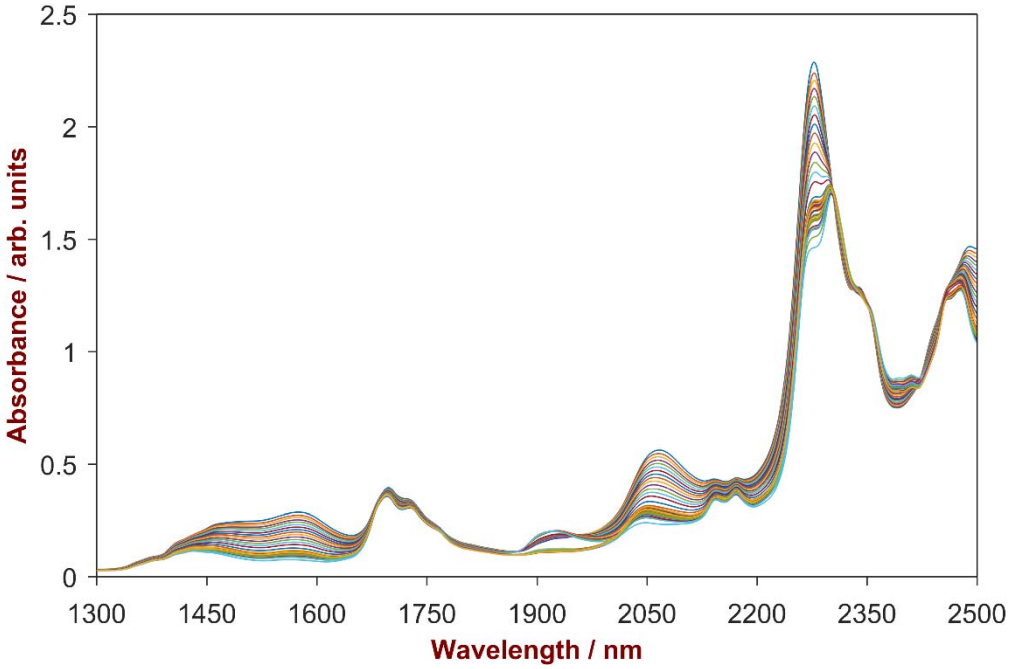
NIR Application Note NIR–056

Quantification of five effective components in pesticides by visible near-infrared spectroscopy



This Application Note shows that visible near-infrared spectroscopy (Vis-NIRS) can be used for the quantification of five effective insecticide and herbicide components (Abamectin emulsifiable concentrate (EC), Emamectin EC, Cyhalothrin EC, Cypermethrin and Glyphosate) in pesticides. Vis-NIRS is an excellent alternative to conventional lab methods, saving both cost and time.

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Method description

Introduction

Pesticides are chemical compounds that are used to kill pests, including insects, rodents, fungi and unwanted plants (weeds). They are used in public health to kill vectors of disease, such as mosquitoes and in agriculture to kill pests that damage crops. By their nature pesticides are potentially toxic to other organisms, including humans, and need to be used safely and disposed of properly. [1]

People who face the greatest health risks from exposure to pesticides are those coming into contact with them at work, at home or in gardens, such as through contaminated food. To protect people from adverse effects of pesticides, WHO reviews evidence and develops internationally-accepted maximum residue limits. [2]

Determination of the concentration of effective components in pesticides is commonly done by reversed-phase HPLC. However, HPLC involves toxic solvents, is time-consuming and requires a well-trained operator, resulting in relatively high costs for routine analysis. In this application note, it is demonstrated that Vis-NIRS is an excellent alternative to HPLC of the listed and tested effective components (**Tab.1**) for saving both time and money.

Tab. 1: Analyzed compounds and the effect as pesticide. [3]

Compound	Effect
Abamectin	• Control insect and mite pests
Emamectin	• Controlling lepidopterous pests
Cyhalothrin	• Control insects in cotton crops
Cypermethrin	• Fast-acting neurotoxin in insects • Moderate toxicity through skin contact or ingestion
Glyphosate	• Broad-spectrum systemic herbicide and crop desiccant

Experimental

In this study pesticide samples were tested for their content of Abamectin EC, Emamectin EC, Cyhalothrin EC, Cypermethrin and Glyphosate. 24–37 samples with different concentrations of the effective compound of interest were prepared to evaluate the correlation between changes in spectral data and reference values. **Tab. 2** shows the actual sample number and the concentration ranges of each effective compound.

Tab. 2: Sample number and concentration range of the five effective compounds of interest.

Ingredient	No. of samples	Concentration range [wt-%]
Abamectin	18	1.8–3.8
Emamectin	35	1.5–3.5
Cyhalothrin	24	2.3–4.2
Cypermethrin	27	4.0–5.8
Glyphosate	33	21.0–40.5

The spectra were collected in transmission on a NIRS RapidLiquid Analyzer over its full wavelength range (400–2500 nm), thus also the visible spectral range is analyzed. The samples were filled into disposable glass vials with 4 mm diameter. The software package Vision Air 2.0 Complete was used for data acquisition, data management and development of the quantification method (see **Tab. 3 / Fig. 1**).

Tab. 3: Used equipment and software.

Equipment	Metrohm code
NIRS RapidLiquid Analyzer	2.921.1410
NIRS disposable glass vials, 4 mm diameter	6.7402.010
Vision Air 2.0 Complete	6.6072.208

Fig. 1: The NIRS XDS RapidLiquid Analyzer was used for spectral data acquisition over the full range from 400 nm to 2500 nm.

NIR Application Note NIR-056
Version 1, first published October 30, 2017

Metrohm NIRSystems

Method description

Results

Depending on the effective compound of interest various spectral regions were selected. A Partial Least Squares (PLS) regression was performed for each analyte. Internal cross-validation (leave-one-out) was applied to verify the performance of the derived quantitative models during method development.

Abamectin:

The wavelength regions of 1360–1850 nm and 2050–2500 nm (**Fig. 2**) were subsequently used to build a robust prediction model. For the quantification of Abamectin in pesticide, a model using 2 factors was developed with a Standard Error of Calibration (SEC) of 0.05% and a Standard Error of Cross Validation (SECV) of 0.06%. A high correlation between the provided reference values and the calculated values (R^2 = 0.9946) was achieved, see **Fig. 3**. Parameters used for method development and the Figures of Merit (FoM) are listed in **Tab. 4**.

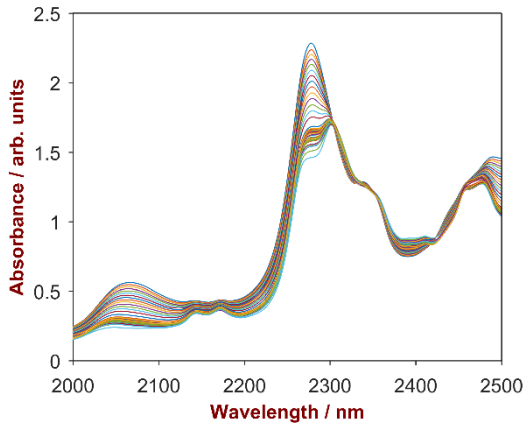

Fig. 2: Raw data spectrum of 18 pesticide samples with Abamectin concentrations ranging from 1.8–3.8%.

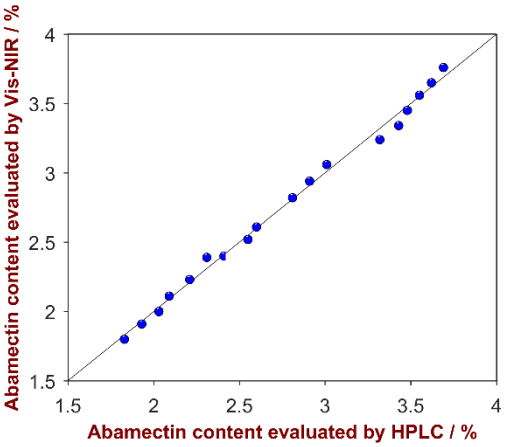

Fig. 3: Correlation plot of the predicted Abamectin content by Vis-NIRS versus the reference values evaluated by HPLC.

Tab. 4: Results of the quantitative method development for Abamectin content.

Regression model	PLS with 2 factors
Pre-treatment	Raw data
Wavelength range	1360 – 1850 nm 2050 – 2500 nm
R	0.9946
SEC	0.05%
SECV	0.06%

Emamectin:

The wavelength regions of 1300-1790 nm (**Fig. 4**) was used to build a robust prediction model. For the quantification of Emamectin in pesticide, a 1 factor model with a SEC of 0.61% and a SECV of 0.62% was developed. A high correlation between the provided reference values and the calculated values (R^2 = 0.9911) was achieved, see **Fig. 5**. Parameters used for method development and the FoM are listed in **Tab. 5**.

NIR Application Note NIR-056
Version 1, first published October 30, 2017

Metrohm NIRSystems

Method description

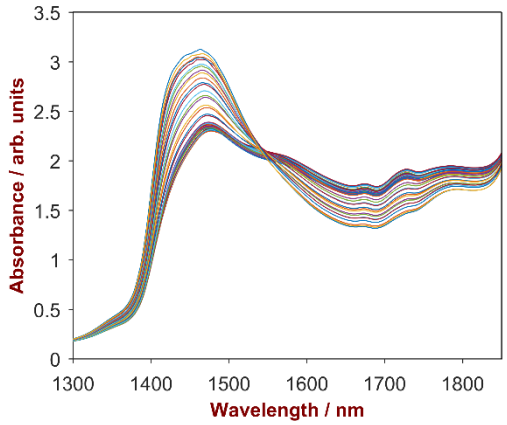

Fig. 4: Raw data spectrum of 35 pesticide samples with Emamectin concentrations ranging from 1.5–3.5%.

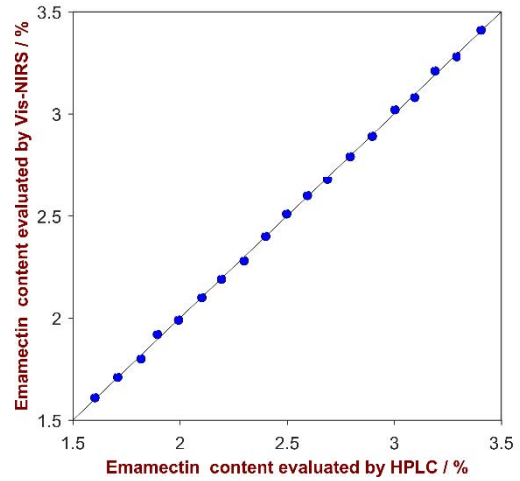

Fig. 5: Correlation plot of the predicted Emamectin content by Vis-NIRS versus the reference values evaluated by HPLC.

Tab. 5: Results of the quantitative method development for Emamectin content.

Regression model	PLS with 1 factor
Pre-treatment	Raw data
Wavelength range	1300 – 1790 nm
R^2	0.9911
SEC	0.61%
SECV	0.62%

Cyhalothrin:

The wavelength regions of 400–1080 nm and 1300–2200 nm (**Fig.6**) were used to build a robust prediction model. For the quantification of Cyhalothrin in pesticide, a 1 factor model with a SEC of 0.042% and a SECV of 0.043% was developed. A high correlation between the provided reference values and the calculated values (R^2 = 0.9952) was achieved, see **Fig. 7**. Parameters used for method development and FoM are listed in **Tab. 6**.

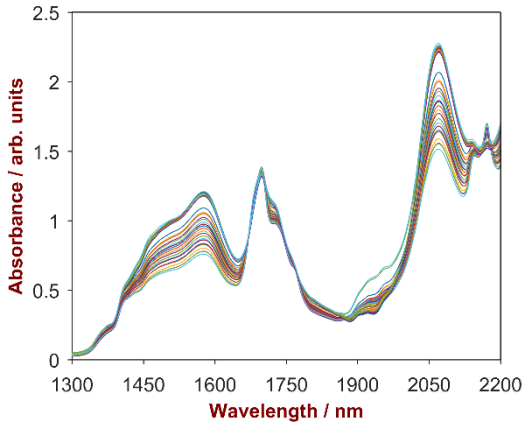

Fig. 6: Raw data spectrum of 24 pesticide samples with Cyhalothrin concentrations ranging from 2.3–4.2%.

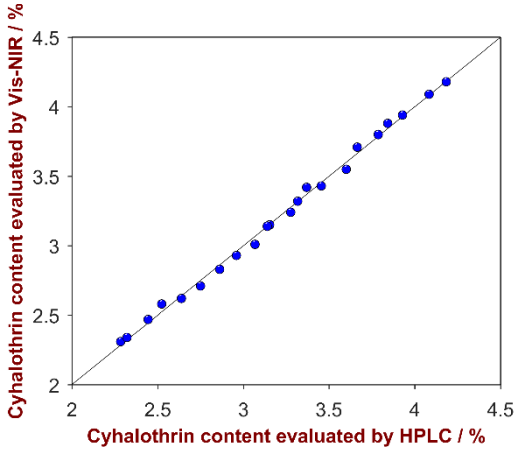

Fig. 7: Correlation plot of the predicted Cyhalothrin content by Vis-NIRS versus the reference values evaluated by HPLC.

NIR Application Note NIR-056
Version 1, first published October 30, 2017

Metrohm NIRSystems

Method description

Tab.6: Results of the quantitative method development for Cyhalothrin content.

Regression model	PLS with 2 factors
Pre-treatment	Raw data
Wavelength range	400–1080 nm 1300–2200 nm
R^2	0.9952
SEC	0.05%
SECV	0.05%

Cypermethrin:

The wavelength regions of 1300–2200 nm (**Fig. 8**) were subsequently used to build a robust prediction model. For the quantification of Cypermethrin in pesticide, a 1 factor model with a SEC of 0.016% and a SECV of 0.016% was developed. A high correlation between the provided reference values and the calculated values (R^2 = 0.9952) was achieved, see **Fig. 9**. Parameters used for method development and FoM are listed in **Tab. 7**.

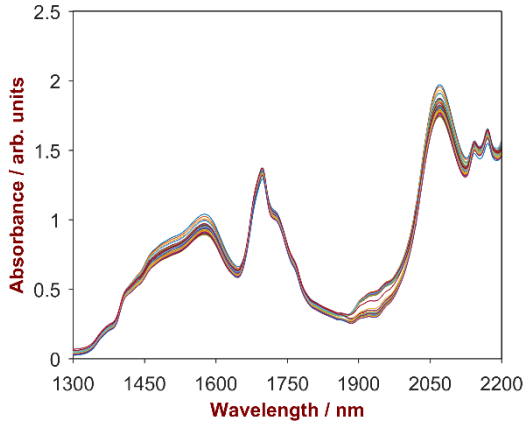

Fig. 8: Raw data spectrum of 27 pesticide samples with Cypermethrin concentrations ranging from 4.0–5.8%.

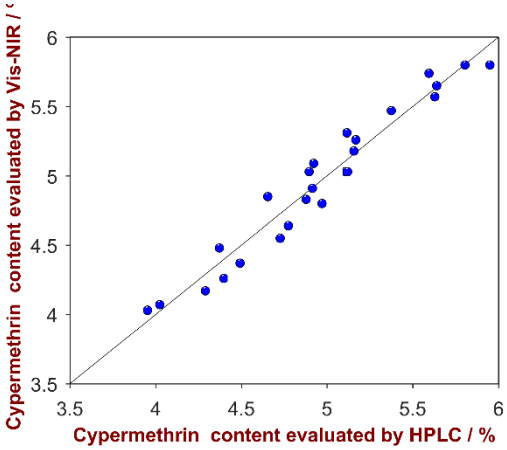

Fig. 9: Correlation plot of the predicted Cypermethrin content by Vis-NIRS versus the reference values evaluated by HPLC.

Tab. 7: Results of the quantitative method development for Cypermethrin content.

Regression model	PLS with 2 factors
Pre-treatment	Raw data
Wavelength range	1300-2200 nm
R^2	0.9286
SEC	0.16%
SECV	0.16%

Glyphosate:

The wavelength regions of 1300–2200 nm (**Fig. 10**) were subsequently used to build a robust prediction model. For the quantification of Glyphosate in pesticide, a 1 factor model with a SEC of 0.03% and a SECV of 0.03% was developed. A high correlation between the provided reference values and the calculated values (R^2 = 0.9952) was achieved, see **Fig. 11**. Parameters used for method development and FoM are listed in **Tab. 8**.

NIR Application Note NIR-056
Version 1, first published October 30, 2017

Metrohm NIRSystems

Method description

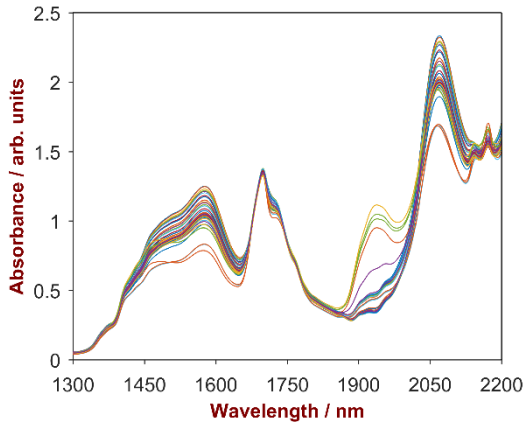

Fig. 10: Raw data spectrum of 33 pesticide samples with Glyphosate concentrations ranging from 21.0–40.5%.

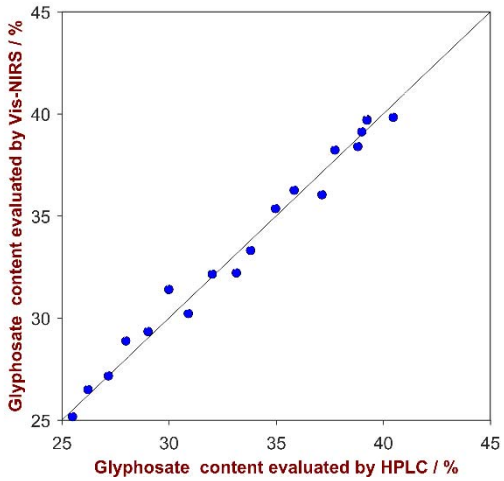

Fig. 11: Correlation plot of the predicted Glyphosate content by Vis-NIRS versus the reference values evaluated by HPLC.

Tab. 8: Results of the quantitative method development for Glyphosate content.

Regression model	PLS with 2 factors
Pre-treatment	Raw data
Wavelength range	1300–2170 nm
R^2	0.9987
SEC	0.03%
SECV	0.03%

External Validation:

The prediction models were tested on an external data set. **Tab. 9** shows the predicted Vis-NIR values and the comparison with the HPLC reference values. Residual and RSD are listed.

Tab. 9: Comparison of predicted Vis-NIR values with the HPLC reference values.

Compound	Vis-NIR [%]	HPLC [%]	Residual	RSD
Abamectin	2.63	2.74	-0.11	-3.87
Abamectin	2.58	2.60	-0.02	-0.91
Abamectin	2.70	2.64	0.06	2.34
Abamectin	2.59	2.57	0.02	0.82
Abamectin	2.51	2.61	-0.10	-3.81
Abamectin	2.48	2.58	-0.10	-3.96
Abamectin	2.53	2.58	-0.05	-2.10
Abamectin	2.58	2.62	-0.04	-1.39
Abamectin	2.57	2.56	0.01	0.29
Abamectin	2.55	2.63	-0.08	-2.92
Abamectin	2.54	2.63	-0.09	-3.45
Abamectin	2.57	2.69	-0.12	-4.35
Emamectin	2.47	2.36	0.11	4.58
Emamectin	2.44	2.45	-0.01	-0.52
Emamectin	2.31	2.39	-0.08	-3.54
Emamectin	2.47	2.36	0.11	4.58
Cyhalothrin	3.14	3.14	0.00	0.14
Cyhalothrin	3.27	3.16	0.11	3.47
Cyhalothrin	3.19	3.13	0.06	1.97
Cyhalothrin	3.13	3.17	-0.04	-1.22
Cyhalothrin	3.17	3.16	0.01	0.37
Cyhalothrin	3.24	3.16	0.08	2.68
Cyhalothrin	3.26	3.15	0.11	3.37
Cyhalothrin	3.20	3.32	-0.12	-3.69
Cyhalothrin	3.30	3.17	0.13	4.01
Cyhalothrin	3.10	3.08	0.02	0.77
Cypermethrin	4.93	4.84	0.09	1.91
Cypermethrin	5.03	4.98	0.05	1.04
Cypermethrin	4.88	5.02	-0.14	-2.73
Cypermethrin	5.05	4.97	0.08	1.51
Cypermethrin	5.11	5.10	0.01	0.16
Cypermethrin	5.08	4.92	0.16	3.17
Cypermethrin	5.12	5.07	0.05	1.04
Cypermethrin	5.09	5.03	0.06	1.15
Cypermethrin	5.01	4.95	0.06	1.28
Cypermethrin	4.97	4.83	0.14	2.98
Cypermethrin	4.96	4.97	-0.01	-0.20
Cypermethrin	5.03	5.10	-0.07	-1.36
Glyphosate	39.61	39.16	0.45	1.14
Glyphosate	39.19	39.86	-0.67	-1.69
Glyphosate	39.16	39.08	0.08	0.19
Glyphosate	39.56	39.46	0.10	0.25
Glyphosate	39.74	39.35	0.39	0.99
Glyphosate	39.09	39.14	-0.05	-0.13
Glyphosate	39.83	39.35	0.48	1.21

NIR Application Note NIR-056
Version 1, first published October 30, 2017

Metrohm NIRSystems

Method description

Summary

This application note shows that quantification of Abamectin, Methylamino abamectin, Cyhalothrin, Cypermethrin and Glyphosate in a pesticides can be conveniently done with Vis-NIR spectroscopy. For all analyses, calculated standard errors are close to standard errors of the reference method highlighting the suitability of Vis-NIR spectroscopy as a highly reliable and much faster quality control method for pesticide manufacturers.

References

[1] http://www.who.int/topics/pesticides/en/
[2] http://www.who.int/mediacentre/factsheets/pesticide-residues-food/en/
[3] https://en.wikipedia.org/

NIR Application Note NIR-056
Version 1, first published October 30, 2017

Metrohm NIRSystems