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Abstract

This study reports about how to integrate the environmental contaminant perchlorate into the QuPPe multiresidue method for the analysis of polar pesticides. Perchlorate, along with a number of polar pesticides, was extracted with acidified methanol. The extracts were filtered and subjected to liquid chromatography-triple quadrupole mass spectrometry (LC-MS/MS). 18O-labeled perchlorate was used as internal standard. The assay was validated for apple and barley matrix at 0.01 and 0.1 mg kg^{-1}, showing average recoveries between 93 % and 108 % and relative standard deviations (RSDs) between 2.2 % and 5.0 %. Up to now, we have analyzed 350 conventionally and 78 organically grown food samples (vegetables, fruits, cereals, legumes, mushrooms and processed foods) from the local market for perchlorate. Perchlorate could be detected in 66 (19 %) of the conventional samples and in two (2.6 %) of the organic samples; in six samples the provisional maximum tolerable daily intake (PMTDI) of 0.01 mg kg^{-1} bodyweight was exceeded.

Introduction

In 2012, the environmental contaminant perchlorate was frequently detected in conventionally and organically grown fruit and vegetable samples from the local market. Perchlorates are salts of perchloric acid ($HClO_4$) arising from natural as well as from anthropogenic sources. The perchlorate anion is a stable but strong oxidant as the chlorine atom possesses an oxidation state of +7. Most perchlorates are soluble in water and circulate within the hydrologic cycle [1]. They naturally occur ubiquitous in atmospheric water and soil compartments in low concentrations [2]. However, perchlorate contamination in food cannot result from natural sources as the appearing environmental concentrations are too low. Aside from natural occurrence, perchlorates are anthropogenically spread, since they are widely used in the metalworking industry, in paper upgrading and, as oxidants, for propellants in pyrotechnic materials like rockets, fireworks and explosives [1, 2]. In diagnostic radiology, perchlorates are medically applied in iodine contrast agents keeping the exposure to high iodine concentrations at a low level by blocking the thyroid [2, 3]. Another source of perchlorate contamination are fertilizers or sewage sludge which are both widely applied in agriculture [2]. Perchlorates also come along with chlorate, a substance which has formerly been used as a herbicide in plant protection products. However, pesticides containing chlorate as an active substance have been banned within the EU since May 2010 [4]. Like chlorate, perchlorate can act as a herbicide [1], but is not approved as a pesticide within the European Union [5] and there is no maximum residue level listed in Regulation (EC) 396/2005 [6].

Perchlorate inhibits the production of thyroxine (T4) and triiodothyronine (T3) in the thyroid by blocking the uptake of iodide from the blood into the thyroid [7, 8]. This effect is reversible as the perchlorate acts as a competitive inhibitor. The Joint FAO/WHO Expert Committee on Food Additives proposed a provisional maximum tolerable daily intake (PMTDI) of 0.01 mg per kilogram bodyweight for perchlorate [9], whereas the National Academy of Sciences (NAS) determined a Reference Dose (RfD) of 0.007 mg per kilogram bodyweight [10]. Both values are based on the same human toxicity study on perchlorate, in which adult human beings were exposed to perchlorate from drinking water for 14 days [8]. The study resulted in a NOEL (No Observed Effect Level) of 0.007 mg kg^{-1} bodyweight per day for perchlorate, which means that from this concentration or above, perchlorate inhibits the uptake of iodide into the thyroid.

Ion chromatography, mostly coupled to conductivity detection has been the method of choice to determine perchlorate [3, 11–13]. Other possibilities to analyze the target anion are photometry [14], potentiometry [15, 16], electrophoresis [17, 18], atomic absorption spectrometry [19, 20], and Raman spectrometry [21]. In the last few years, scientist tended to develop methods including ion chromatography or liquid chromatography coupled to mass spectrometry detection [22–24]. Up to now, the predominant subject of perchlorate analysis has been drinking water and soil [17, 18, 24–28]. To our knowledge, fewer investigations have been made in determining perchlorate in food samples [12, 29–31].

In our study, we analyzed samples of plant origin applying the QuPPe method following liquid chromatography and triple quadrupole mass spectrometry. The QuPPe-method (short for “Quick Method for the Analysis of Residues of numerous Highly Polar Pesticides in Foods of Plant Origin involving Simultaneous Extraction with Methanol and LC-MS/MS Determination”) was developed by the European Reference Laboratory for pesticide residues requiring Single Residue Methods (EURL-SRM). It includes a simple extraction with methanol followed by a filtration step. The extracts are directly analyzed via LC-MS/MS without any further cleanup. The method was validated for apple (high in water) and barley (dry) matrix and was applied to monitor conventionally and organically grown real samples.

Experimental

Chemicals and standards

Acetonitrile and methanol of gradient grade were purchased from Merck (Darmstadt, Germany). Water for liquid chromatography was deionized in the laboratory using a Direct-Q 3 UV Ultrapure Water Purification System (Billerica, MA, USA). Dry ice for sample comminution was delivered in blocks by a local provider, stored at -80 °C until use and was tested not to contain perchlorate at relevant levels. Ammonium formate was purchased from Sigma-Aldrich (Steinheim, Germany). The analytical pesticide standard sodium perchlorate (purity > 98 %) was obtained from Sigma-Aldrich (Steinheim, Germany), the internal standard 18O-labeled perchlorate (heavy oxygen > 90 %) was purchased from Cambridge Isotope Laboratories Inc. (Andover, USA). For perchlorate, a stock solution of 1 mg mL^{-1}, considering standard purity and the sodium part, was prepared in methanol. The stock solution of the internal standard perchlorate 18O (100 µg mL^{-1} in water) was diluted to 10 µg mL^{-1} and 1 µg mL^{-1} (working solution) with methanol. All solutions were stored in the dark at 4 °C.

Samples and commodities

Different crops of plant origin were sampled from the local market. Representative parts of the fresh samples were pre-chopped and deep-frozen at -18 °C overnight after arriving in the laboratory. The pre-chopped samples were subsequently milled with dry ice and stored at -18 °C until extraction.

Dry samples (e.g. barley) were ground thoroughly without adding water and were stored at room temperature until extraction.

Apparatus

Frozen samples were chopped with dry ice using a Prime Cut UM5 universal machine from Stephan Machinery GmbH (Hameln, Germany). Dry samples were ground at room temperature using a Grindomix GM 200 knife mill by Retsch (Haan, Germany). The automatic shaking machine Geno Grinder 2010 (SPEX Sample Prep, Metuchen, USA) was used for automated extraction. The centrifuge Rotanta 460 by Hettich (Tuttlingen, Germany), appropriate to the centrifuge tubes employed in the procedure and capable of achieving 4000×g, was used. Electronic pipettes applicable for volumes of 10–100 µL and 200–1000 µL, respectively, and manual pipettes applicable for volumes of 1–10 mL were from Eppendorf (Hamburg, Germany). Analytical balances capable of weighing to 0.1 mg or to 0.01 g were from Mettler-Toledo (Greifensee, Switzerland). The Fortuna Optifix 10 mL Universal Dispenser was used to add solvent to the samples. The automatic dispenser system Opus (20–50 mL; Ex 20 °C; Hirschmann Laborgeräte, Eberstadt, Germany) was used for dilution of the working solutions.

50-mL PP (114×28 mm) single-use tubes with screw caps for the sample extraction were from Sarstedt (Nümbrecht, Germany). 1.5-mL LC autosampler vials and 20-mL screw-cap vials were from Ziemer GmbH (Mannheim, Germany). 6 mL single-use syringes from Henke Sass Wolf (Tuttlingen, Germany) and disposable polyester syringe filters (0.45 µm pore size, 15 mm diameter) from Machery-Nagel (Düren, Germany) were used to filter the QuPPe extracts.

An Agilent 1200 HPLC system (Agilent, Waldbronn, Germany), consisting of a binary pump, a standard autosampler and a column oven, combined with the mass spectrometer API 5500 Q-Trap (ABSCIEX, Darmstadt, Germany), run in ESI negative mode, was used for the analysis of the QuPPe extracts. The samples were injected on a Hypercarb 2.1 x 100 mm column with 5 µm particle size (Thermo Fisher Scientific, Waltham, USA), equipped with a Hypercarb Guard (2.1 x 10 mm, 5 µm particle size) and a Supelco column saver 2 µm-precolumn filter (Sigma-Aldrich, Steinheim, Germany).

QuPPe extraction

For the QuPPe method 10 ± 0.1 g (in the case of cereals 5 ± 0.1 g plus 10 mL water) of the prepared frozen samples were weighed into 50-mL PP tubes. 10 mL of acidified methanol followed by 100 µL of the internal standard working solution (10 µg mL^{-1}) were added to the samples. The tube was closed and shaken by a mechanical shaker for one minute. The tube was centrifuged for 5 min at 4000 rpm and the upper methanol phase was filtered through a syringe filter (0.45 µm) into sealable storage vessels. An aliquot of the extract was transferred into autosampler vials and was subsequently diluted with acidified methanol by a factor of 1:10 (depending on the matrix, see “Results and Discussion” below). The extracts were applied to LC-MS/MS measurement.

LC-MS/MS analysis

Mobile phase A consisted of 1 % acetic acid in purified water containing 5 % of methanol, mobile phase B was 1 % acetic acid in methanol. A gradient program was applied starting at a flow rate of 0.2 mL min^{-1} and 100 % of mobile phase A (0 % B) at injection time, gradually changing to 70 % A (30 % B) over 10 minutes. Then, the flow was set to 0.4 mL min^{-1} within 1 minute and the conditions were kept for another 7 minutes. Mobile Phase A was then shifted to 10 % (90 % B) within 1 minute and this composition was kept for 3 minutes. Then, mobile phase composition and the flow were shifted back to starting conditions within 0.1 minutes and kept for approximately 8 minutes in order to re-equilibrate the column. Total run time was 30 minutes; the injection volume was 5 µL. The column temperature was set to 40 °C. ESI interface in negative mode was applied, the MS/MS detection was performed in the multiple reaction monitoring (MRM) mode. The ion spray voltage was -4500 V, the curtain gas was nitrogen at 30 psi, the nebulizer gas and the turbo gas were synthetic air, both at 60 psi, the source temperature was 420 °C and the collision gas was set to “medium”.

Two precursor-product ion transitions were monitored for perchlorate in the multiple reaction monitoring mode (MRM). The first transition (m/z 99/83) was used for quantification, while the second transition (m/z 101/85) served for confirmation. For the internal standard perchlorate 18O m/z 107/89 was monitored. Insight to additional method details is given at the web page of the European Reference Laboratory for pesticide residues requiring Single Residue Methods (EURL-SRM) [32].

Method validation

The method was validated at levels of 0.01 and 0.1 mg kg^{-1} for apple matrix (commodity with high water content) and barley matrix (dry commodity). Blank samples were spiked with perchlorate at 0.01 and 0.1 mg kg^{-1} (n=5) following QuPPe extraction and LC-MS/MS analysis. All blank samples were proved not to contain perchlorate in relevant amounts right before validation. We applied matrix matched calibration standards at concentrations representing 60 and 120 % of the validation level for each matrix. Quantification was carried out via the ratio between analyte peak area and ISTD peak area for both, calibration standards and the extracts of the recovery samples. Results of on-going validations can be obtained via the Datapool of the EU Reference Laboratories for Residues of Pesticides [33].

Results and Discussion

In LC-MS/MS analysis we applied a porous graphitic carbon column for chromatographic separation. By using this column it was possible to avoid laborious washing procedures coming along with ion chromatography. The Thermo Hypercarb column consists of 100 % porous graphitic carbon with no micropores or chemically bonded phases. The carbon atoms are hexagonally arranged and form flat sheets. Highly polar analytes or charged compounds induce dipoles at the graphic surface and interact with the induced partial charges. Perchlorate showed a narrow and well-shaped peak at a retention time of 12.20 minutes. Figure 1 and 2 show typical chromatograms of perchlorate (0.01 mg kg^{-1}) and the 18O-labeled internal standard (0.05 µg mL^{-1}) in a QuPPe extract from apples.

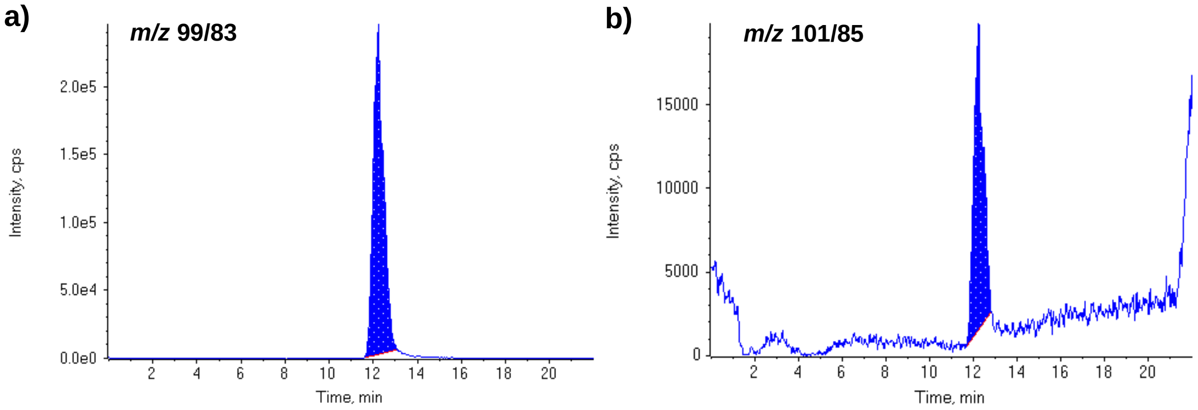

Figure 1: LC-MS/MS chromatogram of perchlorate in apple matrix (0.01 mg kg^{-1})
a) *m/z* 99/83 **b)** *m/z* 101/85

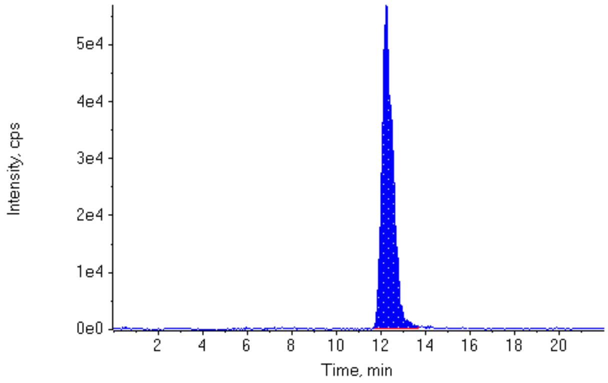

Figure 2: LC-MS/MS chromatogram of 18O-labeled perchlorate *m/z* 107/89 (internal standard) in apple matrix (0.05 µg mL^{-1})

Being a strong solvent, methanol tends to co-extract matrix ingredients that may cause matrix effects in instrumental analysis. Diluting the QuPPe extracts results in less co-extracted matrix ingredients per injection and matrix effects in LC-MS/MS analysis can be avoided or reduced thereby [34]. In our case, matrix effects should be eliminated by the use of the 18O-labeled internal standard. However, we observed unshaped and uneven peaks for perchlorate in certain matrices while method development. We noticed improved peak shapes in those matrices when QuPPe extracts were diluted with acidified methanol. Figure 3 shows chromatograms of a diluted and an undiluted QuPPe extract from kale containing perchlorate.

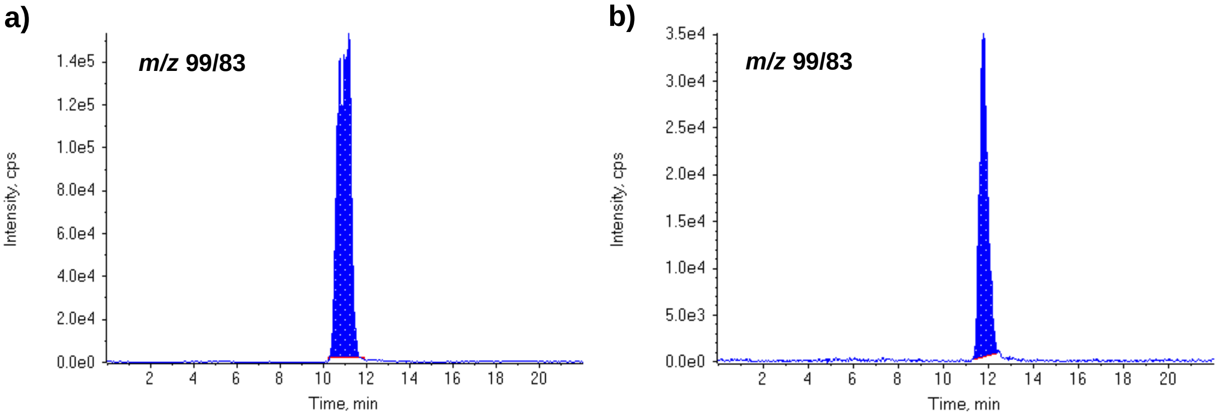

Figure 3: LC-MS/MS chromatogram of perchlorate m/z 99/83 in kale **a)** without dilution **b)** 1:10-diluted extract

The limit of quantification (LOQ) was estimated from the undiluted extracts as the level showing a signal-to-noise ratio of at least 10 to 1. LOQ for perchlorate was 0.002 mg kg^{-1} in cucumber, apple, barley, orange and tomato matrix. The validation in apple and barely matrix (n=5) showed satisfying recoveries between 70–120 % and relative standard deviations (RSDs) well below 10 %. For apple, the average recovery was 108 % at 0.01 mg kg^{-1} and 98 % at 0.1 mg kg^{-1}. RSDs were 2.6 % and 2.2 %, respectively. For barley, the average recovery was 106 % for the 0.01-level and 93 % for the 0.1-level and RSDs were 2.3 % and 5.0 %, respectively.

The method was applied to 350 conventionally and 78 organically grown samples from the local market. Perchlorate was detected in 66 (19 %) of the conventional samples and in two (2.6 %) of the organic samples. In six of all analyzed samples the PMTDI of 0.01 mg kg^{-1} bodyweight was exceeded. The average perchlorate amount of all 66 samples containing perchlorate was 0.043 mg kg^{-1}, the highest perchlorate amount detected was 0.4 mg kg^{-1} in a tomato sample from Spain.[1]

Figure 4 a) and b) show an overview of perchlorate findings in all analyzed fruit and vegetable samples. It was remarkable, that perchlorate could most frequently be detected in melon (50 % of all analyzed melon samples), sweet pepper (53 %), tomato (40 %) and citrus (23 %) commodities. However, the number of analyzed samples is yet not representative

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[1] The data only includes samples that were analyzed after the method validation was completed.

enough and does not allow general statements, especially since not all commodity groups have been implemented to a significant number.

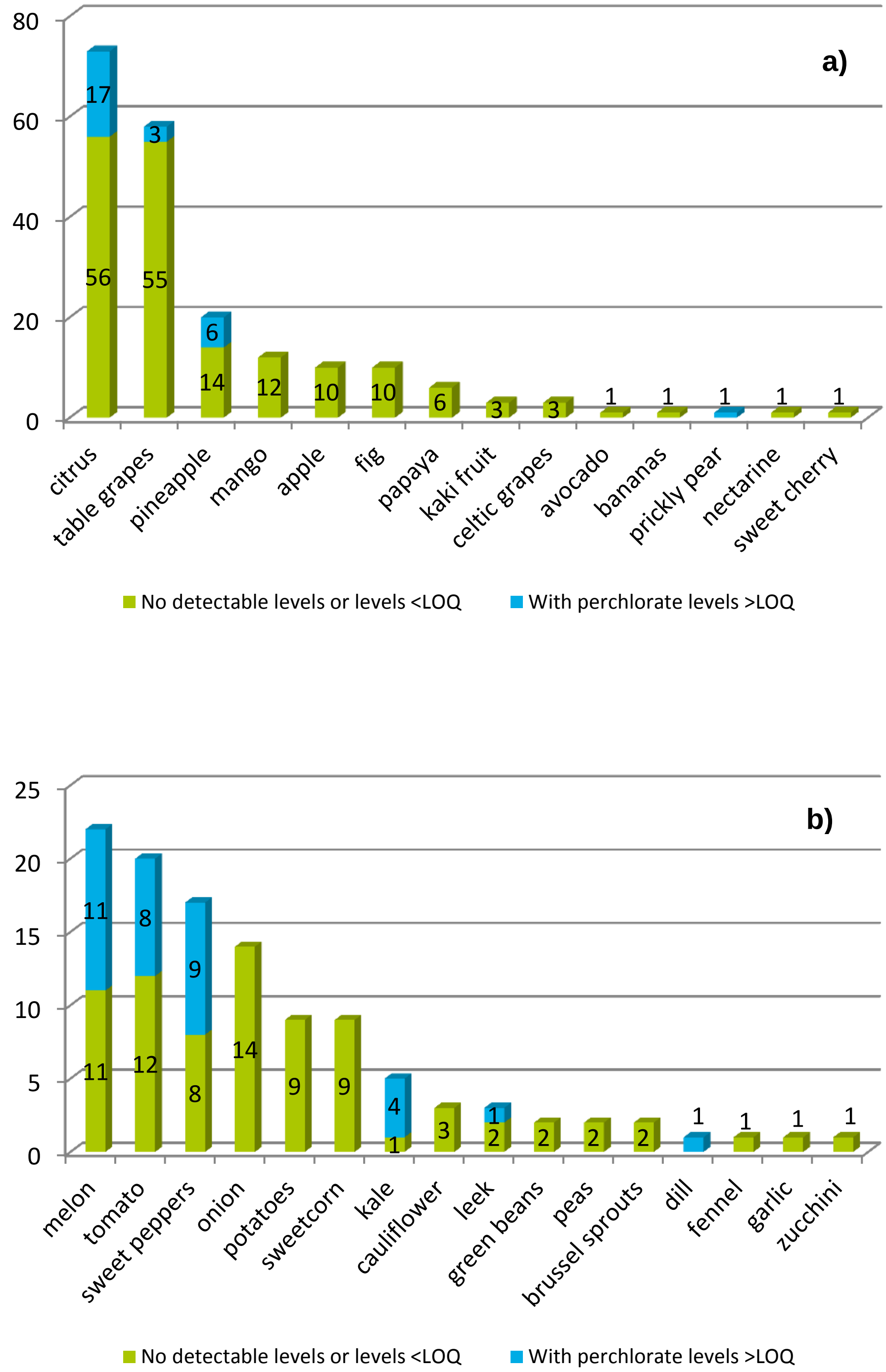

Figure 4: Number of samples with and without perchlorate findings in **a)** fruit commodities **b)** vegetable commodities

Figure 5 shows how many samples from each country of origin contained perchlorate, irrespective if of conventional or organic cultivation. 37 % of all samples from Spain and 28 % of all samples originating from Turkey contained perchlorate. In contrast, only 7 % of all samples from Germany contained perchlorate. Once again, the number of analyzed samples does not allow general statements and more samples have to be analyzed for perchlorate.

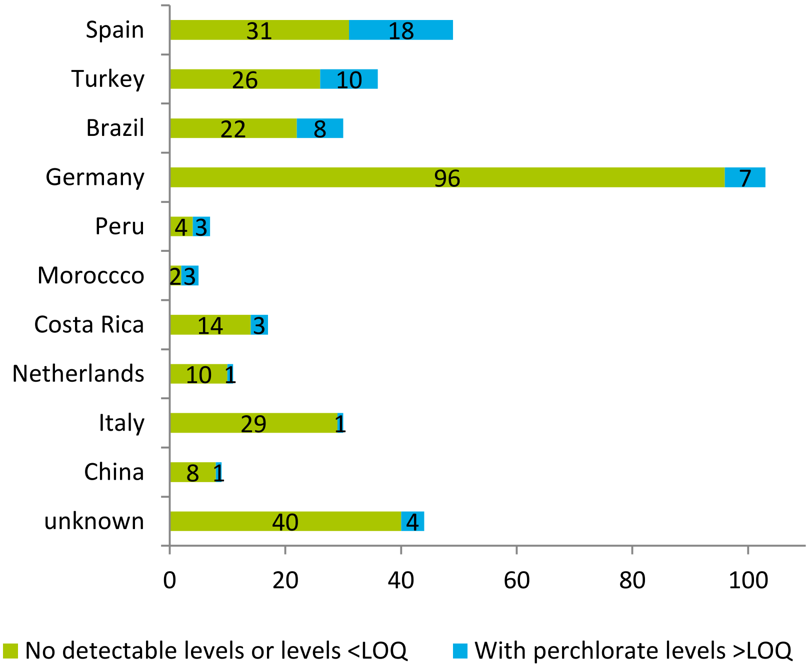

Figure 5: Country of origin **-** Number of samples with and without perchlorate residues

Table 1 shows in which types of samples perchlorate was found and from which countries these samples originated from. The highest perchlorate findings detected were 0.4 mg kg^{-1} in a tomato sample from Spain, 0.18 mg kg^{-1} in a grapefruit from Spain and 0.31 mg kg^{-1} in a tomato sample with no specified country of origin.

Table 1: Perchlorate findings in different commodities and their country of origin

Country of origin	Commodity	Perchlorate levels in mg kg^{-1}
Spain	tomato (5x)	0.003 – 0.4
	clementine (3x)	0.018 – 0.028
	grapefruit (3x)	0.008 – 0.18
	lemon (2x)	0.011 – 0.017
	mandarin (2x)	0.019 – 0.027
	orange (2x)	0.011 – 0.077
	table wine grape white	0.035
Turkey	sweet pepper (8x)	0.002 – 0.086
	melon	0.023
	grapefruit	0.014
Brazil	melon (8x)	0.009 – 0.037
Germany	kale (5x)	0.013 – 0.032
	porree	0.059
	table wine grape white	0.012
Peru	clementine	0.064
	mandarin	0.063
	table wine grape red	0.015
Morocco	sweet pepper	0.090
	tomato (2x)	0.010 – 0.043
Costa Rica	pineapple (3x)	0.003 – 0.073
Ghana	pineapple (3x)	0.020 – 0.054
Belgium	kale (2x)	0.019 – 0.022
Chile	mandarin	0.20
Netherlands	frozen pre-fried French fries	0.027
Italy	prickly pear	0.017
China	pomelo	0.010
Honduras	melon	0.010
unknown	dill	0.016
	frozen pre-fried French fries	0.012
	melon	0.015
	tomato	0.31

Conclusions

Our study demonstrates that the QuPPe method is well applicable for the monitoring of the environmental contaminant perchlorate. Determinative analysis is achieved by LC-MS/MS along with a number of highly polar pesticides. Isotope labeled perchlorate is used as internal standard. The validation of the method showed satisfying recoveries and RSDs in apple and barley matrix. We recommend the use of the 18O-labeled internal standard, if available. Otherwise the use of matrix matched calibration and the dilution of QuPPe extracts should be mandatory.

Validation experiments for perchlorate additional commodities such as citrus fruit and dry fruit are in process. Moreover, the routine monitoring of perchlorate in fruit and vegetable samples from the local market will be continued.

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