluted samples, we assessed the mass accuracy without sample dilution. The spiked samples were injected without final dilution in the vial (0.5 g sample/mL). The SDLs obtained were 0.01 mg kg^{-1} for 30% of the compounds, 0.02 mg kg^{-1} for 28% of the compounds, and 0.1 mg kg^{-1} for 24% of the compounds. Moreover, 18% of the compounds showed an SDL above 0.1 mg kg^{-1} (Figure 1). Lower SDLs were obtained without the final dilution; however, using 0.5 g of sample/mL rather than 0.25 g of sample/mL would also increase the amount of matrix introduced into the instrument (liner, column, and ion source) and more maintenance would be required. Another approach to increase sensitivity is increasing the injection volume. The PTV injector allows use of high injection volumes [20]. However, an increase in sensitivity will not necessarily be accompanied by an increase in mass accuracy.

The SDLs were re-evaluated by considering a mass accuracy threshold of 10 ppm, in accordance with the US-FDA guidelines [21]. More satisfactory results in this case were obtained: 50% of the compounds showed an SDL of 0.01 mg kg^{-1}, 22% of the compounds showed an SDL of 0.02 mg kg^{-1}, and 16% of the compounds showed an SDL of 0.1 mg kg^{-1}.

Those results prompt the question of whether a resolving power of 4 GHz, 12000 FWHM, might be sufficient for screening pesticides at low concentrations in difficult matrices as cereals, without the use of any standard.

Second approach

HRMS instruments were expected to allow the identification of compounds without the use of standards, by relying only on the mass accuracy of two fragment ions. However, given the poor results obtained with the first approach, even though three ions were assessed, the data were re-evaluated with identification criteria commonly applied to unit mass data [14]. For unit mass spectrometry, using certified standards and comparing the ion ratios obtained for a sample with that of a standard is a key requirement for identification [14]. Thus, identification is inadequate without the use of standards. Fortunately, in simultaneous screening and quantification studies, standards were also injected, thus enabling the ion ratios to be used for identification. When this second approach was applied, 85% of the compounds achieved an SDL of 0.01 mg kg^{-1}, 6% of the compounds had an SDL of 0.02 mg kg^{-1}. Only 2% of the compounds showed an SDL of 0.1 mg kg^{-1}, and 7% of the compounds had an SDL above 0.1 mg kg^{-1} (Figure 1).

To improve understanding the differing results obtained with the two approaches, the correlation between the two identification criteria used was studied: the mass accuracy (first approach) and the ion ratio (second approach). Figure 2 provides a summary of the percentage of compounds that met the mass accuracy requirement (± 5 ppm or < 1 mDa compared with the database) and/or the requirement to ion ratio (± 30% of standard) for identification.

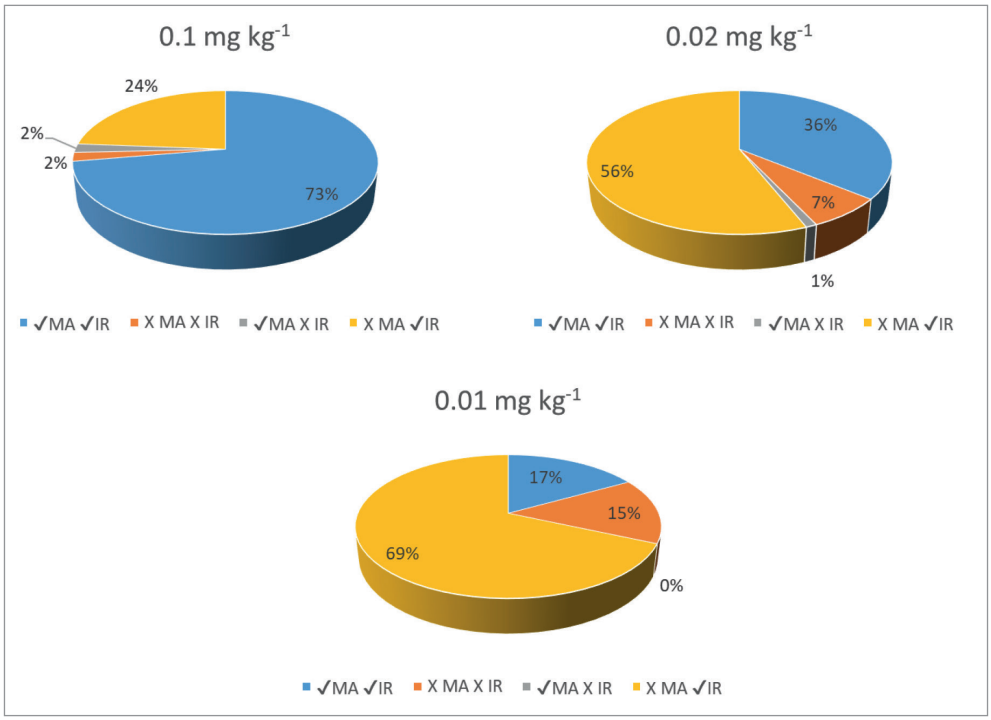

Figure 2. Correlation between mass accuracy and ion ratio at 0.1, 0.02 and 0.01 mg kg^{-1} (blue: percentage of compounds for which fragment ions have fulfilled both mass accuracy and ion ratio criteria. Orange: percentage of compounds that did not fulfill both ion ratio and mass accuracy criteria. Grey: percentage of compounds that have fulfilled the mass accuracy criterion but failed the ion ratio criterion. Yellow: percentage of compounds that have failed the mass accuracy criterion but have met the ion ratio criterion).

At 0.1 mg kg^{-1}, 75% of the compounds showed a positive correlation between the ion ratio and mass accuracy; when the mass accuracy criterion is met, so did the ion ratio results, and when the mass accuracy did not meet the criterion for peak identification, so did the ion ratio results. Therefore, peak identification based on mass accuracy was completely acceptable in that case, without the use of the ion ratio criterion (use of standards), because the two criteria gave the same indication. At 0.02 mg kg^{-1}, 43% of the compounds showed a good correlation between mass accuracy and ion ratio. At 0.01 mg kg^{-1}, the percentage of compounds was even lower: only 32% of the compounds showed a good correlation between mass accuracy and ion ratio. Therefore, the criterion of mass accuracy at low concentrations was insufficient in the last cases for compound identification.

At all the concentrations studied, a mass accuracy less than 5 ppm was accompanied by an ion ratio less than 30%, but not vice versa. At 0.1 mg kg^{-1}, 24% of the compounds showed high mass error (>5 ppm) but acceptable ion ratio (< 30%). At 0.02 and 0.01 mg kg^{-1}, approximately 56% and 69% of the compounds, respectively, showed good ion ratio but low mass accuracy (above 5 ppm or 1 mDa). These compounds met not only the ion ratio criterion but also the signal to noise ratio criterion, and the fragment ions were fully overlapping in the EIC. In the EIC of carfentrazone-ethyl and fenoxaprop-p-ethyl (Figure 3), carfentrazone-ethyl showed a good ion ratio and good mass accuracy for both qualifiers. Fenoxaprop-ethyl showed a good ion ratio, but a high mass error was observed with both qualifiers. Ignoring these compounds because of their low mass accuracy might have resulted in false positive detection.

Therefore, at high concentrations, the first approach relying solely on mass accuracy was applicable. However, at low concentrations, the use of standards and the evaluation of ion ratio was found to be an applicable identification criterion. Relying only on mass accuracy resulted in many false positives.

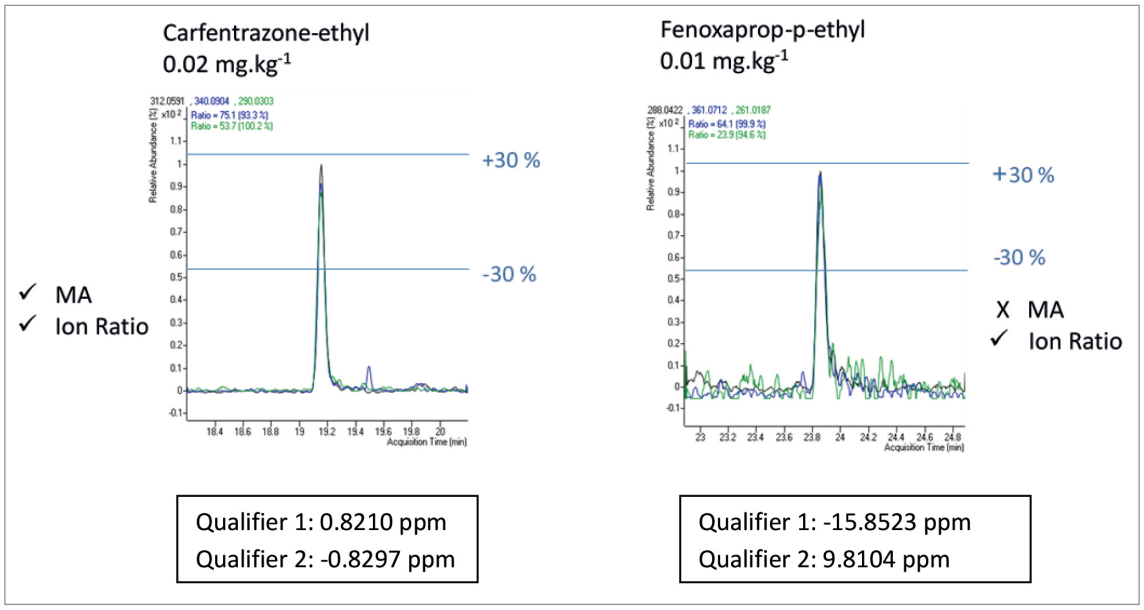

Figure 3. The extracted ion chromatograms of the two qualifiers of carfentrazone-ethyl and fenoxaprop-p-ethyl; ion ratio and mass accuracy.

The question was addressed again about how much resolution is needed to reach low detection limits with high accuracy. Regarding the identification criteria for screening pesticide residues in cereals at a resolving power of 12000 FWHM, the use of standards remains the most important tool for identification. With the availability of different HRMS with different resolving power, the identification requirements cannot be generalised. The limitations of equipment offering a resolution of 12000 FWHH or less must be considered when analysing pesticide residues in difficult matrices.

The EU MRLs in force for the studied compounds in cereals vary from 0.01 up to 0.1 mg kg^{-1}. Among the 102 compounds, 60 compounds had established EU MRLs. Using the extraction procedure described above and applying the first approach, SDLs equal to or below the corresponding EU MRLs were achieved for only 35% of the compounds. When the dilution step was omitted, 47% of the compounds fulfilled the MRL requirements. If the ion ratio was considered along with the mass accuracy, *i.e.,* the second approach was applied, 90% of the compounds were suitable for MRL compliance check. Table I lists the SDLs obtained by the application of both the first and the second approach along with the MRLs in force for each compound.

Table I. The SDLs achieved with 0.25 g sample/mL of extract and with 0.5 sample/mL of extract considering the identification requirements of the SANTE guidelines (Mass accuracy (MA), S/N, peaks overlapping), and the SDLs obtained with 0.25 g of sample/mL by considering the ion ratio (IR) criteria, and the EU MRLs established for cereals.

			SDL (mg kg^{-1})		
	Compounds	**MRLs (mg kg^{-1})**	**SDL (0.25 g sample/mL)+MA**	**SDL (0.5 g sample/mL)+MA**	**SDL (0.25 g sample/mL)+MA+IR**
1	1-Naphthylacetic acid	0.06	0.02	0.02	0.01
2	1-Naphtylacetamide	0.06	0.1	0.02	0.01
3	8-Hydroxyquinoline	0.01	>0.1	>0.1	>0.1
4	Acetochlor	0.01	0.02	0.02	0.01
5	Aclonifen	0.01	0.1	0.1	0.01
6	Ametoctradin	0.05	>0.1	>0.1	0.02

Table I. The SDLs achieved with 0.25 g sample/mL of extract and with 0.5 sample/mL of extract considering the identification requirements of the SANTE guidelines (Mass accuracy (MA), S/N, peaks overlapping), and the SDLs obtained with 0.25 g of sample/mL by considering the ion ratio (IR) criteria, and the EU MRLs established for cereals. (Cont.)

			SDL (mg kg^{-1})		
	Compounds	**MRLs (mg kg^{-1})**	**SDL (0.25 g sample/mL)+MA**	**SDL (0.5 g sample/mL)+MA**	**SDL (0.25 g sample/mL)+MA+IR**
7	Amidosulfuron	0.01	>0.1	>0.1	0.01
8	Amisulbrom	0.01	>0.1	>0.1	0.01
9	Anthraquinone	0.01	>0.1	>0.1	0.01
10	Benalaxyl	0.05	0.02	0.02	0.01
11	Benfluralin	0.02	0.02	0.01	0.01
12	Biphenyl	0.01	0.01	0.01	0.01
13	Bixafen		0.1	0.1	0.01
14	Butralin	0.01	0.1	0.02	0.01
15	Carbophenothion		0.1	0.02	0.01
16	Carfentrazone-ethyl	0.05	0.1	0.02	0.01
17	Carvone		>0.1	>0.1	>0.1
18	Chlorantraniliprole		>0.1	>0.1	0.01
19	Chloridazon	0.1	>0.1	>0.1	>0.1
20	Chloropropylate		0.02	0.01	0.01
21	Chlorthal-dimethyl	0.01	0.1	0.02	0.01
22	Cinidon-ethyl	0.05	>0.1	>0.1	0.01
23	Clodinafop-propargyl	0.02	>0.1	0.1	0.01
24	Cycloxydim		>0.1	>0.1	>0.1
25	Cyflufenamid		0.1	0.01	0.01
26	Cyromazine	0.05	>0.1	>0.1	>0.1
27	Dialifos		>0.1	>0.1	0.1
28	Dichlobenil	0.01	0.01	0.01	0.01
29	Dichlofenthion		0.02	0.01	0.01
30	Dicrotofos		>0.1	>0.1	0.01
31	Diflufenican		0.02	0.01	0.01
32	Dimetachlor	0.02	0.02	0.02	0.01
33	Dimethenamid	0.01	0.01	0.01	0.01
34	Dimoxystrobin		>0.1	>0.1	0.02
35	Diniconazole	0.01	0.02	0.01	0.01
36	Dioxathion	0.01	>0.1	>0.1	0.01
37	Ethalfluralin	0.01	0.1	0.02	0.01
38	Ethofumesate	0.03	0.01	0.01	0.01
39	Etoxazole	0.01	0.1	0.1	0.01
40	Etridiazole	0.05	0.1	0.02	0.01
41	Etrimfos		0.1	0.1	>0.1
42	Famoxadone		0.1	0.1	0.01
43	Fenchlorphos	0.01	0.01	0.01	0.01

Table I. The SDLs achieved with 0.25 g sample/mL of extract and with 0.5 sample/mL of extract considering the identification requirements of the SANTE guidelines (Mass accuracy (MA), S/N, peaks overlapping), and the SDLs obtained with 0.25 g of sample/mL by considering the ion ratio (IR) criteria, and the EU MRLs established for cereals. (Cont.)

			SDL (mg kg^{-1})		
	Compounds	**MRLs (mg kg^{-1})**	**SDL (0.25 g sample/mL)+MA**	**SDL (0.5 g sample/mL)+MA**	**SDL (0.25 g sample/mL)+MA+IR**
44	Fenoxaprop-p-ethyl	0.1	0.1	0.02	0.01
45	Flonicamid		0.02	0.02	0.01
46	Fluazinam	0.02	>0.1	>0.1	0.01
47	Flucythrinate I and II	0.01	0.1	0.1	0.01
48	Flufenacet		0.1	0.02	0.01
49	Flumetralin	0.01	0.01	0.02	0.01
50	Flumioxazin	0.02	>0.1	0.1	0.01
51	Fluopicolide	0.01	0.01	0.01	0.01
52	Fluopyram		0.01	0.01	0.01
53	Flurochloridone	0.1	0.02	0.02	0.01
54	Flurprimidol	0.02	0.01	0.01	0.01
55	Flurtamone	0.01	>0.1	0.1	0.02
56	Flutolanil		0.01	0.01	0.01
57	Fluxapyroxad		0.02	0.01	0.01
58	Fonofos		0.01	0.01	0.01
59	Fuberidazole		>0.1	>0.1	0.02
60	Furathiocarb	0.01	0.01	0.01	0.01
61	Heptachlor	0.01	0.02	0.01	0.01
62	Isocarbofos		0.1	0.1	0.01
63	Isofenfos		0.01	0.01	0.01
64	Isoprocarb		0.01	0.01	0.01
65	Isopyrazam		0.1	0.02	0.01
66	Isoxaflutole	0.02	0.1	0.02	0.01
67	Isoxathion		0.1	>0.1	0.01
68	Metazachlor	0.02	0.1	0.02	0.01
69	Metobromuron		0.1	0.1	0.01
70	Metolachlor	0.05	0.02	0.1	0.01
71	Metrafenone		>0.1	0.1	0.01
72	Molinate	0.01	0.1	0.1	0.01
73	Napropamide	0.05	>0.1	0.1	0.02
74	Novaluron	0.01	0.1	0.1	0.01
75	Oxadiargyl	0.01	0.1	0.1	0.02
76	Oxasulfuron	0.01	0.1	0.02	0.01
77	Oxyfluorfen	0.05	0.1	0.02	0.01
78	Penflufen		0.02	0.01	0.01
79	Pentachloroaniline	0.02	0.01	0.01	0.01
80	Penthiopyrad		0.02	0.01	0.01

Table I. The SDLs achieved with 0.25 g sample/mL of extract and with 0.5 sample/mL of extract considering the identification requirements of the SANTE guidelines (Mass accuracy (MA), S/N, peaks overlapping), and the SDLs obtained with 0.25 g of sample/mL by considering the ion ratio (IR) criteria, and the EU MRLs established for cereals. (Cont.)

			SDL (mg kg^{-1})		
	Compounds	**MRLs (mg kg^{-1})**	**SDL (0.25 g sample/mL)+MA**	**SDL (0.5 g sample/mL)+MA**	**SDL (0.25 g sample/mL)+MA+IR**
81	Picolinafen		0.02	0.01	0.01
82	Picoxystrobin		0.02	0.01	0.01
83	Piperonylbutoxide		0.1	0.01	0.01
84	Pirimiphos-ethyl		0.02	0.02	0.01
85	Propachlor	0.02	0.1	0.02	0.01
86	Propanil	0.01	0.1	0.02	0.01
87	Proquinazid	0.02	0.02	0.02	0.01
88	Pyraclofos		0.1	0.1	0.01
89	Pyridalyl	0.01	0.1	0.02	0.01
90	Quinalphos	0.01	0.1	0.1	0.01
91	Quintozene	0.02	0.1	0.1	0.01
92	Siafluofen		0.02	0.01	0.01
93	Spiromesifen	0.02	0.02	0.01	0.01
94	Sulfotep		0.1	0.1	0.01
95	Terbuthylazine		>0.1	0.1	0.01
96	Tetrachlorvinphos		0.1	0.02	0.01
97	Tetrasul		0.1	0.02	0.01
98	Thiobencarb	0.01	0.01	0.01	0.01
99	Tralkoxydim	0.01	>0.1	>0.1	0.1
100	Tralomethrin		>0.1	>0.1	0.01
101	Trichloronate		0.02	0.01	>0.1
102	Triflumizole	0.1	0.1	0.02	0.01

Method validation for quantification

Recoveries and repeatability

At 0.01 mg kg^{-1}, the percentages of compounds exhibiting good recovery values between 70 and 120% were 82% in rye, 76% in wheat, 75% in barley, and 33% in rice. Among the cereals injected, and as mentioned before, rice is the most difficult matrix because of the relatively high amount of fat. At low concentrations, the pesticides may be discriminated by the high signal to noise of the co-extractive components of rice. Some non-polar compounds may also remain in the fat precipitate, such as tralomethrin (log P: 5). At 0.02 mg kg^{-1}, good recoveries were obtained with rye, wheat, barley, and rice for 90%, 81%, 92%, and 90% of the compounds, respectively. At 0.1 mg kg^{-1}, 94% of the compounds showed good recoveries in rye, 89% showed good recoveries in wheat, 94% showed good recoveries in barley, and 95% showed good recoveries in rice. Some compounds exhibited poor recoveries for all four matrices at all three concentrations studied, *e.g.,* carvone, cycloxidim, chloridazon, cyromazine, and 8-hydroxyquinoline.

RSDs obtained for almost all the compounds were below 20% except for some compounds analysed in barley and rice at the lowest concentration of 0.01 mg kg^{-1}.

Intra-day precision and inter-day precision

The intra-day precision is influenced by many factors, such as the efficiency of the extraction procedure and potential errors during the extraction. It is also influenced by the instrument calibration and stability during the sequence; an internal mass calibration with perfluorotributylamine was performed before each injection on the TOFMS, to improve the resolution and accuracy of mass operation. Another parameter that may influence the results is the different types of cereals used for this study, which exhibited different responses depending on the matrix effect. The poor recoveries obtained for rice and barley at 0.01 mg kg^{-1} were the main reason why only 40% of the compounds showed an RSD for intra-day precision below 20%. The results were quite different at 0.02 and 0.1 mg kg^{-1}, at which almost all compounds showed an intra-day precision below 20%

The inter-day precision indicates the reproducibility of the method applied on different days. In our study, the different matrices used were also considered. Only 33% of the compounds showed good inter-day precision at 0.01 mg kg^{-1}, whereas 84% of the compounds showed good reproducibility below 20% at 0.02 mg kg^{-1}, and 98% of the compounds showed good inter-day precision standard deviation at 0.1 mg kg^{-1}.

Uncertainty

The results of uncertainty were consistent with the intra-day and inter-day precision results. Figure 4 shows the estimated uncertainty obtained at the three concentrations. Only 58% of the compounds showed low uncertainty below 50% at 0.01 mg kg^{-1}. At 0.02 mg kg^{-1} and 0.1 mg kg^{-1}, 90% and 98% of the compounds showed low uncertainty, respectively. On the basis of the recovery and uncertainty results, the LOQs of the method ranged between 0.01 and 0.02 mg kg^{-1}.

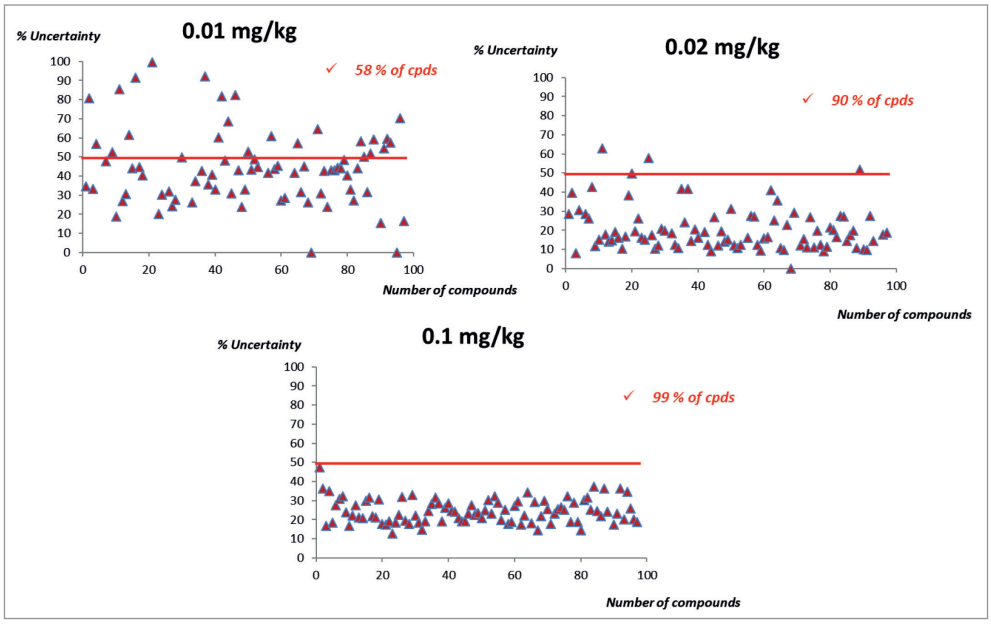

Figure 4. Uncertainty estimation in percentage obtained for the 102 compounds at 0.01, 0.02 and 0.1 mg kg^{-1}.

Matrix effect

The matrix effect is a well-known problem in GC-EI [22] that can influence the accuracy of the results, producing signal suppression or enhancement depending on the compound. Matrix effects can be decreased through efficient sample preparation methods resulting in very clean extracts and therefore less interference. However, this approach may also lead to loss of analytes. Matrix effects are also decreased with dilution of the sample extract. Another way to diminish the matrix effect is to use HRMS; the accurate

mass measurements yielded by HRMS decrease the chance of isobar detection, thus decreasing the matrix effect. According to our laboratory experience, rye was chosen as a representative matrix among the cereals included in the present study. Rye matrix provides good protection of the analytes and has a moderate matrix effect compared with those in other types of cereal matrices. Thus, matrix-matched calibration standards are commonly prepared with rye. The matrix effects presented in this study for barley, wheat, and rice were therefore calculated as percentage increases or decreases in response, normalized to that for rye. Figure 5 shows the matrix effects obtained with the comparison of slopes of the calibration curves prepared with each matrix. The results indicated that 94% of the compounds in wheat showed a weak matrix effect compared with rye (≤ ±20% signal suppression or enhancement). Only 6% of the compounds showed a moderate matrix effect (|20–50|% signal enhancement or suppression). In barley, 83% of the compounds showed a weak or non-significant matrix effect, 14% showed a moderate matrix effect, and 3% showed a strong matrix effect (≥ ±50% signal suppression or enhancement). In rice, 77% of the compounds showed a weak matrix effect, 21% of the compounds showed a moderate matrix effect, and only 2% of the compounds showed a strong matrix effect. Most of the compounds that showed any matrix effect at all exhibited a signal enhancement (approximately 60% of the compounds in wheat and rice, and 88% of the compounds in barley). The combination of an effective extraction method and a relatively high accurate mass measurement decreases the matrix effect. Therefore, the quantification of any cereal sample could be performed with a matrix-matched calibration prepared in rye.

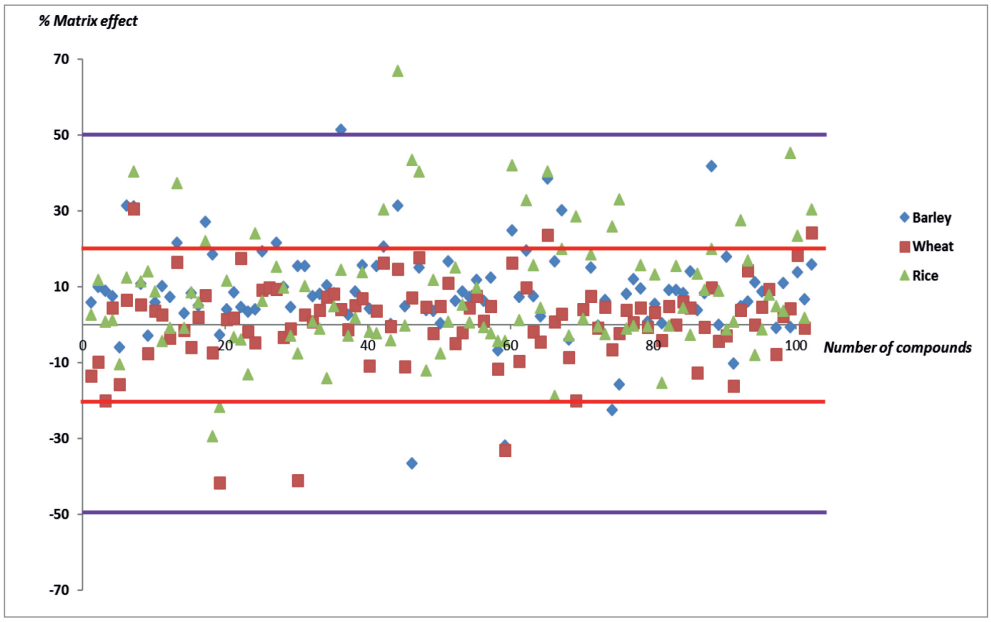

Figure 5. Percentage of matrix effect obtained from the comparison of slopes of matrix-matched calibrations of wheat, barley and rice to the slope of matrix-matched calibration prepared with rye.

Real samples

Only one pesticide was detected in real cereal samples, piperonyl butoxide, which is not included in the EU monitoring program for cereals [23]. Piperonyl butoxide is used as an insecticide synergist. It was detected in two parboiled rice samples, one jasmine rice sample, and one basmati rice sample at concentrations of 0.020, 0.021, 0.055 and 0.113 mg kg^{-1}, respectively. Piperonyl butoxide was detected at a high concentration exceeding the MRL of 0.060 mg kg^{-1}, only in jasmine rice. The presented analytical method and evaluation approach was also applied to the green beans sample of the European Union Proficiency Test for screening methods (EUPT-SM10). All the spiked compounds were identified, among them, etoxazole, isopyrazam, metrafenone, penflufen, pentachloroaniline, penthiopyrad, and proquinazid,

which demonstrate the applicability of the screening method described in this paper not only for cereal samples, but also for fruits and vegetables.

CONCLUSION

In recent years, the application of GC-TOFMS has been demonstrated to be a valuable and highly effective analytical tool in the analysis of pesticide residues in food. High mass accuracy TOF instruments can produce spectra with narrow mass peaks enabling high mass resolution. The benefit of high resolution is the elimination of background interference by using narrow mass window settings for extracting target ions, thus providing high selectivity. The resolution required for pesticide screening at lower concentrations depends on the complexity of the matrix analysed. High sensitivity is considered necessary for each application in food and pesticide food control. Cereals have relatively high lipid content, and the amount of interfering matrix retrieved in the extracts may affect the results. Accurate results are obtained through a combination of highly effective extraction procedures and instrumentation with adequate resolving power. The SDLs for cereals assessed without the use of any standards, through the citrate buffered QuEChERS method followed by GC-TOFMS analysis at 12000 FWHM, were in the range of 0.01 to 0.1 mg kg^{-1} or higher. Considering the injection of standards for identification, 85% of the compounds would show an SDL of 0.01 mg kg^{-1}. Therefore, the recommendation for third countries laboratories disposing of mass spectrometry of insufficient resolution to use standards for the identification of compounds if they are economically unable to switch to instruments offering higher mass resolving power and higher mass accuracy. Simultaneous screening and quantification are possible with HRMS. On the basis of recovery studies and uncertainty estimation, almost all the compounds achieved an LOQ between 0.01 and 0.02 mg kg^{-1}.

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Supplementary Material

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions.

Compounds		CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
1	1-Naphthylacetic acid	86-87-3	13.3	186.068080	C12H10O2	C11H9	141.069876	141.070425
						C9H7	115.054226	115.054775
						C11H7	139.054226	139.054775
2	1-Naphtylacetamide	86-86-2	13.2	185.084064	C12H11NO	C12H11NO	185.083515	185.084064
						C9H7	115.054226	115.054775
						C11H10	142.077701	142.078250
3	8-Hydroxyquinoline	148-24-3	7.7	145.052764	C9H7NO	C9H7NO	145.052215	145.052764
						C8H7N	117.057300	117.057849
						C7H6	90.046401	90.046950
4	Acetochlor	34256-81-1	12.4	269.118256	C14H20ClNO2	C10H12N	146.096425	146.096974
						C9H10N	132.080775	132.081324
						C11H12NO	174.091340	174.091889
5	Aclonifen	74070-46-5	18.2	264.030171	C12H9ClN2O3	C12H9ClN2O3	264.029622	264.030171
						C12H8N2O2	212.058029	212.058578
						C12H9NO	183.067865	183.068414
6	Ametoctradin	865318-97-4	23.7	275.210995	C15H25N5	C8H10N5	176.093071	176.093620
						C9H12N5	190.108721	190.109270
						C8H11N5	177.100896	177.101445
7	Amidosulfuron	120923-37-7	27.7	369.041294	C9H15N5O7S2	C4H5N4O4S2	236.974676	236.975225
						C5H11N4S	159.069894	159.070443
						C4H5N4O4(34S)S	238.971086	238.971635
8	Amisulbrom	348635-87-0	23.8	464.957638	C13H13BrFN5O4S2	C5H2N5O2S2	227.963656	227.964205
						C8H4FNO2S2	228.966202	228.966751
						C9H6BrFN	225.966214	225.966763
9	Anthraquinone	84-65-1	13.9	208.052430	C14H8O2	C14H8O2	208.051880	208.052429
						C13H8O	180.056966	180.057515
						C12H7	151.054226	151.054775

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

	Compounds	CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
10	Benalaxyl	71626-11-4	19.1	325.167794	C20H23NO3	C11H14NO	176.106990	176.107539
						C12H16NO2	206.117555	206.118104
						C13H16NO3	234.112470	234.113019
11	Benfluralin	1861-40-1	10.1	335.109291	C13H16F3N3O4	C10H9F3N3O4	292.053967	292.054516
						C8H5F3N3O4	264.022667	264.023216
						C7H5F3N2O2	206.029763	206.030312
12	Biphenyl	92-52-4	7.8	154.078250	C12H10	C12H10	154.077701	154.078250
						C12H9	153.069876	153.070425
						C12H8	152.062051	152.062600
13	Bixafen	581809-46-3	27.0	413.030951	C18H12Cl2F3N3O	C18H12Cl(37Cl)F3N3O	415.027453	415.028002
						C18H12Cl2F3N3O	413.030403	413.030952
						C6H5F2N2O	159.036445	159.036994
14	Butralin	33629-47-9	14.5	295.153207	C14H21N3O4	C12H16N3O4	266.113533	266.114082
						C11H14N3O2	220.108053	220.108602
						C9H10N3O4	224.066583	224.067132
15	Carbophenothion	786-19-6	19.0	341.973862	C11H16ClO2PS3	C7(35Cl)H6S	156.987326	156.987875
						C7(37Cl)H6S	143.979501	158.984925
						C3H6ClOS	124.982241	124.982790
16	Carfentrazone-ethyl	128639-02-1	19.2	411.036432	C15H14Cl2F3N3O3	C13H9F3N3O3	312.059052	312.059601
						C15H13F3N3O3	340.090352	340.090901
						C11H8ClF3N3O	290.030250	290.030799
17	Carvone	99-49--0	8.9	150.104465	C10H14O	C7H7	91.054226	91.054775
						C7H9	93.069876	93.070425
						C6H7	79.054226	79.054775
18	Chlorantraniliprole	500008-45-7	21.5	480.970792	C18H14BrCl2N5O2	C13H8Cl2N2O	278.000820	278.001369
						C9H14BrClN2O	279.997253	279.997802
						C13H8ClN2O	243.031967	243.032516
19	Chloridazon	2698-60-8	19.4	221.035590	C10H8ClN3O	C10H8ClN3O	221.035041	221.035590
						C10H8(37Cl)N3O	223.032091	223.032640
						C6H5	77.038576	77.039125

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

	Compounds	CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
20	Chloropropylate	5836-10-2	17.9	338.047651	C17H16Cl2O3	C7H4ClO	138.994519	138.995068
						C13H9Cl2O	251.002500	251.003046
						C6H4Cl	110.999604	111.000153
21	Chlorthal-dimethyl	1861-32-1	14.4	329.902022	C10H6Cl4O4	C9H3Cl4O3	298.883083	298.883632
						C10H6Cl4O4	329.901473	329.902022
						C7Cl3O2	220.895840	220.896389
22	Cinidon-ethyl	142891-20-1	31.2	393.053465	C19H17Cl2NO4	C17H13ClNO4	330.052763	330.053312
						C19H17ClNO4	358.084063	358.084612
						C15H9ClNO4	302.021463	302.022012
23	Clodinafop-propargyl	105512-06-9	19.5	349.051715	C17H13ClFNO4	C11H6ClFNO2	238.006560	238.007110
						C13H10ClFNO2	266.037860	266.038410
						C17H13ClFNO4	349.051170	349.051715
24	Cycloxydim	101205-02-1	24.0	325.171165	C17H27NO3S	C10H12NO2	178.086255	178.086804
						C6H6NO	108.044390	108.044939
						C5H9S	101.041948	101.042497
25	Cyflufenamid	180409-60-3	17.7	412.121018	C20H17F5N2O2	C7H6	90.046401	90.046950
						C8H2F4N	188.011787	188.012336
						C7H7	91.054226	91.054775
26	Cyromazine	66215-27-8	11.2	166.096694	C6H10N6	C5H7N6	151.072670	151.073219
						C6H9N6	165.088320	165.088869
						C4H5N4	109.050872	109.051421
27	Dialifos	10311-84-9	23.7	393.002510	C14H17ClNO4PS2	C10H7ClNO2	208.015983	208.016532
						C7H4O	104.025666	104.026215
						C10H7(37Cl)NO2	210.013033	210.013582
28	Dichlobenil	1194-65-6	7.6	170.964255	C7H3Cl2N	C7H3Cl2N	170.963706	170.964255
						C7H3(37Cl)ClN	172.960756	172.961305
						C7H2N	100.018174	100.018723
29	Dichlofenthion	97-17-6	12.4	313.970011	C10H13Cl2O3PS	C6H5ClO3PS	222.938009	222.938558
						C10H13ClO3PS	279.000609	279.001158
						C8H9ClO3PS	250.969309	250.969858

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

	Compounds	CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
30	Dicrotofos	141-66-2	10.0	237.076612	C8H16NO5P	C2H6O3P	109.004909	109.005458
						C3H6NO	72.044390	72.044939
						C6H10O5P	193.026039	193.026588
31	Diflufenican	83164-33-4	20.1	394.074068	C19H11F5N2O2	C13H7F3NO2	266.042339	266.042888
						C19H11F5N2O2	394.073519	394.074068
						C13H6F2N2O	246.036110	246.036659
32	Dimetachlor	50563-36-5	12.5	255.102607	C13H18ClNO2	C9H12N	134.096425	134.096974
						C10H12ClNO	197.060193	197.060742
						C9H10NO	148.075690	148.076239
33	Dimethenamid	87674-68-8	12.5	275.074679	C12H18ClNO2S	C8H12NS	154.068497	154.069046
						C10H13ClNOS	230.040090	230.040639
						C8H10ClNOS	203.016615	203.017164
34	Dimoxystrobin	149961-52-4	21.1	326.163043	C19H22N2O3	C8H6N	116.049475	116.050024
						C7H5	89.038576	89.039125
						C11H13N2O2	205.097154	205.097703
35	Diniconazole	83657-24-3	18.1	325.074868	C15H17Cl2N3O	C11H8Cl2N3O	268.003894	268.004443
						C11H7ClN3O	232.027216	232.027765
						C8H5Cl	136.007429	136.007978
36	Dioxathion	78-34-2	25.1	456.008753	C12H26O6P2S4	C8H16O4PS2	271.022218	271.022767
						C4H10O2PS2	184.985438	184.985987
						C4H10O2PS	153.013366	153.013915
37	Ethalfluralin	55283-68-6	9.9	333.093641	C13H14F3N3O4	C10H9F3N3O3	276.059052	276.059601
						C13H13F3N3O3	316.090352	316.090901
						C10H9F3N3O4	292.053967	292.054516
38	Ethofumesate	26225-79-6	13.5	286.087497	C13H18O5S	C10H9O2	161.059705	161.060254
						C12H15O3	207.101571	207.102120
						C8H9O2	137.059705	137.060254
39	Etoxazole	153233-91-1	21.5	359.169685	C21H23F2NO2	C7H3F2O	141.014647	141.015196
						C18H16F2NO	300.119446	300.119995
						C13H18NO	204.138290	204.138839

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

	Compounds	CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
40	Etridiazole	2593-15-9	8.3	245.918819	C5H5Cl3N2OS	C3HCl2N2OS	182.918117	182.918666
						C5H5Cl2N2OS	210.949417	210.949966
						C5H5(35Cl)ClN2OS	212.946467	212.947016
41	Etrimfos	38260-54-7	11.8	292.064668	C10H17N2O4PS	C9H13N2O2	181.097154	181.097703
						C10H17N2O4PS	292.064119	292.064668
						C7H9N2O2	153.065853	153.066402
42	Famoxadone	131807-57-3	29.8	374.126658	C22H18N2O4	C21H18N2O2	330.136279	330.136828
						C15H12O2	224.083181	224.083730
						C14H12O	196.088266	196.088815
43	Fenchlorphos	299-84-3	13.1	319.899739	C8H8Cl3O3PS	C8H8Cl2O3PS	284.930337	284.930886
						C8H8(37Cl)ClO3PS	286.927387	286.927936
						C2H6O2PS	124.982066	124.982615
44	Fenoxaprop-p-ethyl	71283-80-2	23.9	361.071702	C18H16ClNO5	C15H11ClNO3	288.042198	288.042747
						C18H16ClNO5	361.071152	361.071701
						C13H8ClNO3	261.018723	261.019272
45	Flonicamid	158062-67-0	9.4	229.046295	C9H6F3N3O	C7H3F3NO	174.016124	174.016673
						C6H3F3N	146.021209	146.021758
						C6H4F3N	147.029034	147.029583
46	Fluazinam	79622-59-6	15.1	463.951380	C13H4Cl2F6N4O4	C13H4Cl2F6N3O2	417.957927	417.958476
						C13H4Cl2F6N2	371.965023	371.965572
						C13H4(37Cl)ClF6N3O2	419.954977	419.955526
47	Flucythrinate I and II	70124-77-5	26.6	451.159515	C26H23F2NO4	C8H7F2O	157.045947	157.046496
			27.0			C11H13F2O	199.092897	199.093446
						C14H11NO2	225.078430	225.078979
48	Flufenacet	142459-58-3	14.1	363.066461	C14H13F4N3O2S	C9H10FN	151.079178	151.079727
						C5H2F3N2O2S	210.978360	210.978909
						C8H7FN	136.055703	136.056252
49	Flumetralin	62924-70-3	16.2	421.045247	C16H12ClF4N3O4	C7H5ClF	143.005832	143.006381
						C7H5(37Cl)F	145.002882	145.003431
						C16H11ClF4N3O3	404.041958	404.042507

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

	Compounds	CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
50	Flumioxazin	103361-09-7	27.9	354.101586	C19H15FN2O4	C19H15FN2O4	354.101037	354.101586
						C13H8FN2O3	259.051347	259.051896
						C18H15FN2O3	326.106122	326.106671
51	Fluopicolide	239110-15-7	19.7	381.965431	C14H8Cl3F3N2O	C7H3Cl2O	172.955547	172.956096
						C14H8Cl2F3N2O	346.996029	346.996578
						C6H3Cl2	144.960632	144.961181
52	Fluopyram	658066-35-4	15.3	396.046409	C16H11ClF6N2O	C8H4F3O	173.020875	173.021424
						C7H4F3	145.025960	145.026509
						C8H7ClF3N2	223.024436	223.024985
53	Flurochloridone	61213-25-0	14.3	311.009153	C12H10Cl2F3NO	C8H4F3NO	187.023949	187.024498
						C8H7F3N	174.052509	174.053058
						C12H10Cl2F3NO	311.008605	311.009154
54	Flurprimidol	56425-91-3	12.5	312.108562	C15H15F3N2O2	C12H8F3N2O2	269.053238	269.053787
						C5H3N2O	107.023989	107.024538
						C8H4F3O2	189.015790	189.016339
55	Flurtamone	96525-23-4	22.2	333.097663	C18H14F3NO2	C8H10N	120.080775	120.081324
						C18H14F3NO2	333.097114	333.097663
						C10H8F3N	199.060334	199.060883
56	Flutolanil	66332-96-5	16.6	323.113313	C17H16F3NO2	C8H4F3O	173.020875	173.021424
						C7H4F3	145.025960	145.026509
						C17H16F3NO2	323.112764	323.113313
57	Fluxapyroxad	907204-31-3	21.3	381.090052	C18H12F5N3O	C6H5F2N2O	159.036445	159.036994
						C18H12F5N3O	381.089503	381.090052
						C12H6F3N	221.044684	221.045233
58	Fonofos	944-22-9	11.3	246.030197	C10H15OPS2	C2H6OPS	108.987151	108.987700
						C4H10OPS	137.018451	137.019000
						C10H15OPS2	246.029648	246.030197
59	Fuberidazole	3878-19-1	12.7	184.063663	C11H8N2O	C11H8N2O	184.063114	184.063663
						C10H8N2	156.068199	156.068748
						C10H7N2	155.060374	155.060923

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

	Compounds	CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
60	Furathiocarb	65907-30-4	22.2	382.156245	C18H26N2O5S	C10H11O2	163.075356	163.075905
						C10H10O2S	194.039603	194.040152
						C7H7O	107.049140	107.049690
61	Heptachlor	76-44-8	12.9	369.821096	C10H5Cl7	C5H2Cl6	271.809619	271.810168
						C5H5Cl	100.007429	100.007978
						C5H2(37Cl)Cl5	273.806669	273.807218
62	Isocarbofos	24353-61-5	14.2	289.053769	C11H16NO4PS	C7H4OS	135.997738	135.998287
						C7H4O2	120.020581	120.021130
						C6H4O	92.025666	92.026215
63	Isofenfos	25311-71-1	15.2	345.116369	C15H24NO4PS	C7H5O2	121.028406	121.028955
						C9H10O4P	213.031124	213.031673
						C7H6O4P	184.999824	185.000373
64	Isoprocarb	2631-40-5	8.9	193.110279	C11H15NO2	C8H9O	121.064790	121.065339
						C9H12O	136.088266	136.088815
						C8H7	103.054226	103.054775
65	Isopyrazam	881685-58-1	23.9	359.180918	C20H23F2N3O	C6H5F2N2O	159.036445	159.036994
						C20H23F2N3O	359.180369	359.180918
						C12H10NO	184.075690	184.076239
66	Isoxaflutole	141112-90-0	14.4	359.043914	C15H12F3NO4S	C14H8F3NO2	279.050550	279.050713
						C7H3F3O	160.013500	160.013599
						C13H7F3O2	252.039990	252.039814
67	Isoxathion	18854-01-8	17.5	313.053769	C13H16NO4PS	CH5OS	105.033491	105.034040
						C9H7NOS	177.024287	177.024836
						C11H12NO4PS	285.021920	285.022469
68	Metazachlor	67129-08-2	14.9	277.098190	C14H16ClN3O	C9H10N	132.080775	132.081324
						C11H12ClNO	209.060193	209.060742
						C4H5N2	81.044724	81.045273
69	Metobromuron	3060-89-7	7.0	258.000389	C9H11BrN2O2	C7H4BrNO	196.947076	196.947625
						C6H4BrN	168.952161	168.952710
						C6H4N	90.033825	90.034374

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

Compounds		CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
70	Metolachlor	51218-42-2	13.9	283.133907	C15H22ClNO2	C11H16N	162.127725	162.128274
						C13H17ClNO	238.099318	238.099867
						C13H17(37Cl)NO	240.096368	240.096917
71	Metrafenone	220899-03-6	23.8	408.057236	C19H21BrO5	C18H18BrO5	393.033212	393.033761
						C18H18BrO4	377.038297	377.038846
						C11H13O4	209.080836	209.081385
72	Molinate	2212-67-1	8.9	187.103086	C9H17NOS	C7H12NO	126.091340	126.091889
						C6H12N	98.096425	98.096974
						C9H17NOS	187.102537	187.103086
73	Napropamide	15299-99-7	16.5	271.157229	C17H21NO2	C4H10N	72.080775	72.081324
						C7H14NO	128.106990	128.107539
						C9H7	115.054226	115.054775
74	Novaluron	116714-46-6	7.8	492.012310	C17H9ClF8N2O4	C6H5ClNO	142.005418	142.005967
						C6H5(37Cl)NO	144.002468	142.005967
						C9H6ClF6NO2	308.998576	308.999125
75	Oxadiargyl	39807-15-3	18.2	340.038149	C15H14Cl2N2O3	C8H5ClN	150.010503	150.011052
						C9H5Cl2NO	212.974271	212.974820
						C8H5Cl2N	184.979356	184.979905
76	Oxasulfuron	144651-06-9	12.5	406.094707	C17H18N4O6S	C8H12NS	154.068497	154.069046
						C5H5N3O6	203.017288	203.017837
						C6H7S	111.026298	111.026847
77	Oxyfluorfen	42874-03-3	17.2	361.032871	C15H11ClF3NO4	C13H7F3O2	252.039265	252.039814
						C13H6ClF3NO2	300.003367	300.003916
						C15H11ClF3NO4	361.032322	361.032871
78	Penflufen	494793-67-8	18.7	317.190340	C18H24FN3O	C6H6FN2O	141.045867	141.046416
						C15H17FN3O	274.135016	274.135565
						C18H24FN3O	317.189791	317.190340
79	Pentachloroaniline	527-20-8	12.3	262.862988	C6H2Cl5N	C6H2Cl5N	262.862440	262.862988
						C6H4Cl5N	264.878090	264.878639
						C6H6Cl5N	266.893740	266.894289

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

	Compounds	CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
80	Penthiopyrad	183675-82-3	18.4	359.127918	C16H20F3N3OS	C12H11F3N3OS	302.056944	302.057493
						C16H20F3N3OS	359.127369	359.127918
						C6H4F3N2O	177.027023	177.027572
81	Picolinafen	137641-05-5	21.2	376.083490	C19H12F4N2O2	C12H7F3NO	238.047424	238.047973
						C19H12F4N2O2	376.082941	376.083490
						C12H8F3NO	239.055249	239.055798
82	Picoxystrobin	117428-22-5	16.5	367.103143	C18H16F3NO4	C10H9O	145.064791	145.065340
						C17H12F3NO3	335.076379	335.076928
						C9H7	115.054226	115.054775
83	Piperonylbutoxide	51-03-6	20.2	338.209325	C19H30O5	C11H12O2	176.083181	176.083730
						C9H9O2	149.059705	149.060254
						C9H11	119.085526	119.086075
84	Pirimiphos-ethyl	23505-41-1	14.7	333.127602	C13H24N3O3PS	C7H10N3S	168.058995	168.059544
						C12H21N3O3PS	318.103578	318.104127
						C11H19N3O3PS	304.087928	304.088477
85	Propachlor	1918-16-7	9.5	211.076392	C11H14ClNO	C8H10N	120.080775	120.081324
						C11H14NO	176.106990	176.107539
						C8H8ClNO	169.028893	169.029442
86	Propanil	709-98-8	12.4	217.006120	C9H9Cl2NO	C6H5Cl2N	160.979356	160.979905
						C6H5(37Cl)ClN	162.976406	162.976955
						C9H9Cl2NO	217.005571	217.006120
87	Proquinazid	189278-12-4	20.0	381.965431	C14H8Cl3F3N2O	C8H5IN2O2	287.939031	287.939580
						C7H4INO	244.933217	244.933766
						C8H3INO2	271.920307	271.920856
88	Pyraclofos	89784-60-1	23.7	360.046431	C14H18ClN2O3PS	C9H7ClN2O	194.024142	194.024691
						H2O2PS	96.950766	96.951315
						C14H18ClN2O3PS	360.045882	360.046431
89	Pyridalyl	179101-81-6	26.8	488.967990	C18H14Cl4F3NO3	C9H9F3NO	204.063074	204.063623
						C3H3Cl2	108.960632	108.961181
						C6H5F3NO	164.031774	164.032323

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

	Compounds	CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
90	Quinalphos	13593-03-8	15.3	298.054103	C12H15N2O3PS	C8H6N2O	146.047464	146.048013
						C10H8N2	156.068199	156.068748
						C10H9N2	157.076024	157.076573
91	Quintozene	82-68-8	11.3	292.837169	C6Cl5NO2	C5Cl5	234.843716	234.844265
						C6Cl4	211.874851	211.875400
						C6Cl5	246.843716	246.844265
92	Siafluofen	105024-66-6	27.0	408.192086	C25H29FO2Si	C10H15OSi	179.088669	179.089218
						C15H15FOSi	258.087072	258.087621
						C17H19FOSi	286.118372	286.118921
93	Spiromesifen	283594-90-1	20.7	370.214410	C23H30O4	C17H20O3	272.140700	272.141245
						C17H18O2	254.130130	254.130679
						C17H21O3	273.148520	273.149070
94	Sulfotep	3689-24-5	10.2	322.022740	C8H20O5P2S2	C8H20O5P2S2	322.022196	322.022745
						C4H11O3PS2	201.988178	201.988727
						C2H8O5P2S2	237.928296	237.928845
95	Terbuthylazine	5915-41-3	11.2	229.109423	C9H16ClN5	C8H13ClN5	214.085399	214.085948
						C5H8ClN5	173.046274	173.046823
						C5H8N5	138.077421	138.077970
96	Tetrachlorvinphos	22248-79-9	16.1	363.899260	C10H9Cl4O4P	C10H9Cl3O4P	328.929858	328.930407
						C2H6O3P	109.004909	109.005458
						C10H9Cl4O4	332.924948	332.925497
97	Tetrasul	2227-13-6	18.5	321.894434	C12H6Cl4S	C12H6Cl2S	251.956179	251.956728
						C12H6(37Cl)ClS	253.953229	253.953778
						C12H6(37Cl)Cl3S	323.890935	323.891484
98	Thiobencarb	28249-77-6	13.7	257.064114	C12H16ClNOS	C5H10NO	100.075690	100.076239
						C3H6NO	72.044390	72.044939
						C7H6Cl	125.015254	125.015803
99	Tralkoxydim	87820-88-0	22.8	329.199094	C20H27NO3	C7H7NO2	137.047130	137.047679
						C6H7NO	109.052215	109.052764
						C18H21NO2	283.156680	283.157229

The database of 102 compounds including: CAS number, retention times, molecular formula and exact mass of the compounds, and the formula, neutral mass and exact ion mass of fragment ions. (Cont.)

Compounds		CAS number	Rt (min)	Exact molecular mass	Molecular formula	Ion formula	M^+ , M+2	Neutral mass
100	Tralomethrin	66841-25-6	29.0	660.809838	C22H19Br4NO3	C13H9O	181.064791	181.065340
						C7H9Br2	250.906548	250.907097
						C6H9Br2O	254.901462	254.902011
101	Trichloronate	327-98-0	14.4	331.936124	C10H12Cl3O2PS	C2H6OPS	108.987151	108.987700
						C8H8Cl2O2PS	268.935422	268.935971
						C10H12Cl2O2PS	296.966722	296.967271
102	Triflumizole	68694-11-1	15.6	345.085574	C15H15ClF3N3O	C8H4ClF3N	205.997887	205.998436
						C7H3ClF3	178.986988	178.987537
						C12H12ClF3NO	278.055402	278.055951