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Environmental Protection Agency

Control of Pesticides and Biocides 2012

The Analytical Chemical Control of
Pesticides and Biocides on the Danish
Market

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Foreword

50 different types of products, covered by the pesticide and biocide regulation, were included in the Danish authority control in 2012.

All collected products were examined for content of one or more active substances according to the declared content and the specification of the product given by the authorisation holder. Some products were examined for their content of relevant impurities and a chemical marker.

For the 2012 programme, all 50 tested products comply with the tolerance limits defined by the Danish Statutory Order on pesticides No. 702 of 24 June 2011 incl. revisions, and in Regulation 1107/2009 concerning marketing of plant protection products¹⁺²⁺³.

Konklusion og sammenfatning

Denne rapport beskriver den analytisk kemiske kontrol af biocid- og pesticidprodukter på det danske marked, der er udført af den danske Miljøstyrelse, Afdeling for Pesticider og Genteknologi, i 2012.

50 produkter fra udvalgte typer af bekæmpelsesmidler er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med produktspecifikationen og det deklarerede indhold. Grænsen for en accepteret afvigelse i indholdet af et aktivstof i forhold til det deklarerede indhold og produktspecifikationen er fastsat i bekendtgørelsen om bekæmpelsesmidler Nr. 702 af 24. juni 2011 inkl. revisioner og i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler¹⁺²⁺³.

50 forskellige produkter er inkluderet i den analytisk kemiske kontrol, der blev udført af myndighederne i 2012:

- 17 insekticider indeholdende Deltamethrin og Imidacloprid
- 28 herbicider indeholdende Diflufenican, MCPA, Metamitron og Metsulfuron-methyl
- 4 fungicider indeholdende Pyraclostrobin
- 1 feromone indeholdende 1-Dodecanol og 1-Tetradecanol.

Indholdet af aktivstoffet i alle de analyserede produkter var indenfor den accepterede tolerance:

TABLE 1
OVERSIGT OVER ANTAL ANALYSEREDE PRODUKTER OG KONKLUSION

Aktivstof	Antal analyserede produkter	Antal inden for tolerance	Antal uden for tolerance
Deltamethrin	6	6	0
Diflufenican	7	7	0
Imidacloprid	11	11	0
MCPA	13	13	0
Metamitron	3	3	0
Metsulfuron-methyl	5	5	0
Pyraclostrobin	4	4	0
1-Dodecanol og 1-Tetradecanol	1	1	0
Total	50	50	0

Produkter indeholdende imidacloprid blev undersøgt for en kemisk markør, som ikke blev påvist.

De fem produkter indeholdende Metsulfuron-methyl blev desuden undersøgt for fem udvalgte urenheder. To produkter overholdt specifikationerne. Et produkt er blevet tilbagekaldt fra markedet af godkendelsesindehaveren, og to produkter afventer yderligere undersøgelser.

Conclusion and Summary

This report describes the analytical chemical control of pesticide and biocide products on the Danish market that was carried out by the Danish Environmental Protection Agency (Danish EPA), Division for Pesticides and Gene Technology, in 2012.

50 products from selected types of pesticides and biocides were collected and analysed to verify whether or not the content of the active substances in the products in question complied with the product specification and the declared content. The tolerance of an accepted deviation in the content of an active substance compared to the declared content and product specification is determined in the Danish Statutory Order on pesticides No. 702 of 24 June 2011 incl. revisions, and in Regulation 1107/2009 concerning Marketing of Plant Protection Products¹⁺²⁺³.

50 different products are covered by the analytical chemical control that was carried out by the authorities in 2012:

- 17 insecticides containing Deltamethrin and Imidacloprid
- 28 herbicides containing Diflufenican, MCPA, Metamitron, Metsulfuron-methyl, and Pyraclostrobin
- 4 fungicides containing Pyraclostrobin
- 1 pheromone containing 1-Dodecanol, and 1-Tetradecanol

The content of the active substance in all 50 of the analysed products was within the accepted tolerance:

TABLE 1
OUTLINE OF TOTAL OF ANALYSED PRODUCTS AND CONCLUSION

Active substances	Number of analysed products	Number of product comply	Number of products non-comply
Deltamethrin	6	6	0
Diflufenican	7	7	0
Imidacloprid	11	11	0
MCPA	13	13	0
Metamitron	3	3	0
Metsulfuron-methyl	5	5	0
Pyraclostrobin	4	4	0
1-Dodecanol and 1-Tetradecanol	1	1	0
Total	50	50	0

Products containing imidacloprid were investigated for a chemical marker that was not proven.

Furthermore, the five products containing Metsulfuron-methyl were investigated for five selected impurities. Two products were in compliance. One authorization holder withdrew his product from the Danish market, whereas two products await further investigations.

1. Control campaigns in 2012

1.1 Selected active substances

The control campaigns conducted in 2012 covered 9 active substances in pesticides. Overall, pesticides are distinguished in two types: plant protection products and biocides (non-agricultural pesticides).

An overview of the selected active substances is given in following table:

TABLE 2
OVERVIEW OF SELECTED ACTIVE SUBSTANCES IN CONTROL CAMPAIGNS IN 2012

Type	Active substance	CAS no.	Area of application
Biocides	Deltamethrin	55918-63-5	Insecticide
Pesticides	Diflufenican	83164-33-4	Herbicide
	MCPA	94-74-6	Herbicide
	Metamitron	41394-05-2	Herbicide
	Metsulfuron-methyl	74223-64-6	Herbicide
	Pyraclostrobin	175013-18-0	Fungicide
	1-Dodecanol	112-53-8	Pheromone, Insecticide
	1-Tetradecanol	112-72-1	Pheromone, Insecticide
Biocides and Pesticides	Imidacloprid	138261-41-3	Insecticide

1.2 Collecting products

Product samples of the various pesticide and biocide formulations from different manufacturers, covered in the 2012 control campaigns, were collected by the Chemical Inspection Service from the Danish Environmental Protection Agency, Division of Pesticides and Gene Technology, during the period from March to August 2012. The product samples were bought from either wholesale dealers/importers or at retailer outlets.

A total of 50 products were collected. From them, 17 were insecticides, 32 were herbicides, and 1 was a pheromone.

The collected product samples were stored at Danish Technological Institute (DTI) in the original packaging until the chemical analyses were initiated. The product samples were stored at ambient temperature and protected from light for the entire storage period. One product was stored in a refrigerator.

1.3 Tolerance for active substances

The Danish EPA aims to examine the content of active substances in the products and will compare the result of the chemical analysis with the content according to the specification of the products and the declared content on the label supplied by the authorisation holder.

The Danish Statutory Order on pesticides No. 702 of 24 June 2011 incl. revisions, and the Regulation 1107/2009 concerning Marketing of Plant Protection Products specify the general tolerance of deviation from the declared content¹⁺²⁺³. These tolerances are listed in the following table:

TABLE 3
THE TOLERANCE OF DEVIATION FROM THE DECLARED CONTENT OF ACTIVE SUBSTANCES 2012

Content of active substances in g/kg or g/l at 20°C	Tolerance of deviation
Up to 25	± 15% homogeneous formulation
	± 25% non-homogeneous formulation
More than 25 up to 100	± 10%
More than 100 up to 250	± 6%
More than 250 up to 500	± 5%
More than 500	± 25 g/kg or ± 25 g/l

1.4 Chemical analysis 2012

The analyses of the products for the active substances were performed by Danish Technological Institute, Laboratory for Chemistry and Microbiology. DTI is a self-owned and not-for-profit institute⁷.

The Laboratory for Chemistry and Microbiology is accredited by DANAK (Danish Accreditation and Metrology Fund), registration no. 90, according to ISO 17025⁸. The Laboratory also complies with the GMP regulation of the Danish Medicines Agency regarding analysis of medicinal products and intermediate products (§ 39).

1.4.1 Analysing active substances

The chemical analyses were performed as eight freshly prepared samples of each product. The analyses were distributed over two days (four samples each day), typically within the same week. The mean value of the eight analyses and the SD (standard deviation) were calculated for each day and for all eight results.

Validation of the applied analytical method was carried out. The method was validated with regard to linearity, specificity, accuracy, and control tests at two levels spread over 2 days. Eight samples

were analysed from each product to which a known amount of the relevant active substance had been added in order to calculate the recovery.

The density of liquid products was determined by measuring with a densimeter called Densito 30 PX and as average of triple determination. The mean value and the SD were calculated.

The result in % (w/w) has been converted to g/L by using the measured density: $\text{Result (g/L)} = \text{Result \% (w/w)} * \text{density (kg/L)} * 10$.

For each product, the expanded uncertainty ($k=2$) was calculated on the basis of the spread of the results of the eight analyses, spread of the three density measurements (only included if the product is liquid), and bias was calculated on the basis of the eight recovery investigations. The expanded analysis uncertainty is used to determine a 95% confidence interval concerning the analysis result.

The results \pm the expanded uncertainty were compared with the tolerance of deviation calculated from the declared content of active substances.

1.4.2 Analysing for impurities

Products containing Metsulfuron-methyl were investigated for five selected impurities.

The chemical analyses were performed as eight analyses per pesticide product spread over two days. The mean value of the eight analyses and the SD (standard deviation) were calculated for each day and for all eight results.

1.4.3 Analysing for chemical marker

Products containing Imidcloprid were investigated for a chemical marker. A chemical marker can be used to identify products that are not legal.

2. Biocides

For the Danish 2012 Pesticide Control Campaign, 11 biocides were selected (all insecticides). The selected active substances were Deltamethrin and Imidacloprid.

2.1 Insecticides (Biocides)

Insecticides containing Deltamethrin and Imidacloprid as active substances were selected for the control campaign for 2012. All products were examined for their content of active substances.

2.1.1 Deltamethrin

Deltamethrin is an insecticide and the selected products are sold in Denmark to control crawling insects, and some flying insects indoors and around houses and buildings, e.g., ants, cockroaches, silverfish, earwigs, beetles, bedbugs, moths, small flies, and mosquitoes. Chemically, it belongs to the group of pyrethroid insecticides that inhibits the sodium channels from functioning, thereby ensuring that no transmission of nerve impulses can take place. Mode of action is as non-systemic insecticide with contact and stomach action. Fast-acting.⁹⁺¹⁰ Products with Deltamethrin were previously selected in 2003 by the Danish EPA for control.

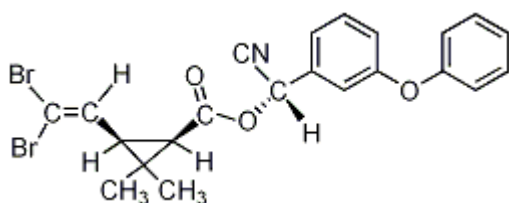


FIGURE 1 MOLECULE STRUCTURE OF DELTAMETHRIN¹⁰, CAS. NO. 55918-63-5

2.1.2 Imidacloprid

Imidacloprid is an insecticide, and the products selected for the control program are sold in Denmark to control ants in houses and buildings, as well as on terraces, flagged paths and footpaths around houses, or to control flies in stables. Chemically, it belongs to the group of neonicotinoid insecticides, and it acts as an antagonist by binding to postsynaptic nicotinic receptors in the insect central nervous system. Mode of action as biocide is as systemic insecticide with translaminar activity and with contact and stomach action.⁹⁺¹⁰ Products with Imidacloprid were previously selected in 2004 by the Danish EPA for control.

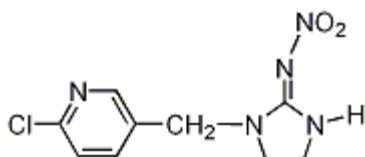


FIGURE 2 MOLECULE STRUCTURE OF IMIDACLOPRID¹⁰, CAS. NO. 138261-41-3

2.1.3 Analysis methods

Deltamethrin was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved or diluted in methanol and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC method no. 333¹¹.

Imidacloprid was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved in acetonitrile/water and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC method no. 582¹¹.

Details concerning the implementation of the analyses, and the calculation of the result and expanded analysis uncertainty, are described in chapter 1.4.1.

2.1.4 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following tables. % RSD is the percentage relative reproducibility of 8 determinations of the product. % UE is the calculated expanded measurement uncertainty described in section 1.4.1.

TABLE 4
ANALYSIS RESULTS OF INSECTICIDES (BIOCIDES), CONTENT IN G/KG

TI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	U _E %	Analysis interval	Comply/ Non-Comply
36752-1	Delta-methrin	0.5	0.43 - 0.58	0.38	1.7	15	0.33 - 0.44	Comply
36752-53	Delta-methrin	0.5	0.43 - 0.58	0.42	3.3	10	0.37 - 0.46	Comply
36752-7	Imidacloprid	0.3	0.23 - 0.38	0.27	2.3	12	0.24 - 0.30	Comply
36752-8	Imidacloprid	0.5	0.43 - 0.58	0.54	2.4	13	0.47 - 0.61	Comply
36752-9	Imidacloprid	0.3	0.26 - 0.35	0.29	4.9	24	0.22 - 0.36	Comply
36752-11	Imidacloprid	0.3	0.23 - 0.38	0.27	5.3	10	0.24 - 0.30	Comply
36752-29	Imidacloprid	5.0	4.3 - 5.8	5.1	6.6	14	4.4 - 5.8	Comply

TABLE 5
ANALYSIS RESULTS OF INSECTICIDES (BIOCIDES), CONTENT IN G/L

TI sample no.	Active substance	Label claim g/l	Tolerance interval	Analysis result g/l	RSD %	U _E %	Analysis interval	Comply / Non-Comply
36752-2	Delta-methrin	0.153	0.13 - 0.18	0.13	4.8	20	0.11 - 0.16	Comply
36752-3	Delta-methrin	7.5	6.4 - 8.6	7.7	5.3	26	5.7 - 9.7	Comply
36752-4	Delta-methrin	7.5	6.4 - 8.6	7.2	4.7	28	5.2 - 9.2	Comply
36752-52	Delta-methrin	26.65	23.9 - 29.3	25	9.6	32	17 - 33	Comply

2.1.5 Conclusion

The measured content of Deltamethrin and Imidacloprid complies with the declared content of all 11 products and is in compliance with applicable Danish law, because of the overlap between the range of analysis results and tolerance.

3. Pesticides

In the 2012 Danish Pesticide Control Campaign, a total of 39 pesticide products were selected: 28 herbicides, 4 fungicides, and 7 seven insecticides. The active substances in the selected pesticide products were Diflufenican, MCPA, Metamitron, Metsulfuron-methyl, Pyraclostrobin, Imidacloprid, 1-Dodecanol, and 1-Tetradecanol.

3.1 Herbicides (Pesticides)

Herbicides containing Diflufenican, MCPA, Metamitron and Metsulfuron-methyl as active substances were selected for the control campaign for 2012. All products were examined for their content of active substances.

3.1.1 Diflufenican

Diflufenican is a herbicide used in Denmark for weed control in private gardens and in agriculture e.g. winter crops, spring barley, spring wheat, and Christmas trees. It is normally used in combination with other cereal herbicides. Chemically, it belongs to the group of pyridinecarboxamide, and it acts by blocking the carotenoid biosynthesis by inhibition of phytoene desaturase. Mode of action is selective contact and residual herbicide; absorbed principally by the shoots of germinating seedlings, with limited translocation.⁹⁺¹⁰ Products with Diflufenican were previously selected in 2007 by the Danish EPA for control of content of active substances.

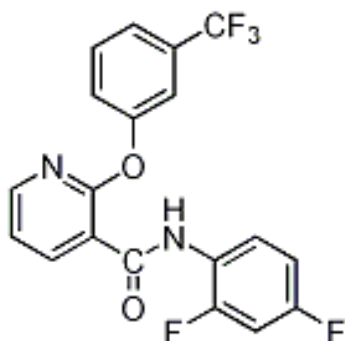


FIGURE 3 MOLECULE STRUCTURE OF DIFLUFENICAN¹⁰, CAS. NO. 83164-33-4

3.1.2 MCPA

MCPA is an herbicide and used in Denmark for weed control in corn and control of broad-leaved weeds in established grass areas such as e.g. lawns, sports grounds, and golf courses. It is often used in combination with other herbicides. Chemically, it belongs to the group of phenoxyacetic acid. Mode of action is selective, systemic, hormone-type herbicide, absorbed by the leaves and roots, with translocation. Concentrates in the meristematic regions, where it inhibits growth.⁹⁺¹⁰ Products with MCPA were previously selected in 2004 by the Danish EPA for control of content of active substances.

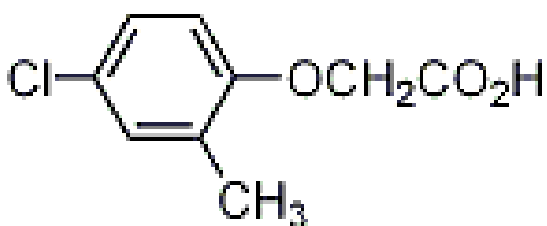


FIGURE 4 MOLECULE STRUCTURE OF MCPA¹⁰, CAS. NO. 94-74-6

3.1.3 Metamitron

Metamitron is a herbicide used in Denmark to control seed weeds in beets. Chemically, it belongs to the group of triazinone. Metamitron acts as a photosynthetic electron transport inhibitor on the photosystem II receptor site. Metamitron is a selective systemic herbicide; absorbed predominantly by the roots, but also by the leaves, with translocation acropetally.⁹⁺¹⁰ Products with Metamitron were previously selected in 2006 by the Danish EPA for control of content of active substances.

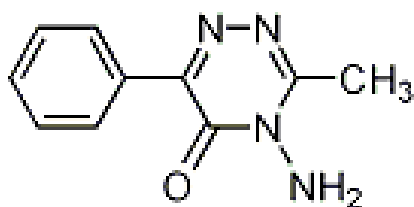


FIGURE 5 MOLECULE STRUCTURE OF METAMITRON¹⁰, CAS. NO. 41394-05-2

3.1.4 Metsulfuron-methyl

Metsulfuron-methyl is a herbicide used in Denmark for weed control in corn during spring and for weed control in winter wheat, winter barley, and spring barley. Chemically, it belongs to the group of sulfonyleurea. Metsulfuron-methyl affects sensitive weeds through inhibition of the enzyme acetolactate synthase (ALS). Inhibition of ALS leads to the rapid cessation of cell division and subsequent growth processes in plants. Metsulfuron-methyl is a selective systemic herbicide absorbed through the roots and foliage, and translocated to the apex of the plants. Symptoms appear within days, and death appears within 2–4 weeks.⁹⁺¹⁰ Products with Metsulfuron-methyl were previously selected in 2005 by the Danish EPA for control of content of active substances.

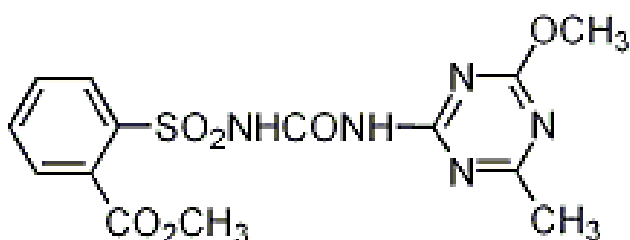


FIGURE 6 MOLECULE STRUCTURE OF METSULFURON-METHYL¹⁰, CAS. NO. 74223-64-6

3.1.5 Analysis

Diflufenican was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved in acetonitrile/water and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC-method no. 462¹¹.

MCPA was analysed by reversed phase high-performance liquid chromatography combined with UV detection or mass spectrometry, HPLC-UV, and LC-MS. All samples were dissolved or diluted in methanol or acetonitrile and were ultrasound treated before the analysis. The method is a modified HPLC method according to method no. AOAC-CIPAC 1983, MCPA-2, 4,4 HPLC p. 2139¹¹.

Metamitron was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved or diluted in methanol and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC method no. 381¹¹.

Metsulfuron-methyl was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved in acetonitrile/water and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC method no. 441¹¹.

Details concerning the implementation of the analyses and calculation of the result and expanded analysis uncertainty are described in chapter 1.4.1.

3.1.6 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following tables. % RSD is the percentage relative reproducibility of 8 determinations of the product. % UE is the calculated expanded measurement uncertainty described in section 1.4.1.

TABLE 6
ANALYSIS RESULTS OF HERBICIDES (PESTICIDES), CONTENT IN G/L

TI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	U _E %	Analysis interval	Comply / Non-Comply
36752-27	Diflufenican	417	396 - 438	425	5.5	14	365 - 485	Comply
36752-20	MCPA	5.0	4.3 - 5.8	4.1	4.8	15	3.5 - 4.7	Comply
36752-17	Metsulfuron-methyl	200	168 - 212	205	0.6	6.7	191 - 218	Comply
36752-40	Metsulfuron-methyl	200	188 - 212	205	2.0	10	184 - 225	Comply
36752-51	Metsulfuron-methyl	500	475 - 525	528	0.7	17	438 - 618	Comply
36752-56	Metsulfuron-methyl	200	168 - 212	211	1.1	11	188 - 234	Comply
36752-57	Metsulfuron-methyl	200	188 - 212	204	2.9	19	165 - 243	Comply

TABLE 7
ANALYSIS RESULTS OF HERBICIDES (PESTICIDES), CONTENT IN G/KG

TI sample no.	Active substance	Label claim g/l	Tolerance interval	Analysis result g/l	RSD %	U _E %	Analysis interval	Comply / Non-Comply
36752-5	Diflufenican	40	36-44	37	1.6	7.3	35 - 40	Comply
36752-19	Diflufenican	500	475-525	449	1.6	8.9	409 - 489	Comply
36752-25	Diflufenican	40	36 - 44	37	1.0	7.1	35 - 40	Comply
36752-36	Diflufenican	500	475 - 525	461	0.59	8.3	423 - 499	Comply
36752-37	Diflufenican	500	475-525	448	2.0	9.1	407 - 489	Comply
36752-46	Diflufenican	500	475 - 525	463	1.1	9.3	420 - 506	Comply
36752-12	MCPA	78.0	70.2 - 85.8	72	1.8	7.2	67 - 77	Comply
36752-13	MCPA	5.20	4.42 - 5.98	5.3	0.41	4.7	5.0 - 5.5	Comply
36752-14	MCPA	70	63 - 77	63	3.7	14	54 - 72	Comply
36752-15	MCPA	0.7	0.60 - 0.81	0.65	6.5	23	0.50 - 0.80	Comply
36752-23	MCPA	75	68 - 83	77	3.1	15	65 - 89	Comply
36752-28	MCPA	70	63 - 77	61	4.0	21	48 - 74	Comply
36752-30	MCPA	76.5	68.9 - 84.2	69	1.1	5.3	66 - 73	Comply
36752-32	MCPA	750	725 - 775	733	1.9	5.6	692 - 774	Comply
36752-35	MCPA	750	725 - 775	729	1.8	6.7	678 - 778	Comply
36752-39	MCPA	200	188 - 212	195	0.22	4.6	186 - 204	Comply
36752-41	MCPA	0.7	0.60 - 0.81	0.61	4.1	25	0.46 - 0.76	Comply
36752-42	MCPA	70	63 - 77	58	3.9	21	46 - 70	Comply
36752-16	Meta-mitron	700	675 - 725	707	1.1	6.3	662 - 752	Comply
36752-43	Meta-mitron	700	675 - 725	709	0.78	6.0	666 - 752	Comply

TI sample no.	Active substance	Label claim g/l	Tolerance interval	Analysis result g/l	RSD %	U _E %	Analysis interval	Comply / Non-Comply
36752-44	Meta-mitron	700	675 - 725	681	1.2	5.3	645 - 717	Comply

3.1.7 Conclusion

The measured content of Diflufenican, MCPA, Metamitron, and Metsulfuron-methyl complies with the declared content of all 28 products and is in compliance with applicable Danish law because of the overlap between the range of analysis results and tolerance.

3.2 Fungicides (Pesticides)

Fungicides containing Pyraclostrobin as active ingredient were selected for the Danish Pesticide Control Campaign in 2012. All targeted products were examined for their content of active substances.

3.2.1 Pyraclostrobin

Pyraclostrobin is a fungicide used in Denmark to control fungal diseases in e.g. vegetables, corn, seed grass, beets, and maize. Chemically, it belongs to the group of methoxycarbamate. Pyraclostrobin is a Quinone outside Inhibitor. It inhibits mitochondrial respiration by blocking electron transfer at the cytochrome bc₁ complex. Pyraclostrobin is a fungicide with protectant, curative, and translaminar properties.⁹⁺¹⁰ Products with Pyraclostrobin were previously selected in 2005 by the Danish EPA for control of content of active substances.

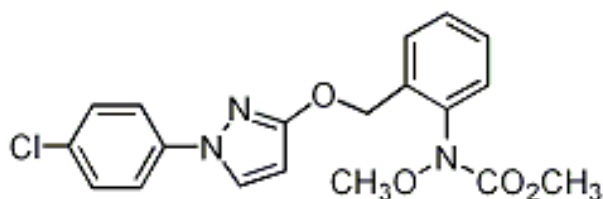


FIGURE 7 MOLECULE STRUCTURE OF PYRACLOSTROBIN¹⁰, CAS NO. 175013-18-0

3.2.2 Analysis

Pyraclostrobin was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved or diluted in methanol and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC method no. 333¹¹.

Details concerning the implementation of the analyses and calculation of the result and expanded analysis uncertainty are described in chapter 1.4.1.

3.2.3 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following tables. % RSD is the percentage relative reproducibility of 8 determinations of the product. % UE is the calculated expanded measurement uncertainty described in section 1.4.1.

TABLE 6
ANALYSIS RESULTS OF FUNGICIDES (PESTICIDES), CONTENT IN G/KG

TI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	U _E %	Analysis interval	Comply / Non-Comply
36752-34	Pyraclostrobin	67	60 - 74	77	7.3	24	59 - 95	Comply
36752-45	Pyraclostrobin	67	60 - 74	72	5.3	13	63 - 81	Comply

TABLE 7
ANALYSIS RESULTS OF FUNGICIDES (PESTICIDES), CONTENT IN G/L

TI sample no.	Active substance	Label claim g/l	Tolerance interval	Analysis result g/l	RSD %	U _E %	Analysis interval	Comply / Non-Comply
36752-21	Pyraclostrobin	250	235 - 265	213	2.8	26	158 - 268	Comply
36752-22	Pyraclostrobin	133	125 - 141	133	0.98	10	120 - 146	Comply

3.2.4 Conclusion

The measured content of Pyroclostrobin complies with the declared content of all 4 products, and is in compliance with applicable Danish law because of the overlap between the range of analysis results and tolerance.

3.3 Insecticides (Pesticides)

Insecticides containing Imidacloprid, 1-Dodecanol, and 1-Tetradecanol as active substances were selected for the 2012 control campaign. All products were examined for their content of active substances.

3.3.1 Imidacloprid

Imidacloprid is an insecticide used in Denmark to control insect pests in ornamental plants, tomatoes, cucumbers and peppers in greenhouses, as well as garden chafer larvae on lawns, and fungicide treatment of seed potatoes. Chemically, it belongs to the group of neonicotinoid. Imidacloprid acts as an antagonist by binding to postsynaptic nicotinic receptors in the insect's central nervous system. Imidacloprid acts as a systemic insecticide with translaminar activity and with contact and stomach action. Readily taken up by the plant and further distributed acropetally, with good root-systemic action.⁹⁺¹⁰ Products with Imidacloprid were previously selected in 2004 by the Danish EPA for control of content of active substances.

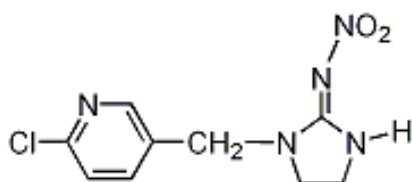


FIGURE 7 MOLECULE STRUCTURE OF IMIDACLOPRID[®], CAS. NO. 138261-41-3

3.3.2 1-Dodecanol and 1-Tetradecanol

1-dodecanol and 1-tetradecanol are used in combination with the (E, E) -8, 10-dodecadiene-1-ol, (Z)-11-tetradecene-1-yl acetate, and (Z)-9-tetradecene-1-yl acetate as pheromone confusion mixture for controlling pests on plants, e.g., codling moths and leaf wrappers. In Denmark, the product is used for insect control in apples and pears. Mode of action is to prevent mating of codling moths and several species of leaf wrappers, whereby propagation is prevented. That results in a reduced moth (leaf rollers) population and therefore less damage to the coops. The product has not previously been selected by the Danish EPA for control of content of active substances.

3.3.3 Analysis methods

Imidacloprid was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved in acetonitrile/water and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC method no. 582¹¹.

Dodecanol and 1-Tetradecanol were analysed by gas chromatography combined with mass spectrometry, GC-MS. Acetone was added to all samples before the analysis. The method is a modified GC-MS method according to a method validated for the product ISOMATE¹². It was not possible to obtain chemical standards of (E,E)-8, 10-dodecadien-1-ol, (Z)-11-tetradecen-1-yl acetate, and (Z)-9-tetradecen-1-yl acetate. Therefore, they have not been included in the survey.

Details concerning the implementation of the analyses and calculation of the result and expanded analysis uncertainty are described in chapter 1.4.1.

3.3.4 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following tables. % RSD is the percentage relative reproducibility of 8 determinations of the product. % UE is the calculated expanded measurement uncertainty described in section 1.4.1

TABLE 8
ANALYSIS RESULTS OF INSECTICIDES (PESTICIDES), CONTENT IN G/KG

TI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	U _E %	Analysis interval	Comply/Non-Comply
36752-6	Imidacloprid	25.0	23.8 - 26.3	23	5.5	20	19 - 28	Comply
36752-24	Imidacloprid	0.5	0.43 - 0.58	0.51	14	31	0.35 - 0.66	Comply
36752-31	Imidacloprid	5.0	4.3 - 5.8	6.7	7.0	21	5.4 - 8.0	Comply

TI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	U _E %	Analysis interval	Comply/ Non-Comply
36752-33	Imidacloprid	700	675 - 725	610	1.3	18	500 - 720	Comply
36752-38	Imidacloprid	700	675 - 725	614	3.9	20	491 - 737	Comply
36752-55	Dodecan-1-ol	59	53 - 65	53	6.4	18	44 - 63	Comply
36752-55	Tetradecan-1-ol	13	11 - 15	18	6.6	21	14 - 22	Comply

TABLE 9
ANALYSIS RESULTS OF INSECTICIDES (PESTICIDES), CONTENT IN G/L

TI sample no.	Active substance	Label claim g/l	Tolerance interval	Analysis result g/l	RSD %	U _E %	Analysis interval	Comply / Non-Comply
36752-18	Imidacloprid	120	118 - 123	116	4.3	13	101 - 131	Comply

3.3.5 Conclusion

The measured content of Imidacloprid, Dodecanol, and 1-Tetradecanol complies with the declared content of all 7 products and is in compliance with applicable Danish law because of the overlap between the range of analysis results and tolerance.

4. Impurities

The five pesticide products containing Metsulfuron-methyl were in addition to the control of the active ingredient also submitted for the content of five relevant impurities.

4.1.1 Analysis

Metsulfuron-methyl and the impurities were analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved in acetonitrile/ water and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC method no. 441¹¹.

Details concerning the implementation of the analyses and calculation of the result are described in chapter 1.4.2.

4.1.2 Results

Two products were in compliance. Three products contained at least one substance that exceeded the tolerance stated in the product specifications given by the authorisation holders. There might be a risk of formulation ingredients interfering with some of the results, and therefore the authorisation holders were subsequently contacted to explain if that is possible. In reply to the request, one authorization holder withdrew his product from the Danish market, whereas two products await further investigations.

5. Chemical marker

The task was to analyze for chemical markers in products with the active substance Imidacloprid. The identity of the chemical marker is confidential.

5.1.1 Analysis methods

Chemical marker in products containing Imidacloprid were analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. The method is a modified HPLC method according to CIPAC method no. 582¹¹.

Analyses of 8 subsamples of each product were spread over two days.

The detection limit was determined to 1 ppm for a reference standard of the chemical marker. The detection limit for determination of the chemical marker in the products was set to 10 ppm due to interference from other constituents in some of the products.

5.1.2 Results

No content of the chemical marker was demonstrated in the analysed products

5.1.3 Conclusion

Therefore, the analysed products meet the permitted content of possible chemical marker of max. 60 ppm.

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13. Danish Ministry of the Environment, Environmental Protection Agency, Control of Pesticides and Biocides 2010, Working Report No. 6, 2011.
14. Danish Ministry of the Environment, Environmental Protection Agency, Control of Pesticides and Biocides 2011, Working Report No. 1, 2012.

Appendix 1: Pesticide and biocide samples collected on the Danish market for authority control in 2012

TABLE 10
COLLECTED INSECTICIDES (BIOCIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36752-1	Deltamethrin	18-421	K-Otrine Insektpulver	Bayer A/S, Bayer CropScience
36752-2	Deltamethrin	18-504	Kvit D mod myrer	Bayer A/S, Bayer CropScience
36752-3	Deltamethrin	18-507	Baythion mod myrer	Bayer A/S, Bayer CropScience
36752-4	Deltamethrin	18-540	Myremiddel	Bayer A/S, Bayer CropScience
36752-52	Deltamethrin	18-422	K-Otrine SC 25	Bayer A/S, Bayer CropScience
36752-53	Deltamethrin	18-423	Kvik Insektpulver	Bayer A/S, Bayer CropScience
36752-7	Imidacloprid	18-489	Baythion I Myrelokkedåse	Bayer A/S, Bayer CropScience
36752-8	Imidacloprid	18-490	Kvit Ekstra Myregranulat	Bayer A/S, Bayer CropScience
36752-9	Imidacloprid	18-530	Kvit Myre-sirup	Bayer A/S, Bayer CropScience
36752-11	Imidacloprid	18-535	Material Shop I Myrelokkedåse	Bayer A/S, Bayer CropScience
36752-29	Imidacloprid	18-465	Quick Bayt	Bayer A/S, Bayer CropScience

TABLE 11
COLLECTED HERBICIDES (PESTICIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36752-5	Diflufenican	18-498	Keeper L mod ukrudt	Bayer A/S, Bayer CropScience
36752-19	Diflufenican	18-416	DFP	Bayer A/S, Bayer CropScience
36752-25	Diflufenican	18-497	Pistol	Bayer A/S, Bayer CropScience
36752-27	Diflufenican	3-170	Absolute 5	DuPont Danmark ApS
36752-36	Diflufenican	396-26	Legacy 500 SC	Makhteshim Agan Holland BV

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36752-37	Diflufenican	18-514	Quartz	Bayer A/S, Bayer CropScience
36752-46	Diflufenican	594-4	Sempre	AgriChem BV
36752-12	MCPA	49-27	Trim Toxan Plænerens	Klarsø A/S
36752-13	MCPA	49-38	Toxan Plænerens	Klarsø A/S
36752-14	MCPA	361-17	Herbavæk Plænerens	Agriphar S. A.
36752-15	MCPA	361-24	Turflin Plænerens klar til brug	Agriphar S. A.
36752-20	MCPA	49-49	Trim Plænerens	Klarsø A/S
36752-23	MCPA	19-74	Basagran M 75	BASF A/S
36752-28	MCPA	361-7	Dicotex	Agriphar S. A.
36752-30	MCPA	49-104	Herbipur Plænerens Plus	Klarsø A/S
36752-32	MCPA	347-5	Metaxon	Nufarm Deutschland GmbH
36752-35	MCPA	347-11	SweDane MCPA-750	Nufarm Deutschland GmbH
36752-39	MCPA	64-39	Ariane FG S	Dow Agro Sciences Danmark A/S
36752-41	MCPA	361-23	Tanaco Plænerens klar til brug	Agriphar S. A.
36752-42	MCPA	361-19	Tanaco Plænerens	Agriphar S. A.
36752-16	Metamitron	14-252	SweDane Metafol 700 SC	AgroDan A/S
36752-43	Metamitron	396-22	Goltix SC 700	Makhteshim Agan Holland B.V.
36752-44	Metamitron	242-22	ND Metamitron 700	Nedab ApS
36752-17	Metsulfuron-methyl	11-32	Accurate	Cheminova A/S
36752-40	Metsulfuron-methyl	594-1	Finy	AgriChem BV
36752-51	Metsulfuron-methyl	3-168	Ally ST	DuPont Danmark ApS
36752-56	Metsulfuron-methyl	607-1	MiniMet	Rotam Agrochemical

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
				Europe Ltd
36752-57	Metsulfuron-methyl	347-6	Isomexx	Nufarm Deutschland GmbH

TABLE 12
COLLECTED FUNGICIDES (PESTICIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36752-21	Pyraclostrobin	19-143	Comet	BASF A/S
36752-22	Pyraclostrobin	19-144	Opera	BASF A/S

TABLE 13
COLLECTED INSECTICIDES (PESTICIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36752-6	Imidacloprid	18-356	Provado Insektpind	Bayer A/S, Bayer CropScience
36752-18	Imidacloprid	18-400	Prestige FS 370	Bayer A/S, Bayer CropScience
36752-24	Imidacloprid	18-506	Trim mod gåsebille-larver	Bayer A/S, Bayer CropScience
36752-31	Imidacloprid	18-485	Merit Turf	Bayer A/S, Bayer CropScience
36752-33	Imidacloprid	18-365	Confidor WG 70	Bayer A/S, Bayer CropScience
36752-38	Imidacloprid	11-41	Warrant 70 WG (CHA 5760)	Cheminova A/S
36752-55	Dodecan-1-ol Tetradecan-1-ol	699-1	Isomate CLR	CBC Europe Ltd. Milan Branch

Control of Pesticides and Biocides 2012

The analytical chemical authority control of pesticide and biocide products on the Danish market that was carried out in 2012 by the Danish Environmental Protection Agency (Danish EPA), Division for Pesticides and Gene Technology, is described in this report. Samples of selected types of pesticides and biocides were collected on the Danish market and analysed to verify whether or not the content of the active substances in the products in question complied with the product specification and the labelled content. A total of 50 different pesticide products were analysed. The content of active substance in all of the analysed products was within the accepted tolerance that is determined in the Danish Statutory Order on pesticides.

Den analytisk kemiske kontrol af biocid- og pesticidprodukter på det danske marked, der er udført i 2012 af den danske Miljøstyrelses Afdeling for Pesticider og Genteknologi, er beskrevet i denne rapport. Prøver fra udvalgte typer af bekæmpelsesmidler er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med det deklarerede indhold. Der blev undersøgt i alt 50 bekæmpelsesmidler. Indholdet af aktivstoffet i alle af de analyserede produkter var indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler.



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