

FOOD

Analysis of neonicotinoid pesticides in dried plant materials – the effects of different quantification strategies

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Introduction and Objectives

Neonicotinoids constitute a relatively newly-developed pesticide class consisting of Acetamiprid, Imidacloprid, Clothianidin, Nitenpyram, Thiacloprid and Thiamethoxam. These insecticides are acting with a higher selectivity against nicotinic acetylcholine receptors of insects than of mammals, due to the modification of the nicotinic structure. As a result of their systemic mode of action, and their long term stability, neonicotinoids are often used as seed treatment agents but also widely during plant growth, and are nowadays increasingly applied in crop protection. The routine analysis of these compounds in fruits and vegetables are easily accomplished in many laboratories worldwide by different methods.

Unfortunately there are substantial difficulties in the determination of neonicotinoids in dried plant material caused by weak extraction efficiency and high matrix content in the sample extract leading to wrong quantitative results.

The objective of this study was to compare different strategies of extraction and quantification of these pesticides in dried plant materials using the example of non fermented tea.

Material and Methods

A reference sample of green tea, spiked with Acetamiprid, Clothianidin, Imidacloprid, Thiacloprid and Thiamethoxam was extracted in 4 different ways: (1) QuEChERS methodology; (2) DFG-S19 methodology (modified); (3) Methanol/Water Extraction (pH-modified); (4) Oxidative degradation of three of five Neonicotinoid compounds and extraction and determination of their 6-chloronicotinic acid (6-CINA) moiety. The sample extracts were measured by LC-MS-MS and GC-MSD in diverse sample dilutions.

The quantification was carried out by solvent calibration, matrix matched calibration with a similar matrix and by spiking experiments of the test sample. The different results are compared to each other.

Results and Discussion

The differentially quantified concentrations of neonicotinoid pesticides are shown in table 1.

Table 1: Contents of neonicotinoid pesticides in a green tea sample achieved by different extraction and calibration methods

Extraction by MeOH/H ₂ O		c [mg/kg]				
	Acetamiprid	Imidacloprid	Thiacloprid	Clothianidin	Thiamethoxam	
Standard Addition	0,533	0,192	0,349	0,158	0,092	
Matrix Matched Cal.	0,461	0,180	0,293	0,131	0,058	
Calibration Method						
Solvent Cal.	0,330	0,091	0,166	0,054	0,005	
Solvent Cal. (Sample Dilution 1:10)	0,565	0,161	0,308	0,113	0,027	

Extraction by QuEChERS		c [mg/kg]				
	Acetamiprid	Imidacloprid	Thiacloprid	Clothianidin	Thiamethoxam	
Standard Addition	0,636	0,193	0,313	0,171	0,069	
Matrix Matched Cal.	0,528	0,189	0,312	0,168	0,061	
Solvent Cal.	0,318	0,118	0,171	0,082	0,009	
Solvent Cal. (Sample Dilution 1:10)	0,545	0,171	0,318	0,173	0,022	

Extraction by ACE/H ₂ O		c [mg/kg]				
	Acetamiprid	Imidacloprid	Thiacloprid	Clothianidin	Thiamethoxam	
Standard Addition	0,323	0,135	0,228	0,106	0,065	
Matrix Matched Cal.	0,279	0,126	0,191	0,088	0,041	
Solvent Cal.	0,199	0,064	0,108	0,036	0,003	
Solvent Cal. (Sample Dilution 1:10)	0,342	0,113	0,201	0,076	0,015	

The extraction by polar solvents like methanol or acetonitrile is leading to higher values for neonicotinoid compounds compared to the extraction with acetone applied by the DFG-S19 methodology. Whereas the extraction by methanol and acetonitrile is equal with regard to the values obtained by the respective extraction mode.

The calibration by solvent-standard led to a dramatic underestimation of the neonicotinoid content in the sample of regard.

These distinctions aroused by negative matrix effects were corrected adequately by ten-fold dilution of the relevant sample extracts. A good correlation of the calibration curves in dilute sample extracts and solvent standard could be observed.

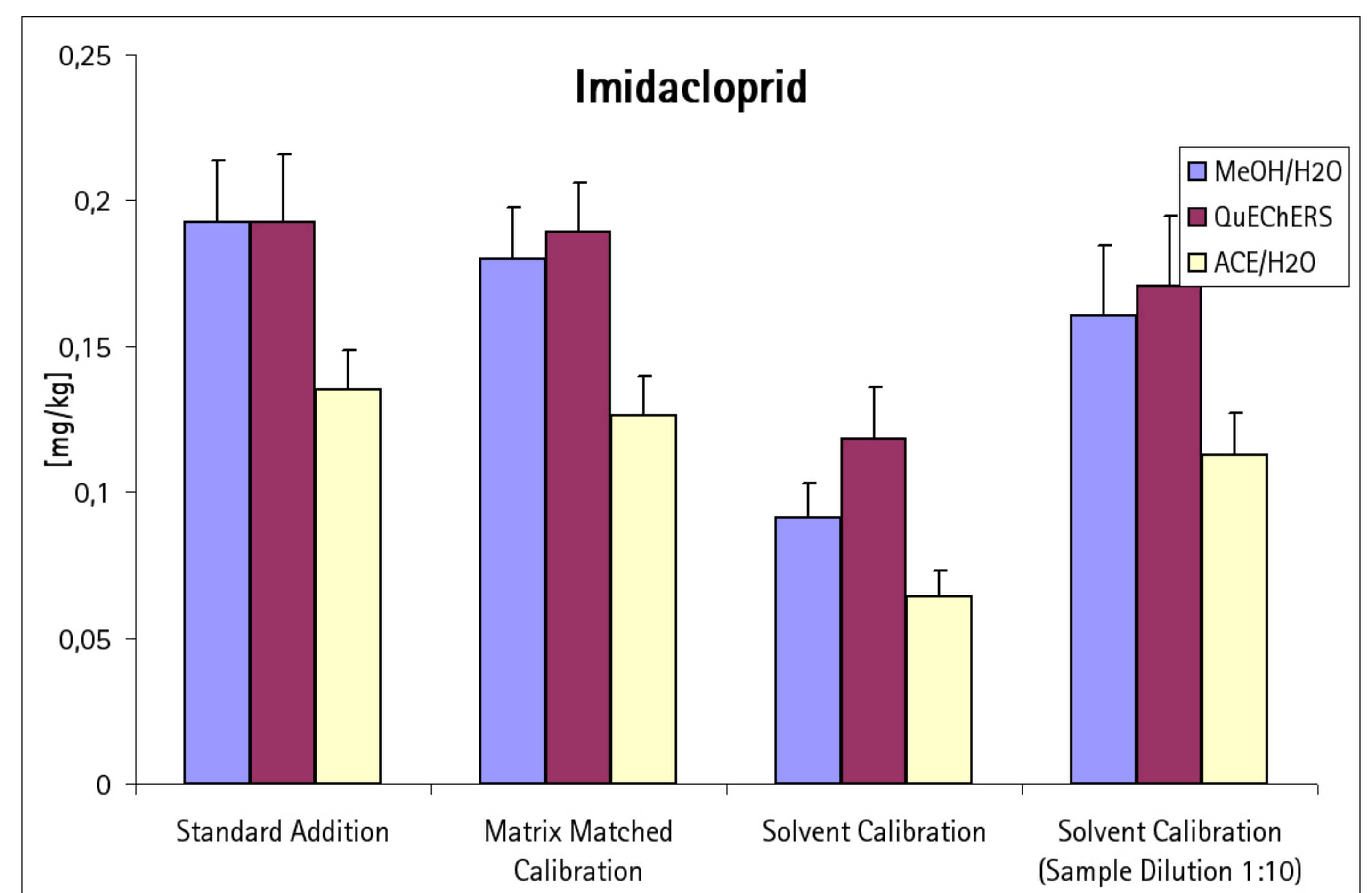


Fig. 1: Content of Imidacloprid in a green tea sample (achieved by different extraction and calibration methods)

The results of the determination of the 6-chloronicotinic acid moiety are shown in table 2 and figure 2. The theoretical concentrations of 6-CINA calculated from the concentrations of the sum of Acetamiprid, Imidacloprid and Thiacloprid calibrated by standard addition measured by LC-MS-MS are compared to the concentration of 6-CINA determined by oxidative degradation under alkaline conditions measured via GC-MSD.

Table 2: Content of 6-chloronicotinic acid in a green tea sample (theoretical and determined by oxidative degradation)

Quantification by Standard Addition	Sum of 6CINA-Moiety [mg/kg]
MeOH/H ₂ O	0,714
QuEChERS	0,764
ACE/H ₂ O	0,454
Ox. Degradation	1,121

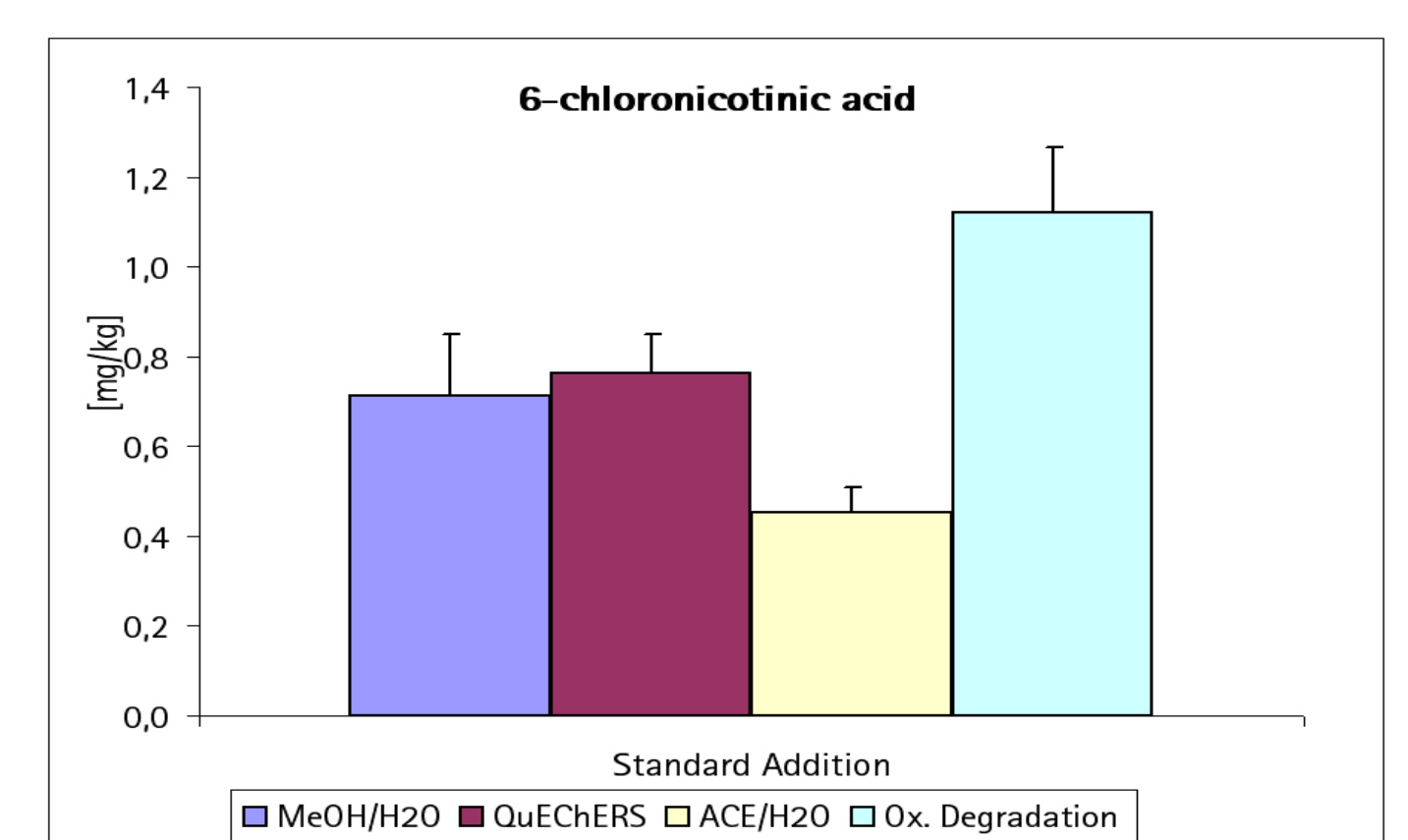


Fig. 2: Content of 6-chloronicotinic acid in a green tea sample (calculated by the results of neonicotinoid pesticides and determined by oxidative degradation)

The determination by oxidative degradation led to higher values of 6-chloronicotinic acid compared to the theoretical calculated values resulting from the determination of the Neonicotinoid compounds (Acetamiprid, Imidacloprid, Thiacloprid) by LC-MS-MS.

A reason for this might be the presence of neonicotinoid pesticide metabolites in the sample, not covered by the determination of the original neonicotinoid substances but by the determination of 6-chloronicotinic acid due to further metabolite degradation. This latter approach allows a more comprehensive consideration of the residue situation in the sample. Unfortunately the identification and quantification of single neonicotinoid compounds is not possible with this method.

Conclusions

- The extraction of neonicotinoid pesticides by aqueous mixtures of polar solvents like methanol or acetonitrile is superior to that of mixtures of acetone.
- The calibration by a solvent-standard will definitely lead to an underestimation of neonicotinoid levels in the sample of regard.
- These matrix effects induced phenomena can be avoided adequately by sufficient dilution of the sample extract.
- The option of determination of 6-chloronicotinic acid for a more comprehensive residue monitoring of neonicotinoid pesticides in food should be discussed.