TRIPLE QUADRUPOLE VS ION TRAP SENSITIVITY IN A MULTIRESIDUE PESTICIDES ANALYSIS IN SELECTED FRUIT AND VEGETABLES

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Mass spectrometry stands for highly selective and sensitive instrumental technique; therefore, it has many applications in various scientific fields. Sensitivity is usually defined as the change in measured signal per unit change in analyte concentration. Several factors such as the effective sample preparation, mobile phase composition, chromatographic column parameters and mass spectrometer features can affect this parameter. By keeping rest of the parameters the same, the effect of mass spectrometer features on the sensitivity of multi-residue pesticides analysis was investigated. Linear ion trap and triple quadrupole, as the two most exploited mass analyzers, were compared. The comparison of sensitivity for solvent-based and QuEChERS treated fruit- and vegetable-based pesticides standards demonstrated triple quadrupole as a highly sensitive instrument. The analysis of solvent-based standards on the triple quadrupole was from 4 to 71 times more sensitive than the analysis on the linear ion trap. Sensitivity enhancement for lemon-based standards ranged from 15 to 138 times, and for vegetable-based standards (tomato, lettuce, cucumber) it ranged from about 5 to about 70 times, when shifting from linear ion trap to triple quadrupole. Sensitivity comparison for solvent- and sample-based standards majorly evidenced the presence of a strong matrix effect, thus reflecting the need to perform analytes quantification against sample-based standards in an actual sample analysis.

Keywords: mass spectrometry, HPLC, multi-residue analysis, vegetables

Introduction

Due to its supreme selectivity and sensitivity, mass spectrometry nowadays represents the most used analytical technique for both qualitative and quantitative purposes in many research areas such as life sciences, forensics, environmental and food monitoring and safety. In mass spectrometry, sensitivity is usually defined as the increment in measured signal per unit change in analyte concentration; it can be related to the detection limits, meaning the higher the sensitivity, the lower the detection limits. In practice, across the specified concentration range this parameter can be estimated via the slope of the calibration function.

The basics of sensitivity lay in the in-source ionization efficiency and subsequent transfer efficiency from the atmospheric pressure to the low-pressure region of the mass spectrometer. Several factors such as the effective sample preparation, mobile phase composition, chromatographic column parameters and mass spectrometer features can enhance analyte signal when carefully chosen and optimized and can result in a highly sensitive method of analysis. Critical factors that may lead to poor sensitivity such as the analyte properties and the mobile phase composition are usually dealt with the analyte structure modification by derivatization, or the change in the mobile phase composition [1]. The use of ultra-high performance liquid chromatography (UHPLC) instead of high-performance liquid chromatography (HPLC) can lead to improvements in speed, resolution and sensitivity of a method. By comparing these two methods in the analysis of several compounds from different chemical classes, Churchwell et al. [2] found as large as 10-fold sensitivity improvement with UHPLC.

In addition to these factors, mass analysis and detection are significant factors in the sensitive analysis. Since the key point of difference between the mass spectrometers is mass analyzer, the improvement in its construction is a promising method for sensitivity enhancement. There are four basic approaches for the improvement of mass spectrometers' sensitivity, which include ion transmission efficiency improvement mainly used in quadrupole mass analyzers, selective enrichment of targeted ions mainly used in ion traps, the improvement of the ion utilization rate, used in time-of-flight (TOF), Fourier transform ion cyclotron (FT-ICR) and Orbitrap mass analyzers and the improvement of the signal-to-noise ratio (S/N) of the spectrum used in quadrupole tandem mass analyzers [3].

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Quadrupole tandem mass analyzer (triple quadrupole, QqQ) combines three transmission quadrupoles in a linear configuration, of which the first and the third quadrupole have the role of scanning or filtering device and the central one has the role of a collision cell. Stages of tandem mass analysis within this analyzer (parent ion isolation, parent ion fragmentation, daughter ions isolation and transmission towards the detector) are performed successively in space. QqQ performs scanning by ramping the DC/RF voltage in time across the quadrupoles, providing ions of one specified m/z ratio are only passed through the analyzer in a unit of time, rejecting all other ions. Due to the small interscan times, the duty cycle of this analyzer is almost 100%.

On the contrary, in the ion trap analyzer stages of tandem mass analysis are performed in the same space, successively in time. Since the ion trap works on the principle of filling and emptying the same space with ion packages, the main phenomenon that can affect sensitivity is the space charge effect which arises from the Coulomb interactions between the ions trapped in small space. This phenomenon is circumvented by the accumulation of a limited number of ions, determined in the instrument cycle called the pre-scan. Ion traps that differ in construction also differ in trapping efficiency and charge capacity. The successor of the originally constructed trap (3D ion trap – quadrupole ion trap), 2D ion trap – linear ion trap has about 10 times higher trapping efficiency and 20 times higher charge capacity than the 3D trap [3], simply due to a larger trapping space, which should lead to higher sensitivity of a linear ion trap.

Due to a pre-scanning, ion traps have a lesser duty cycle than QqQs, which implies smaller number of ions arriving from the source are processed in a unit of time than in the QqQ. Vatansever et al. [6] made a comparison of a linear ion trap and triple quadrupole on the example of large peptides. They noted a milder and single-step fragmentation of peptides on a linear ion trap and more efficient dissociations on a triple quadrupole due to a collision cascade. Furthermore, both analyzers expressed similar sensitivity in MS^1 acquisitions. However, when performing MS^2 acquisitions, the linear trap expressed better sensitivity in comparison to the triple quadrupole.

The aim of this study was to compare the sensitivity of analysis on the two most exploited, fundamentally different mass analyzers, that is on the linear ion trap and triple quadrupole mass analyzer. Performances were evaluated in the simplest MS mode, that is in the MS^1 full scan mode, primarily by the cross-analysis of solvent-based standards of 15 pesticides from different chemical classes. Then, the evaluation was broadened to pesticide standards in selected fruit and vegetable matrices treated with the QuEChERS sample preparation procedure.

Experimental

Chemicals. Formic acid (FA) (98%) and high purity pesticide standards (Table 2) were produced by Sigma-Aldrich®, Germany. Ammonium-formate (AMF) (98%), deionized water and HPLC grade ethanol were produced by Carlo Erba, Italy. HPLC grade methanol (MeOH) and acetonitrile (AcN) were produced by J.T. Baker, USA. Prepacked QuEChERS extraction pouches (1 g of NaCl, 4 g of $MgSO_4$, 1 g of trisodium citrate dihydrate and 0.5 g disodium hydrogen citrate) and dispersion kits (25 mg PSA and 150 mg $MgSO_4$) were produced by Hillium, USA. Syringe microfilters (Nylon Hydrophilic 0.22 μm) were produced by Membrane Solutions, USA. Fresh tomatoes, cucumbers, lettuce and lemons were purchased in a local supermarket.

Instruments and instrumental parameters

Appliances. For high purity standards weighing procedures analytical balance, Sartorius BP110S (Germany) was used. In the sample preparation procedure, the following appliances were used: blender 0.9L BL142A TEFAL (France), balance (acc. ± 0.01 g) KB 2000-2N KERN (Germany) and centrifuge Jouan C4i Thermo Scientific (USA). To facilitate the extraction Digital Vortex-Genie 2 (Scientific Industries, USA) was used. Nitrogen (99%) was supplied by a nitrogen generator (PEAK Scientific, Scotland, UK).

Analytical instruments and instrumental parameters. Samples were analyzed in parallel on two separate LC/MS systems presented in Table 1. 10 μL of the sample was loaded on a column in a partial loop injection mode and eluted with a mixture of: eluent A (solution of 0.10% of FA and 0.03% of AMF in water) and eluent B (MeOH) following the gradient: 0-2 min (90% A), 2-7 min (90-30% A), 7-30 min (30% A), 30-35 min (30-90% A), 35-40 min (90% A) with flow equal to 300 μL min^{-1}.

Table 1. Utilized instruments

	Instruments	
	HPLC/MS system 1	*HPLC/MS system 2*
Autosampler	Surveyor (Thermo Finnigan, USA)	Accela (Thermo Scientific, USA)
MS pump	Accela (Thermo Scientific, USA)	Accela (Thermo Scientific, USA)
Mass spectrometer	LTQ XL (Thermo Electron Corporation, USA) with *linear ion trap analyzer*	TSQ Quantum Ultra (Thermo Electron Corporation, USA) with *triple quadrupole analyzer*
	Analytes' separation and ionization	
Column	Hypersil GOLD (C18, 150mm×2.1mm, particle size 3 μm)	
Ionization type	ESI+	
	Data acquisition and processing	
Software	Thermo Xcalibur™, version 2.1.0, SP1.1160	Thermo Xcalibur™, version 2.0.7

Table 2. LC/MS features of the targeted analytes

Pesticide	Pesticide class	Chemical class	Molar mass	*m/z* of detected $[M+H]^+$ ion (MS^1 spec.)	Retention time, min*
Acetamiprid	Insecticide	Neonicotinoid	222.67	223.52	9.91
Azoxystrobin	Fungicide	Strobilurin	403.40	404.20	12.19
Boscalid	Fungicide	Pyridine carboxamide	343.20	343.40	12.69
Buprofezin	Insecticide	Thiadiazine	305.40	306.21	16.71
Cyprodinil	Fungicide	Anilinopyrimidine	225.29	226.50	12.39
Difenoconazole	Fungicide	Triazole	406.30	406.34	17.84
Fenhexamid	Fungicide	Hydroxyanilide	302.20	302.46	13.35
Kresoxim-methyl	Fungicide	Strobilurin	313.30	314.11	14.52
Metsulfuron-methyl	Herbicide	Sulfonylurea/triazine	381.37	382.15	11.14
Propiconazole	Fungicide	Triazole	342.20	342.46	15.59
Pyraclostrobin	Fungicide	Strobilurin	387.80	388.14	15.93
Pyrimethanil	Fungicide	Anilinopyrimidine	199.25	200.44	11.25
Pyriproxyfen	Insecticide	Aromatic ether/pyridine	321.40	322.26	21.64
Tebuconazole	Fungicide	Triazole	307.82	308.46	15.26
Trifloxystrobin	Fungicide	Strobilurin	408.40	409.17	18.15

*mean value (n=10) for solvent-based standard (5.00 μg mL^{-1}) analyzed on the LC/MS system 1

Table 3. Linear regression parameters ($y = ax + b$, conc. range 0.01 – 15.00 μg mL^{-1}) for the analysis of solvent-, tomato-and cucumber-based pesticides standards on a triple quadrupole instrument

	a (×10^6)	b (×10^6)	Correlation coefficient, R^2	a (×10^6)	b (×10^6)	Correlation coefficient, R^2	a (×10^6)	b (×10^6)	Correlation coefficient, R^2
	Solvent			**Tomato**			**Cucumber**		
Acetamiprid	13.51	11.04	0.9924	10.04	8.89	0.9859	7.86	10.05	0.9590
Azoxystrobin	50.78	-3.57	0.9995	21.95	12.04	0.9883	17.05	16.54	0.9626
Boscalid	1.07	1.67	0.9977	0.63	0.15	0.9986	0.49	0.17	0.9985
Buprofezin	219.41	2.19	0.9999	136.14	67.93	0.9902	106.60	76.23	0.9780
Cyprodinil	213.60	15.60	0.9999	116.38	63.54	0.9890	88.80	81.73	0.9763
Difenoconazole	5.17	0.10	0.9985	15.88	-0.37	0.9996	10.34	3.50	0.9969
Fenhexamid	5.05	-0.65	0.9992	3.20	-0.59	0.9967	2.49	-0.19	0.9994
Kresoxim methyl	2.32	0.05	0.9999	1.64	-0.03	1.0000	1.08	0.19	0.9933
Metsulfuron methyl	2.60	2.29	0.9981	1.26	1.73	0.9992	0.99	2.04	0.9910
Propiconazole	33.96	0.91	1.0000	26.87	-1.52	0.9999	19.02	4.75	0.9954
Pyraclostrobin	22.80	-0.14	1.0000	14.77	2.89	0.9980	10.78	5.23	0.9866
Pyrimethanil	58.54	45.89	0.9907	42.36	40.94	0.9994	33.60	46.83	0.9959
Pyriproxyfen	40.34	-20.23	0.9410	40.23	-40.08	0.9479	31.24	16.34	0.9924
Tebuconazole	38.83	-0.04	1.0000	27.47	-0.65	1.0000	19.45	6.12	0.9940
Trifloxystrobin	46.46	4.43	0.9998	40.88	9.27	0.9973	31.24	16.34	0.9924

Table 4. Linear regression parameters ($y = ax + b$, conc. range 0.01 – 15.00 μg mL^{-1}) for the analysis of lemon-based and lettuce-based pesticides standards on a triple quadrupole instrument

	a (×10^6)	b (×10^6)	Correlation coefficient, R^2	a (×10^6)	b (×10^6)	Correlation coefficient, R^2
	Lemon			**Lettuce**		
Acetamiprid	11.17	9.04	0.9881	9.76	12.20	0.9648
Azoxystrobin	32.20	15.34	0.9931	17.76	16.43	0.9699
Boscalid	0.89	0.22	0.9990	0.58	0.14	0.9985
Buprofezin	69.23	48.51	0.9799	118.17	94.73	0.9748
Cyprodinil	68.28	60.18	0.9790	97.04	90.62	0.9660
Difenoconazole	17.40	3.97	0.9991	13.24	1.32	0.9958
Fenhexamid	6.19	22.7	0.9923	3.00	-0.16	0.9992
Kresoxim methyl	3.18	0.23	0.9999	1.37	0.22	0.9958
Metsulfuron methyl	1.34	2.32	0.9988	1.08	2.95	0.9721
Propiconazole	23.76	3.84	0.9983	22.22	5.04	0.9979
Pyraclostrobin	16.61	2.55	0.9993	12.49	5.41	0.9905
Pyrimethanil	31.86	49.00	0.9947	36.10	51.75	0.9943
Pyriproxyfen	24.84	-19.68	0.9702	36.70	-34.50	0.9570
Tebuconazole	22.70	3.57	0.9987	23.19	6.18	0.9965
Trifloxystrobin	53.91	17.42	0.9970	32.00	18.97	0.9848

Procedures

Stocks preparation. Single-pesticide stock solutions (1 mgmL^{-1} each) were prepared by dissolving high purity pesticide standards in ethanol. Multi-pesticide solutions were prepared by mixing and diluting single stocks in ethanol.

Sample preparation. One kilogram of fresh tomato, cucumber, lettuce and lemon was cut and homogenized by blending for 5 min. Ten grams of the obtained homogenate of each matrix were extracted with 10 mL of acetonitrile, after which an extraction pouch was added. The mixture was immediately vortexed for one minute

and centrifugated (10 min/3000 rpm). A supernatant aliquot was subjected to a dispersive extraction by the addition of one dispersion kit per mL of supernatant. The mixture was vortexed for one minute and centrifugated (10 min/3000 rpm). The supernatant was microfiltered prior to instrumental analysis.

Calibration standards preparation. Solvent-based standard series was prepared by spiking acetonitrile with a multi-pesticide standard solution. For each matrix, standard series with 7 calibration levels was prepared by spiking the obtained blank extracts with multi-pesticides standard solutions.

Results and discussion

Sensitivity, denoted as parameter a of the calibration function $y = ax + b$, for analysis of pesticide standards on a triple quadrupole is given in Tables 3 and 4. The comparison of this parameter across analytes (solvent-based standards) revealed the highest sensitivity of the instrument towards buprofezin and cyprodinil (>200×10^6 arb. units per µg mL^{-1}). Mid-range sensitivity (10 – 60×10^6 arb. units per µg mL^{-1}) was achieved for 8 of 15 analytes; the instrument is the least sensitive to boscalid, difenoconazole, fenhexamid, kresoxim methyl and metsulfuron methyl with the slopes ranging from approx. 1 to 5 ×10^6 arb. units per µg mL^{-1} (Table 3).

Almost the same trend could be observed on the linear ion trap instrument (Table 5). The highest instrumental sensitivity could be observed for buprofezin and cyprodinil, however, the differences between analytes in sensitivity were not as pronounced as on the QqQ instrument. Sensitivity for trifloxystrobin, pyriproxyfen and azoxystrobin was not much lesser than the sensitivity for buprofezin and cyprodinil. On the QqQ instrument sensitivity for buprofezin and cyprodinil was about 4 times higher than the sensitivity for the following three pesticides, however, on the linear ion trap instrument it is higher by only about 1.5 times. Buprofezin on the QqQ instrument expressed about 3.7 times higher sensitivity than the pyrimethanil, but on the linear ion trap its sensitivity is only about 1.7 times higher than the sensitivity of pyrimethanil. Tebuconazole on the QqQ expressed about 3 times higher sensitivity than acetamiprid, however, on the linear ion trap sensitivity for these analytes are comparable (Tables 3 and 5).

When compared across the instruments, much higher sensitivity could be observed for the instrument with QqQ analyzer. Sensitivity enhancement ranged from 4.28 times for boscalid to 71.24 times for buprofezin. Since the separation parameters (column, flow, mobile phases composition) and the ionization type were the same, these differences can be attributed to the two main features that distinguish the instruments used within this study, that is the ion optics and mass analyzers features.

Triple quadrupole performances are often compared to the performances of other analyzers. In some cases, QqQ demonstrated better performances than other analyzers. Pozo *et al*. [7] compared the performances of QqQ, time-of-flight (TOF) and hybrid quadrupole-time-of-flight (QTOF) analyzer for the detection of 10 anabolic steroids in human urine. QqQ provided the detection of all analytes at the minimum required performance limit, while TOF and QTOF were not sensitive enough. Bartolucci et al. [8] investigated the performances of QqQ and ion trap for trace amounts quantitation of sulfamethazine and its metabolite in swine urine. Both instruments were appropriate for rapid, sensitive and specific analysis, but the overall performance of the QqQ was slightly superior in terms of linearity, precision and sensitivity. The paper of Belarbi *et al.* [9] dealing with analysis of 100 pesticides and other contaminants in complex food matrices, however, showed superior sensitivity of Q-Orbitrap method in full scan mode to QqQ method in multiple reaction monitoring mode for 86% of analytes. Also, a comparison between Q-TOF and QqQ for the quantification of six different model peptides by Morin et al. [10], showed equivalent or better sensitivity of the high-resolution Q-TOF instrument for all compounds tested.

The triple quadrupole is often coupled to another analyzer to enhance mass analysis performances. The hybrid mass spectrometer containing QqQ and linear ion trap instead of third quadrupole, that is the QqLIT instrument preserves QqQ scan functions providing at the same time access to sensitive ion trap experiments. The enhanced performances of the instrument in triple-stage MS scanning mode, such as improved sensitivity and selectivity have been confirmed by Kokina *et al.* [11] for the analysis of the content of ochratoxin A (OTA) in coffee samples. The study of Shaner *et al.* [12] has also showed greater sensitivity of the hybrid instrument over QqQ in the quantitative analysis of sphingolipids in mice cells.

In QuEChERS treated tomato the same trend in sensitivity as in the solvent-based standards could be observed (Tables 3 and 5). The highest sensitivity was observed for buprofezin and cyprodinil on the QqQ, while the sensitivity for these analytes on the linear trap was much lower and it was comparable with the sensitivity for azoxystrobin on the same instrument (Tables 3 and 5). A mid-range sensitivity in tomato extracts on the QqQ instrument (10 – 40×10^6 arb. units per µg mL^{-1}) was achieved for 9 of 15 analytes, while the instrument had lower sensitivity (0.6 – 3.0×10^6 arb. units per µg mL^{-1}) for 4 of 15 analytes (Table 3). The highest sensitivity in tomato extracts analyzed on the linear ion trap instrument was 2.23×10^6 arb. units per µg mL^{-1} and it was achieved for cyprodinil; this parameter is 52 times lower than the corresponding one obtained on the QqQ instrument. A mid-range sensitivity on the linear ion trap practically does not exist, since across the analytes, the sensitivity was uniform (Table 5). The lowest sensitivity of 0.02×10^6 arb. units per µgmL^{-1} was achieved for metsulfuron methyl and it was 63 times lower than the sensitivity for this pesticide on the QqQ instrument.

In QuEChERS treated cucumber analyzed on the

QqQ instrument the highest sensitivity was achieved for buprofezin (106×10^6 arb. units per µg mL^{-1}) and it was no more comparable to the sensitivity for cyprodinil, which was about 1.2 times lower (Table 3). A mid-range sensitivity (10 – 33×10^6 arb. units per µg mL^{-1}) was achieved for 8 of 15 analytes, while the instrument had lower sensitivity (0.5 – 7.8×10^6 arb. units per µg mL^{-1}) for 5 of 15 analytes (Table 3). The lowest sensitivity of 0.49×10^6 arb. units per µg mL^{-1} was achieved for boscalid. The highest sensitivity in cucumber extracts analyzed on the linear ion trap instrument of 1.82×10^6 arb. units per µg mL^{-1} was achieved for cyprodinil and it was 49 times lower than the corresponding one on the QqQ instrument. Buprofezin, pyriproxyfen and trifloxystrobin closely followed cyprodinil with sensitivity between 1.12 – 1.44×10^6 arb. units per µg mL^{-1} (Table 5). The lowest sensitivity of 0.02×10^6 arb. units per µg mL^{-1} was achieved for metsulfuron methyl and it was 49 times lower than the sensitivity for this pesticide on the QqQ instrument. In general, sensitivity on the QqQ was higher than the sensitivity on the linear trap, from 5.44 times (boscalid) to 74 times (buprofezin).

In QuEChERS treated lettuce analyzed on the QqQ instrument the highest sensitivity was achieved for buprofezin (118×10^6 arb. units per µg mL^{-1}); the sensitivity for the following cyprodinil was about 1.2 times lower (Table 4). A mid-range sensitivity (9.8 – 36×10^6 arb. units per µg mL^{-1}) was achieved for 9 of 15 analytes, while the instrument had lower sensitivity (0.5 – 3.0×10^6 arb. units per µg mL^{-1}) for 4 of 15 analytes (Table 4). The lowest sensitivity of 0.58×10^6 arb. units per µg mL^{-1} was achieved for boscalid. The highest sensitivity in lettuce extracts analyzed on the linear ion trap instrument of 2.34×10^6 arb. units per µg mL^{-1} was achieved for cyprodinil (Table 6) and it was 41 times lower than the corresponding one on the QqQ instrument. Almost equal sensitivity was achieved for azoxystrobin, buprofezin, pyriproxyfen and trifloxystrobin (Table 6). The lowest sensitivity of 0.02×10^6 arb. units per µg mL^{-1} was achieved for metsulfuron methyl and it was 54 times lower than the sensitivity for this pesticide on the QqQ instrument. In general, sensitivity on the QqQ was higher than the sensitivity on the linear trap from 5.27 times (boscalid) to 68 times (buprofezin).

In QuEChERS treated lemon analyzed on the QqQ instrument the highest sensitivity was achieved for buprofezin and cyprodinil (≈69×10^6 arb. units per µg mL^{-1}) (Table 4). A mid-range sensitivity (11 – 54×10^6 arb. units per µg mL^{-1}) was achieved for 9 of 15 analytes. Lower sensitivity (0.9 – 6.2×10^6 arb. units per µg mL^{-1}) was achieved for 4 of 15 analytes (Table 4). The lowest sensitivity of 0.89×10^6 arb. units per µg mL^{-1} was achieved for boscalid. The highest sensitivity in lemon extracts analyzed on the linear ion trap instrument of 1.13×10^6 arb. units per µg mL^{-1} was achieved for cyprodinil (Table 6) and it was 60 times lower than the corresponding one on the QqQ instrument. On the linear trap, almost equal sensitivity was achieved for azoxystrobin, pyriproxyfen and trifloxystrobin, while on the QqQ sensitivity for these pesticides decreased as follows trifloxystrobin > azoxystrobin > pyriproxyfen. The lowest sensitivity of 0.01×10^6 arb. units per µg mL^{-1} was achieved for metsulfuron methyl and it was 134 times lower than the sensitivity for this pesticide on the QqQ instrument. In general, the sensitivity on the QqQ was higher than the sensitivity on the linear trap from 15 times (boscalid) to 138 times (pyraclostrobin).

Table 5. Linear regression parameters ($y = ax + b$, conc. range 0.01 – 15.00 µg mL^{-1}) for the analysis of solvent-, tomato- and cucumber-based pesticides standards on a linear ion trap instrument

	a (×10^6)	b (×10^6)	Correlation coefficient, R^2	a (×10^6)	b (×10^6)	Correlation coefficient, R^2	a (×10^6)	b (×10^6)	Correlation coefficient, R^2
	Solvent			**Tomato**			**Cucumber**		
Acetamiprid	0.71	0.52	0.9816	0.45	0.33	0.9805	0.38	0.31	0.9752
Azoxystrobin	2.34	2.06	0.9803	1.09	1.19	0.9702	0.93	1.02	0.9685
Boscalid	0.25	0.65	0.9713	0.13	0.54	0.9896	0.09	0.61	0.9999
Buprofezin	3.08	2.27	0.9838	1.66	1.07	0.9872	1.44	0.83	0.9891
Cyprodinil	4.21	2.86	0.9909	2.23	1.95	0.9910	1.82	1.74	0.9892
Difenoconazole	1.13	-0.09	0.9986	0.60	-0.07	0.9987	0.52	-0.07	0.9989
Fenhexamid	0.55	0.10	0.9986	0.28	0.06	0.9990	0.24	0.03	0.9989
Kresoxim methyl	0.19	0.02	0.9979	0.09	0.03	0.9994	0.08	0.02	0.9944
Metsulfuron methyl	0.06	0.18	0.9638	0.02	0.16	0.9736	0.02	0.16	0.9844
Propiconazole	0.79	0.13	0.9991	0.43	0.07	0.9995	0.37	0.03	0.9998
Pyraclostrobin	0.63	0.36	0.9893	0.27	0.21	0.9903	0.24	0.14	0.9913
Pyrimethanil	1.82	1.14	0.9935	0.85	0.21	0.9986	0.66	1.16	0.9905
Pyriproxyfen	2.75	1.02	0.9944	1.33	0.50	0.9948	1.12	0.44	0.9969
Tebuconazole	0.75	0.05	0.9998	0.40	0.05	0.9997	0.35	0.05	0.9999
Trifloxystrobin	2.70	0.63	0.9980	1.32	0.34	0.9977	1.20	0.43	0.9993

Table 6. Linear regression parameters ($y = ax + b$, conc. range 0.01 – 15.00 μg mL^{-1}) for the analysis of lemon-based and lettuce-based pesticides standards on a linear ion trap instrument

	a (×10⁶)	b (×10⁶)	Correlation coefficient, R^2	a (×10⁶)	b (×10⁶)	Correlation coefficient, R^2
	Lemon			Lettuce		
Acetamiprid	0.20	0.17	0.9767	0.43	0.36	0.9698
Azoxystrobin	0.62	0.60	0.9647	1.19	1.46	0.9528
Boscalid	0.06	0.39	0.9997	0.11	0.61	0.9945
Buprofezin	0.81	0.43	0.9876	1.73	1.36	0.9739
Cyprodinil	1.13	0.98	0.9736	2.34	2.70	0.9748
Difenoconazole	0.30	0.04	0.9990	0.57	0.004	0.9945
Fenhexamid	0.14	0.03	0.9991	0.27	0.10	0.9930
Kresoxim methyl	0.05	0.01	0.9974	0.09	0.01	0.9944
Metsulfuron methyl	0.01	0.09	0.9859	0.02	0.15	0.9726
Propiconazole	0.21	0.07	0.9957	0.40	0.10	0.9965
Pyraclostrobin	0.12	0.07	0.9930	0.28	0.14	0.9883
Pyrimethanil	0.37	0.14	0.9961	0.90	0.54	0.9924
Pyriproxyfen	0.68	0.29	0.9925	1.33	0.77	0.9882
Tebuconazole	0.20	0.03	0.9991	0.36	0.09	0.9962
Trifloxystrobin	0.70	0.29	0.9946	1.33	0.68	0.9908

The main phenomenon that causes differences among analytes sensitivity in different matrices is the matrix effect. The matrix effect represents every influence of the co-extractives on analyte signal. The two possible signal deviations are signal enhancement (positive matrix effect) and signal suppression (negative matrix effect). The main issue that develops from the matrix effect manifestation is the uncertainty in both quantitative and qualitative analysis. The mechanism of the matrix effect manifestation in LC/MS techniques of analysis is related to the analyte ionization in the source. Due to the co-elution of analytes and co-extractives, analytes ionization efficiency is deteriorated, directly leading to the lower sensitivity in analysis [13]. Ionization efficiency of analyte molecules is less pronounced, since its number on the ESI drop surface is smaller, due to the presence of matrix constituents. The methods for overcoming the matrix effect are mainly based on the sample dilutions, the use of lower mobile phase flow rates or even a different ionization source [14].

By comparing sensitivity between matrices (solvent and fruit/vegetable), within the same instrument, mainly strong negative matrix effect could be observed for most analytes (Figures 1 and 2). However, there were some differences in the matrix effect between the extracts analyzed on the QqQ and those analyzed on the linear ion trap. In general, the matrix effect was more uniform on the linear trap instrument (Figure 1). In tomato, cucumber and lettuce extracts the matrix effect ranged from -36 to -66%, from -46 to -66% and from -39 to -66%, respectively (Figure 2). In each case, the lower range limit was observed for acetamiprid and the higher range limit for metsulfuron methyl. In lemon matrix somewhat stronger signal suppression was observed. The matrix effect in lemon analyzed on the linear ion trap ranged from -72% (acetamiprid) to -83% (metsulfuron methyl). On the QqQ instrument the matrix effect was less uniform (Figure 2). In tomato, the matrix effect ranged from almost 0% for pyriproxyfen to more than +200% for difenoconazole. In cucumber and lettuce, the matrix effect ranged from -22% to 100% and from -9% to 156%, respectively. In both cases, the lower range limit was observed for pyriproxyfen and the higher range limit for difenoconazole. In lemon, the matrix effect ranged from 16% for trifloxystrobin to 236% for difenoconazole

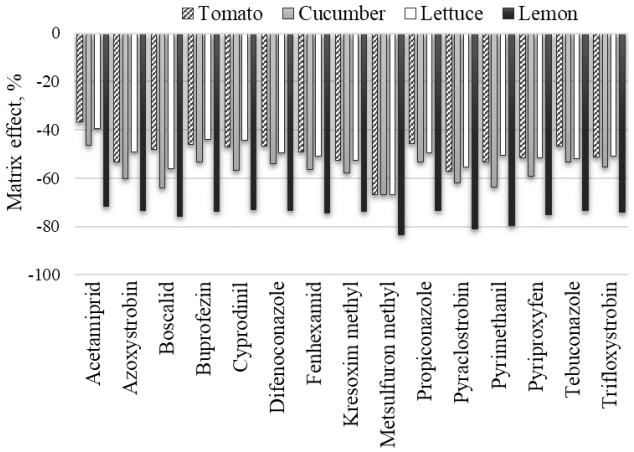

Figure 1. The matrix effect in lemon and vegetable extracts analyzed on linear ion trap instrument

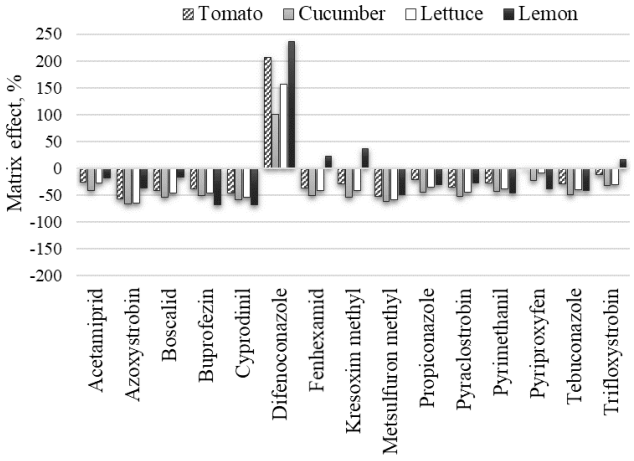

Figure 2. The matrix effect in lemon and vegetable extracts analyzed on triple quadrupole instrument

Conclusion

Sensitivity of analysis on the linear ion trap and triple quadrupole, two most exploited, fundamentally different mass analyzers, was compared. A batch of solvent-based and QuEChERS treated tomato-, cucumber-, lettuce- and lemon-based standards of 15 pesticides from 9 chemical classes was analyzed, with both analyzers operating in full scan MS^1 mode and the sensitivity was estimated from the slopes of calculated calibration functions. A much higher sensitivity was observed in analysis on the triple quadrupole; the sensitivity for boscalid in solvent was about 4 times higher and for buprofezin 71 times higher on the triple quadrupole than on the linear trap. The same trend in sensitivity could be observed in fruit and vegetables extracts. Shifting from linear trap to triple quadrupole, sensitivity enhancement ranged from about 5 to even 134 times. By comparing the slopes calculated for solvent- and fruit- or vegetable-based standards, mostly strong negative matrix effect was observed on both instruments, rising the need to perform analytes quantification against sample-based standards in an actual sample analysis. In conclusion, triple quadrupole instrument has provided much higher sensitivity in multiresidue pesticides analysis. Such instruments should be implemented when highly sensitive analysis is required.

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Izvod

ISPITIVANJE OSETLJIVOSTI ANALIZE PESTICIDA U ODABRANOM VOĆU I POVRĆU NA MASENIM SPEKTROMETRIMA SA TROSTRUKIM KVADRUPOLOM I JONSKOM ZAMKOM

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Masena spektrometrija je jedna od najselektivnijih i najosetljivijih instrumentalnih tehnika koje se primenjuju u različitim naučnim disciplinama. Termin osetljivost u masenoj spektrometriji obično se definiše kao promena u merenom signalu analita sa promenom njegove koncentracije. Faktori poput načina pripreme uzoraka, sastava hromatografske mobilne faze, vrste hromatografske kolone i osobina masenog spektrometra mogu uticati na osetljivost analize. Cilj ovog rada bio je ispitivanje uticaja vrste masenog spektrometra, tačnije masenog analizatora na osetljivost analize pesticida u povrću i limunu, pri konstantnim ostalim faktorima. U ispitivanje su bila uvrštena dva masena spektrometra: maseni spektrometar sa trostrukim kvadrupolom i sa linearnom jonskom zamkom kao analizatorima. Poređenje osetljivosti putem nagiba kalibracione funkcije izračunate za seriju standarda u rastvaraču i u matriksima limuna i povrća tretiranog QuEChERS procedurom pokazalo je da je kod analize pesticida osetljivost mnogo veća na instrumentu sa trostrukim kvadrupolom kao analizatorom. Osetljivost je bila veća od 5 do 134 puta.

Ključne reči: Masena spektrometrija, HPLC, multirezidualna analiza, povrće