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RESEARCH PAPER

Compensation for matrix effects in GC analysis of pesticides by using cucumber extract

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Abstract

Matrix effects (MEs) can adversely affect quantification in pesticide residue analysis using GC. Analyte protectants (APs) can effectively interact with and mask active sites in the GC system, and are added individually or in combination to sample extracts and calibration solutions to minimize errors related to MEs. Unfortunately, APs cannot sufficiently compensate for MEs in all cases. Plant extracts, containing a broad range of natural compounds with AP properties, can also be used for this purpose. In this study, the applicability of cucumber extract as a natural AP mixture was investigated both alone and in combination with traditional APs. Extracts of two selected difficult matrices (onion and garlic) were prepared according to the citrate-buffered QuEChERS (quick, easy, cheap, effective, rugged, and safe) procedure. ME values of 40 representative GC-amenable pesticides were compared when calibrating against standards in pure solvent and in cucumber extract, with and without the addition of APs. Using a GC system with a contaminated inlet liner, the use of a cucumber-based calibration solution decreased MEs remarkably. The combination of APs with cucumber raw extract further decreased MEs, resulting in more than 85% of the tested pesticides showing ≤ 10% ME in onion and ≤ 20% ME in garlic. These results demonstrate that the preparation of calibration standards based on cucumber extracts (with or without the addition of APs) is a very useful and practical approach to compensate for MEs in pesticide residue analysis using QuEChERS and GC-MS/MS. The use of various internal standards is furthermore critically discussed.

Keywords Pesticide residue analysis · QuEChERS · Matrix effects · GC-MS/MS · Matrix-based calibration · Internal standard

Introduction

Combinations of QuEChERS (quick, easy, cheap, effective, rugged, and safe) sample preparation with GC- and LC-separation and massspectrometric detectorion are widely used in pesticide residue analysis to monitor hundreds of pesticide residues at trace levels. But when dealing with complex matrices, analysis is particularly vulnerable to matrix effects (MEs) which adversely affect quantification in both GC and LC applications [1–4].

The causes of MEs in GC-MS and LC-MS are different in nature [5]. In GC, a matrix-induced signal enhancement effect occurs when an analyte is retained or decomposed at active sites in the inlet, column, or detector [6]. Pesticides with polar structures, e.g., hydroxy, amino, and phosphate functional groups, are more likely to bind and react with glass and metal surfaces in a heated gaseous state than nonpolar pesticides, e.g., organic chlorinated pesticides [7].

When injected into the GC, various pesticides tend to interact with active sites of the GC system, which can lead to a stronger retention (mostly visible as tailing) or their degradation. In the presence of plant-derived matrix components in the extract, the interaction of pesticides with active sites is considerably reduced as such matrix components, which are present in excess, occupy most of the active sites, allowing the pesticide molecules to pass through the GC system with strongly reduced surface interactions. The presence of a matrix thus leads to reduced pesticide decomposition and sharper

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peaks. Differences in MEs between sample extracts and reagent-only calibration standards consequently lead to quantification errors.

Various approaches have been reported in literature to compensate for MEs in GC-MS, including the standard additions method [8, 9], the use of isotopically labeled internal standards (ILISs) [10–12], the use of matrix-matched calibration [2, 11, 13], and the use of analyte protectants (APs) [14–16]. Among these approaches, the addition of APs [14, 15, 17] into the standard solution and samples is the most practical for routine measurements of many different commodities as it can be applied to most GC-amenable pesticides and does not require the availability of extracts from blank matrix. APs are compounds entailing multiple hydroxy groups, with which they can effectively interact with the active sites via hydrogen bonds to reduce analyte tailing and decomposition within the GC system [18].

From 92 compounds, Anastassiades et al. [15] selected gulonolactone to be the most effective protecting agent for the most pesticides in GC-MS, and determined 3-ethoxy-1,2-propanediol, gluconolactone, and D-sorbitol as the best combination [14]. Later on, shikimic acid was added to the mixture, which is effective in protecting base-labile pesticides [19]. This AP combination is currently widely used to reduce or overcome MEs in GC analyses of QuEChERS extracts. As AP compounds are very polar in nature, they do not dissolve well in nonpolar solvents and can therefore not be used in a straightforward way with most multiresidue methods in which the final extracts are dissolved in nonpolar solvents.

However, MEs can still occur even when using large amounts of APs [20]. MEs affecting late-eluting pesticides such as pyrethroids are, for example, not properly compensated by the AP mixture. Sánchez-Brunete et al. [21] reported that MEs were reduced in the analysis of soil, juice, and honey by using L-gulonic acid γ-lactone and olive oil as a natural AP. Other studies showed that the detection sensitivity of thermolabile compounds improves by adding a pepper extract [22–24].

In this study, we evaluated the use of cucumber extracts alone and in combination with APs as a practical method to compensate for MEs in routine pesticide residue analysis via QuEChERS and GC-MS/MS.

Materials and methods

Chemicals and apparatus

The 40 pesticide standards and 2 internal standards (IS) used in this study were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), Sigma-Aldrich (Steinheim, Germany), Riedel-del Haen (Seelze, Germany), and LGC Standards GmbH (Wesel, Germany). The stock solution was prepared with acetonitrile at a concentration of 1 mg/mL. The working standard mixture was prepared by diluting acetonitrile to a concentration of 1 μg/mL. The prepared mixture was used for experiments within 1 week. The IS was 20 μg/mL of chlorpyrifos d10 (diethyl d10) and diluted ten times with acetonitrile when added to samples and standard solutions.

The APs, ethyl glycerol, sorbitol, δ-gluconolactone, and shikimic acid were purchased from Sigma-Aldrich. To prepare the AP mixture, 50 mg/mL of sorbitol, 50 mg/mL of δ-gluconolactone, and 50 mg/mL of shikimic acid were made using 40% water in acetonitrile, and further diluted with 40% water in acetonitrile to produce 200 mg/mL of ethyl glycerol, 5 mg/mL of sorbitol, 10 mg/mL of δ-gluconolactone, and 5 mg/mL of shikimic acid [18]. Ultrapure water was prepared using the Direct-Q 3 UV Ultrapure Water Purification System (EMD Millipore Corp., Billerica, MA, USA), and acetonitrile and formic acid (98–100%) were purchased from Merck (Darmstadt, Germany). A 5% formic acid solution (*v*/*v*) was prepared with acetonitrile.

For extraction, pre-packed QuEChERS salt mixtures purchased from UCT (Levittown, PA, USA) were used containing 4 g anh. (anhydrous) $MgSO_4$ + 1 g sodium chloride (NaCl) + 1 g trisodium citrate dehydrate ($Na_3Cit{\cdot}2H_2O$) + 0.5 g disodium hydrogen citrate sesquihydrate ($Na_2HCit{\cdot}1.5H_2O$). For the dispersive solid-phase extraction (d-SPE) cleanup step, anh. $MgSO_4$ grit was purchased from Sigma-Aldrich (Steinheim, Germany), and the silica-based primary-secondary amine (PSA) sorbent Bondesil-PSA, 40 μm, was purchased from Varian (Palo Alto, CA, USA). A Prime Cut UM5 (Stephan Machinery GmbH, Hameln, Germany), Geno Grinder 2010 (SPEX Sample Prep, Metuchen, NJ, USA), and Rotanta 460 (Hettich, Tuttlingen, Germany) were used for sample milling, sample extraction, and centrifugation, respectively.

Sample preparation

The onion and garlic used in the experiment were purchased from an organic farm-product market. The outermost shell surrounding the cloves and stalk of the garlic were removed, and the dry and easily peeled outermost shell of the onion was removed for the experiment. The garlic and onion were placed in separate Styrofoam containers, quickly frozen by adding liquid nitrogen, and comminuted using a chopper.

For the sample preparation, the QuEChERS method using a citrate buffer was applied [19, 25]. Because the water content of garlic is 60% [26], water was added to the garlic as described below. The QuEChERS procedure for onion and garlic was as follows: (1) weigh each sample (10.0 ± 0.1 g of onion and 5.0 ± 0.1 g of garlic) into a 50-mL centrifuge tube and add 6 mL of water to the garlic; (2) add 10 mL of acetonitrile into the tube and shake the tube vigorously using the shaker for 15 min; (3) add 4 g anh. $MgSO_4$, 1 g NaCl, 1 g

$Na_3Cit{\cdot}2H_2O$, and 0.5 g $Na_2HCit{\cdot}1.5H_2O$; (4) seal the tubes, shake vigorously for 1 min using a shaker, and centrifuge at 3500 relative centrifugal force (rcf) for 5 min; (5) transfer 6 mL of supernatant into a d-SPE tube containing 150 mg of PSA and 900 mg of anh. $MgSO_4$; (6) seal the tubes, shake for 30 s, and centrifuge at 3500 rcf for 5 min; (7) transfer 4 mL of extract into a glass container and add 40 μL of acetonitrile containing 5% formic acid; and (8) transfer 800 μL of extract into an autosampler vial, and add 100 μL of the working standard mixture and 100 μL of the IS solution to obtain a final solution concentration of 0.1 μg/mL for pesticides and 0.2 μg/mL for IS.

The cucumber to be used for the cucumber standard was purchased from a local organic product market, cut, frozen, and then comminuted with dry ice using a chopper. For cucumber extraction, steps (1) to (4) were the same as for onion. Sixty microliters of acetonitrile containing 5% formic acid was added to 6 mL raw extract. For solvent- and cucumber-based calibration standards, 800 μL of acetonitrile or cucumber blank extract, respectively, was used instead of onion or garlic extracts. Where APs were used, 30 μL of the AP mixture was added per vial.

ME was calculated separately against solvent-based and cucumber-based standards using the peak areas of the matrix, solvent, and cucumber, as shown in the following equation:

$$\%\mathrm{ME} = \frac{S_{\mathrm{Matr}} - S_{\mathrm{Ref}}}{S_{\mathrm{Ref}}} \times 100$$

S_{Matr} signal (area or area ratio against IS) of compound spiked to onion or garlic extract

S_{Ref} signal (area or area ratio against IS) of compound spiked to pure solvent or cucumber extract

GC-MS/MS analysis

For the GC-MS/MS analysis (Table 1), a Thermo Scientific TSQ 8000 triple quadrupole MS/MS (Waltham, MA, USA) in the electron ionization (EI) mode was connected to a Thermo Scientific Trace 1310 GC system (Waltham, MA, USA). The injection volume was 3 μL using a TriPlus RSH autosampler (Thermo Scientific, Waltham, MA, USA). The CIS 4 programmed-temperature vaporizing (PTV) injector by Gerstel equipped with a cryostatic cooling was maintained at 50 °C for 0.8 min after the sample injection, and the purge flow to the solvent vent was maintained at a vent flow of 20 mL/min with an open purge valve during this time. After the purge valve was closed, the PTV temperature was increased at 12 °C/s to 300 °C, held for 10 min, and then held at 240 °C for 1 min.

The analytical column was a Thermo Scientific TG-5Sil MS (30 m × 0.25 mm, 0.25-μm film thickness), and the flow was maintained at a rate of 2 mL/min. During the experiment, the liner and column were in a relatively poor condition to simulate a bad case scenario. The GC oven temperature was maintained at 40 °C for 2 min, then heated to 220 °C at

Table 1 Retention times (t_R) and selected reaction monitoring (SRM) pairs in GC-MS/MS

Analyte	t_R (min)	SRM1 (*m*/*z*)	SRM2 (*m*/*z*)
Azoxystrobin	19.0	344/172	344/329
Bifenthrin	12.8	181/165	181/166
Biphenyl	6.7	153/152	154/153
Buprofezin	10.6	172/57	305/172
Chlorpyrifos D10 (IS)	9.2	326/262	324/260
Chlorpyrifos	9.3	314/258	314/286
Chlorpyrifos-methyl	8.8	286/271	288/273
Cyprodinil	9.7	225/210	224/208
Dicloran	8.3	206/176	208/178
Dicofol	14.5	139/111	251/139
Dimethomorph	19.5	301/272	387/301
Endosulfan-alpha	10.3	241/206	243/208
Endosulfan-beta	11.2	241/206	243/208
Endosulfan-sulfate	11.9	270/235	272/235
Etofenprox	16.9	163/107	163/135
Fenarimol	14.5	251/139	219/107
Fludioxonil	10.9	248/154	248/182
Iprodione	12.8	314/245	316/247
Kresoxim-methyl	10.6	206/116	206/131
Lambda-cyhalothrin	14.1	197/141	208/181
Malathion	9.2	173/99	173/127
Mepanipyrim	10.3	222/207	222/118
Mepanipyrim, hydroxypropyl-	10.4	243/82	243/186
Metalaxyl	9.0	234/174	249/190
Myclobutanil	10.7	179/125	179/152
2-Phenylphenol	7.5	170/141	170/169
PCB138 (IS)	11.9	358/288	360/290
Pendimethalin	9.7	252/162	252/191
Permethrin	15.3	183/153	183/168
Pirimicarb	8.6	166/71	238/166
Pirimiphos-methyl	9.0	290/233	290/125
Procymidone	9.9	283/96	285/96
Propargite	12.1	173/135	350/201
Pyridaben	15.4	309/147	147/132
Pyrimethanil	8.5	198/118	199/198
Pyriproxyfen	13.5	136/78	136/96
Quinalphos	9.8	146/118	298/156
Quinoxyfen	11.8	307/237	307/272
Tebufenpyrad	13.2	333/171	333/276
Thiabendazole	10.2	201/130	174/103
Trifloxystrobin	11.6	222/130	222/162
Vinclozolin	8.9	285/212	212/172

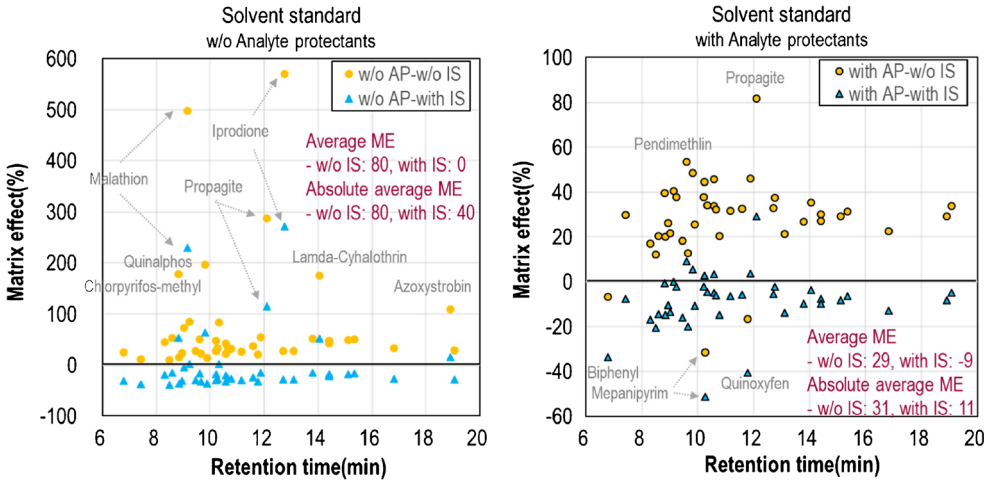

Fig. 1 MEs in GC analysis of onion extract using solvent standard as a reference, results without APs (left) and with APs (right)

30 °C/min, 260 °C at 5 °C/min, and 280 °C at 20 °C/min, and then held for 15 min. The MS/MS condition included a selected ion monitoring (SRM) mode, ionization energy of 70 eV, an ion source temperature of 280 °C, and a transfer line of 280 °C. The data was processed using the Xcalibur 4.0 software.

Results and discussion

In GC analysis, APs are substances that significantly reduce the MEs [14, 15]; however, they cannot sufficiently protect all pesticides [20]. Some previous studies used plant extracts to compensate for the MEs [23, 24].

Cucumbers from organic production are readily available in the market, and compared to other vegetable matrices, their raw extracts contain relatively low amounts of matrix components, thus showing very few chromatographic and mass spectrometric interferences and leading to a very moderate contamination of the GC-inlet system with nonvolatiles. Thus, this study focused on checking cucumbers as possible natural APs. Raw extracts from cucumbers were used without PSA purification to reserve components that could serve as APs [15].

Figure 1 shows the %MEs of various compounds spiked to onion extracts, using a reference standard based on pure solvent (solvent standard), an approach commonly used by several pesticide residue analysis laboratories. When no APs were used (Fig. 1 (left)), the %MEs were very high, including cases with > 400% ME, while most of the %ME values ranged between + 20 and + 100%. The pesticides showing the strongest MEs were azoxystrobin, chlorpyrifos-methyl, endosulfane sulfate, iprodione, lambda-cyhlothrin, malathion, propargite, and quinalphos. As the IS (chlorpyrifos D10) showed strong MEs itself, the %MEs of all compounds decreased considerably when calculating against the IS. But even then, the %ME still exceeded 200% in some cases (iprodione, malathion) while in some other cases (biphenyl, mepanipyrim, quinalphos), there was even an overcompensation, with %ME values dropping below − 25%. When APs were used (Fig. 1 (right)), all pesticides showed decreased MEs, with all but three pesticides (mepanipyrim, propargite, pendimethalin) showing %MEs in the range of + 10 to + 50%. In the case of the above-mentioned iprodione and malathion, for example, the %ME values lowered from > 200% without APs to < 40% when APs were used. Calculation against the IS (chlorpyrifos D10) further lowered the %ME of all but three

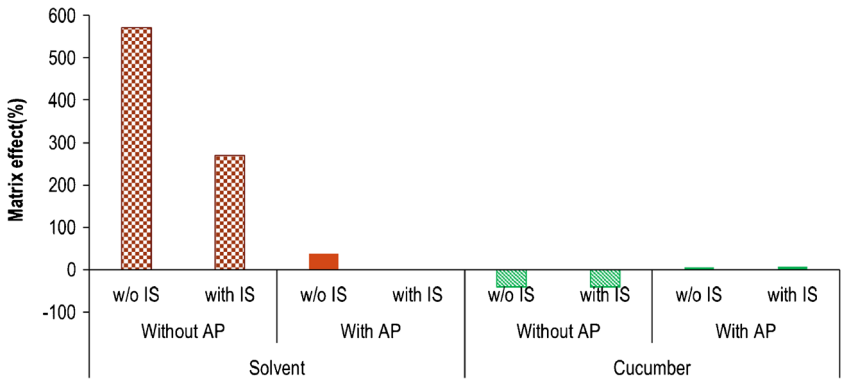

Fig. 2 MEs of iprodione in onion extract using as reference a solvent-based standard (left) and a cucumber-based standard (right) with and without the use of APs

pesticides (biphenyl, mepanipyrim, quinoxyfen) to values from − 22 to + 10%.

The results confirm that when solvent standards are used as reference, the addition of APs significantly reduces MEs. For a substantial number of pesticides, however, the effects were not sufficiently compensated (average %ME 29%). Also, here, the IS (chlorpyrifos D10), which showed strong MEs itself, did not always have a positive impact on the absolute %ME of the target analytes, introducing in some cases a considerable negative bias to compounds such as biphenyl, mepanipyrim, and quinoxafen, which were otherwise not strongly affected much by MEs. The suitability of chlorpyrifos D10 as IS is thus questionable and should be critically evaluated especially when calibration is based on standards in solvent.

Figure 2 shows exemplarily the %ME of iprodione in GC-MS analysis of onion, using as reference a standard in cucumber raw extract and a standard in pure solvent. Calculations were done based on both peak area and peak area ratio against the IS (chlorpyrifos D10). Without the use of IS, the %ME against a solvent standard was as high as 571% if no AP was used but dropped drastically to (still unacceptable) 38% when AP was added to both onion-based and solvent-based standards. Iprodione and the IS showed a similar ME in this experiment, with the IS correcting the %ME of iprodione to an acceptable − 2% (against solvent-based standard and using AP). When using the cucumber standard instead of the solvent standard, the %ME was overall much lower and shifted from − 40% without AP to + 5% with AP. The combination of cucumber and AP provided the overall best results for iprodione with the ME being virtually eliminated. When no AP was used, cucumber-matrix exhibited a stronger protection on iprodione than onion-matrix, resulting in a negative relative ME which was, however, outside the acceptable range. As the IS (chlorpyrifos D10) behaved similarly in cucumber and onion, it had virtually no effect on the %ME calculations when using cucumber-based standards (both using or not using APs).

Figure 3 shows the %ME when using cucumber-based standard with and without APs. Without the use of APs, the %MEs of all pesticides but five (iprodione, endosulfane sulfate, propagate, lamda-cyhothrin, and malathion) were in the range of − 10 to + 15%, with four pesticides showing an absolute ME > 20%. There was little difference in the calculations with and without using the IS. With the use of APs, the %ME decreased further, with the %ME of all pesticides but five (mepanipyrim, quinoxifen, pendimethalin, endosulfan-sulfate, and dichloran) ranging between − 5 and + 10% and with only two pesticides showing an absolute ME > 20% (mepanipyrim and quinoxyfen).

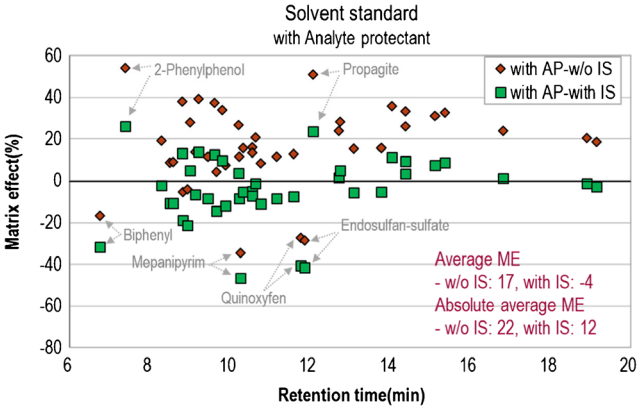

Fig. 4 MEs in GC analysis of garlic using a solvent-based standard with APs as a reference, and impact of the IS chlorpyrifos D10 on the MEs

In the case of garlic, the situation was overall similar to onion. Using solvent standard as a reference and with APs being added to both garlic extract and solvent standard (Fig. 4), all pesticides except six (2-phenylphenol, propagit, biphenyl, mepanipyrim, quinoxyfen, and endosulfan-sulfate) showed %MEs in the range between − 14% and + 40% when the IS was not used for calculation and in the range between − 22% and + 18% when the IS was used.

Using cucumber standard without APs as a reference, the %ME values of all pesticides except five (iprodione, lambda-cyhalothrin, endosulfane sulfate, malathion, and biphenyl) were distributed between − 30 and + 4% when the IS was

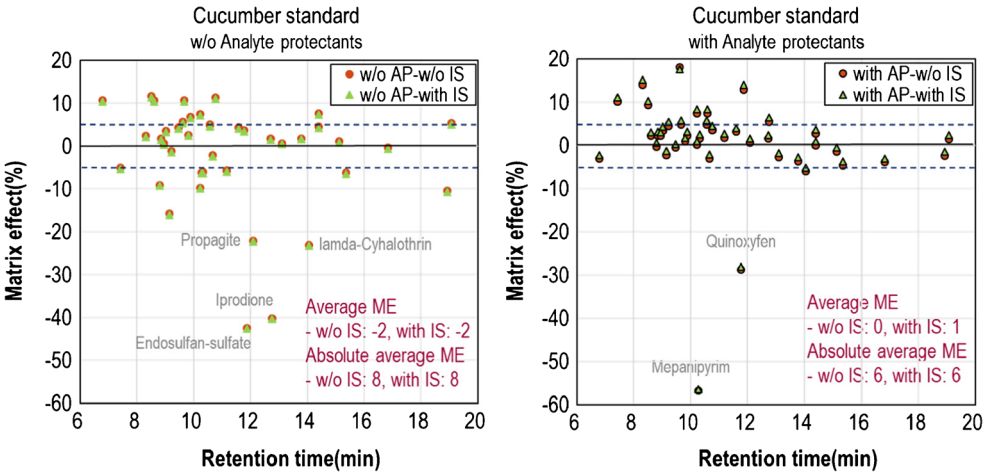

Fig. 3 MEs in GC analysis of onion extract using as reference a cucumber-based standard without APs (left) and with APs (right)

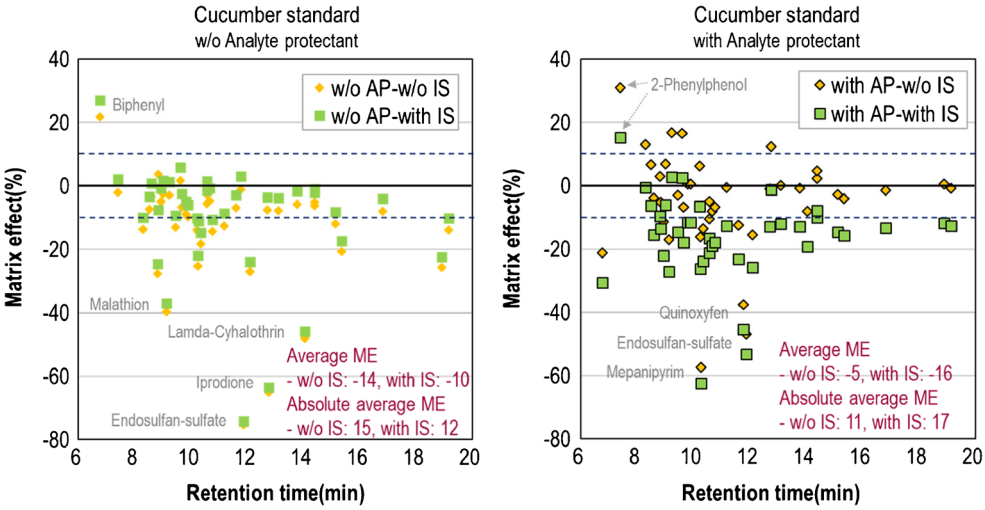

Fig. 5 MEs in GC-MS/MS analysis of garlic extract using as a reference cucumber standard without APs (left) and with APs (right). IS, chlorpyrifos D 10

not used and between − 25 and + 6% when the IS was used (Fig. 5 (left)).

Using cucumber standard in combination with APs (Fig. 5 (right)), the calculation against the IS (chlorpyrifos D10) resulted in an overall increase of the average %ME from − 5 to − 16% and of the absolute %ME from 11 to 17%.

Figure 6 shows the distribution of the absolute %MEs of all tested pesticides in onion and garlic. In onion, using a solvent standard as reference and without using APs and not calculating against the IS (*O-S1*), there was no pesticide with an absolute ME ≤ 10% and only one out of ten pesticides with an absolute ME < 20%. Roughly half of the pesticides showed an absolute ME ≥ 40%. When using the IS for calculation (*O-S2*), the pesticides showing an absolute ME < 20% increased to circa one out of three. Using APs and calculating against the IS (*O-S4*), the average %ME was reduced significantly and the percentage of pesticides with an absolute ME ≤ 10 and ≤ 20% increased to 63 and 90%, respectively.

The cucumber standard strongly reduced the %ME of all the pesticides, with the IS having a considerably reduced influence. When APs were not used, the share of pesticides with an absolute ME ≤ 10% was 76% when calculating without using the IS (*O-C1*) and 81% when using the IS (*O-C2*). When APs were used, these figures increased to 87% (*O-C3*) and 85% (*O-C4*), respectively. Both with and without the use of IS, the percentage of pesticides showing an absolute ME > 20% was 7% using APs and 10% not using APs.

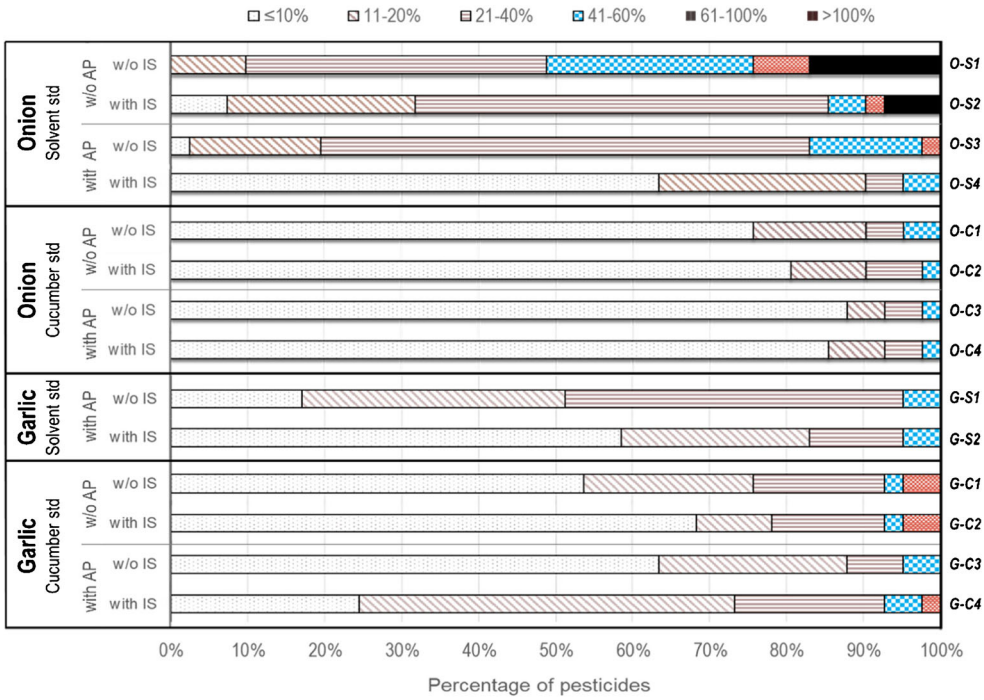

Fig. 6 Influence of calibration type (solvent- versus cucumber-based; with and without APs; with and without IS) on the MEs of the studied pesticides during GC analysis of onion and garlic extracts and grouping of pesticides according to their absolute MEs (in %)

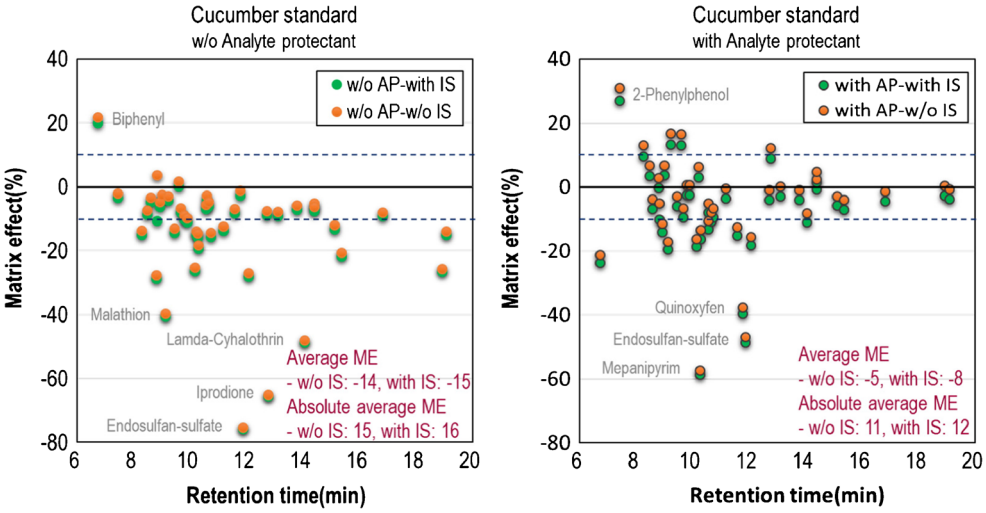

Fig. 7 MEs in GC analysis of garlic extract using as a reference cucumber standard without APs (left) and with APs (right). IS, PCB 138

In garlic, the observed trends were similar to onion, with the use of the IS (chlorpyrifos D10) reducing the %ME when calibrating against a solvent-based standard containing APs (*G-S1* versus *G-S2*) or against a cucumber-based standard without APs (*G-C1* versus *G-C2*), and a negative (though much more pronounced) impact when calibrating against a cucumber-based standard with APs (*G-C3* versus *G-C4*). In particular, using a solvent-based calibration with APs, the share of pesticides showing an absolute ME ≤ 10% raised from 17% without IS (*G-S1*) to 58% when calculating against the IS (*G-S2*), but it dropped from 63% without IS (*G-C3*) to 24% with IS (*G-C4*) when calibrating against a cucumber standard with APs.

The latter effect was mainly correlated to the significant drop (− 14% on average) in the peak area of the IS in the cucumber standard in the presence of APs. This resulted in a shift of all results calculated against the IS. A similar drop of the signal areas when adding APs to cucumber standard was also observed for several others among the compounds injected, including native chlorpyrifos (− 14% on average), chlorpyrifos-methyl (− 18%), and 2-phenylphenol (− 30%). There were also pesticides showing an increase of their signals when adding APs to cucumber standard, such as iprodione (+ 54%) and thiabendazole (+ 18%). Among the compounds injected, the most indifferent one against ME was the alternative IS PCB 138. PCB 138 is well suitable as an IS for the correction of volume deviations, but it has the drawback of experiencing partitioning losses when extracting commodities of high lipid content and when conducting cleanup with graphitized carbon. Among the tested pesticides, the ones affected the least by MEs were buprofezin, cyprodinil, metalaxyl, procymidone, and pyrimethanil. The isotope-labeled analogues of these compounds would thus, in theory, be well suitable as IS for volume corrections.

Considering the overall %ME values, the best way to compensate for MEs in garlic was the calibration against a cucumber-based standard in combination with APs but without using chlorpyrifos D10 as IS. Calculating against the alternative IS PCB 138, the %ME remained practically the same as when calculating with peak areas (see Fig. 7) but the overall

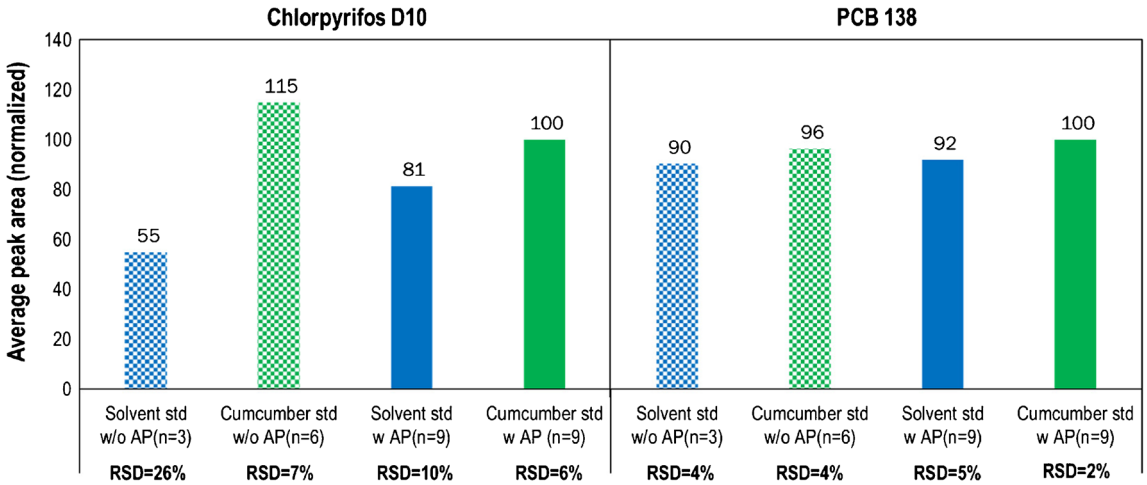

Fig. 8 Relative GC-MS/MS peak areas of chlorpyrifos D10 and PCB 138 in each standard solution normalized against the areas obtained in cucumber standard with AP

fluctuation of results was reduced through volumetric correction (not shown here).

Figure 8 shows a comparison of the relative peak areas and relative standard deviations (RSDs) of chlorpyrifos D10 and PCB138, in each standard solution used for calculating MEs. The peak areas were separately normalized by setting the respective average peak area obtained when injecting cucumber-based standard with APs at 100%. It should be noted that more than 60 injections of various extracts took place between the first and the last injection of the same standards. In the case of chlorpyrifos D10, the ranking in terms of average peak areas was as follows: cucumber standard without APs > cucumber standard with APs > solvent standard with APs > solvent standard without APs. The solvent standard without APs showed the largest variation (RSD = 26%, at $n = 3$). The RSD of the solvent standard with AP was 10% ($n = 9$). The cucumber-based standards with or without AP showed the smallest variations (RSDs were 6 and 7%, respectively). The results indicate that the reproducibility of the cucumber standard was better than that of the solvent standard in the GC-MS system in all conditions with and without APs.

Another interesting aspect observed was the shift in retention times of certain pesticides, i.e., the retention time measured at the peak apex of a smoothed peak. When the standards were prepared in matrix (cucumber, onion, or garlic) or in the presence of APs, retention times and peak shapes were largely comparable. When injecting standards in pure solvent, however, many pesticides showed a more pronounced tailing, which resulted in a shift of the respective peak apex. The compounds most affected by retention time shifts were thiabendazole (+ 0.83 min), hydroxypropyl-mepanipyrim (+ 0.36 min), azoxystrobin (+ 0.24 min), dicloran (+ 0.21 min), 2-phenylphenol (+ 0.21 min), and mepanipyrim (+ 0.20 min). Peak tailing always increases the risk of interferences and affects quantification especially at low levels.

Conclusions

In GC-MS analysis of QuEChERS extracts, the cucumber raw extract-based calibration standards were shown to be more suitable for compensating MEs than standards in pure solvent. Combining cucumber extract with APs was shown to be the best option overall whereas the use of solvent-based standards in combination with APs was not as effective for the tested complex matrices (onion and garlic). The choice of the IS can be very critical, and the use of a nonsuitable IS (showing strong or varying ME) may even contribute to a higher error. Chlorpyrifos D10 proved to be rather unsuitable for GC analyses as its signal was strongly influenced by the presence of the matrix and APs. The cucumber matrix introduced only very small interferences not affecting the detectability of the peaks.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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