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and Food of Denmark**
Environmental
Protection Agency

Control of Pesticides 2018

The Analytical Chemical Control of Pesticides on the Danish Market

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Sources must be acknowledged.

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Preface

This report describes the analytical chemical control of pesticides on the Danish market, which was carried out in 2018 by the Chemical Inspection Service of the Danish Environmental Protection Agency. The control is part of the Danish National Plan of Pesticides 2017-2020. Samples of selected types of pesticides on the Danish market were collected and analysed to verify whether or not the content of active substances in the pesticides complies with the product specifications, the labelled content and the information given to the Danish Environmental Protection Agency.

The Danish National Plan of Pesticides 2017-2020 is also engaged to act against illegal and counterfeit pesticides. Therefore, the objective of the analyses was also to investigate the existence of illegal or counterfeit pesticides.

Sammenfatning og konklusion

Denne rapport beskriver den analytisk kemiske kontrol af pesticidprodukter (plantebeskyttelsesmidler) på det danske marked, der er udført af Miljøstyrelsens Kemikalieinspektion i 2018.^{1,2}

Der er udvalgt og indsamlet 29 pesticidprodukter. Produkterne blev analyseret for at verificere, om indholdet af de respektive aktivstoffer var i overensstemmelse med produktspecifikationen og det deklarerede indhold. Der blev udført i alt 47 analyser for aktivstoffer.

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. 1647 af 17. december 2017 og 815 18/06/2018, samt i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler.^{3,4,5}

Følgende typer af produkter blev analyseret (se tabel på næste side):

- 1 insekticid indeholdende pyrethrin I+II
- 6 herbicider indeholdende pendimethalin, 2,4-D-ethylhexyl, aminopyralid, florasulam, metamitron og pyroxsulam
- 19 fungicider indeholdende azoxystrobin, cymoxanil, difenoconazol, fluopyram, fosetyl-aluminium, mandipropamid, propamocarb, propiconazol, prothioconazol, spiroxamin og tebuconazol
- 3 vækstreguleringsmidler indeholdende ethephon, mepiquat-chlorid, prohexadion-calcium og paclobutrazol.

Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold i alle produkter, idet resultaterne er indenfor tolerancen.

Der blev udført i alt 103 fysisk-kemiske test:

- Densitet blev målt på 25 produkter
- Udseende blev vurderet for 23 produkter
- pH blev bestemt for 23 produkter
- vedvarende skumdannelse blev bestemt for 22 produkter
- emulsionsstabilitet blev vurderet for 7 produkter
- suspensibilitet blev målt for 3 produkter.

Fem produkter, som blev testet for fysisk-kemiske parameter, var ikke i overensstemmelse med produkternes specifikationer for pH. Et enkelt produkt overholdt ikke gældende grænseværdier for vedvarende skumdannelse.

Der blev foretaget screeninger af et parallelprodukt og det tilhørende originalprodukt for at undersøge, om der var forskel på formuleringsingredienser. Der blev ikke fundet forskel mellem parallelproduktet og originalproduktet.

Desuden blev tre pesticidprodukter analyseret for kendte urenheder. To produkter blev screenet for indhold af polychlorerede dibenzodioxiner og polychlorerede dibenzofuraner og et for N-nitroso pendimethalin.

Oversigt over antal analyserede produkter

Aktivstof	Antal analyserede produkter
2.4-D-ethylhexyl & florasulam	1
2.4-D-ethylhexyl, florasulam & aminopyralid	1
Cymoxanil	2
Difenoconazol	1
Difenoconazol & azoxystrobin	2
Difenoconazol & mandipropamid	1
Difenoconazol & propiconazol	1
Ethephon	1
Florasulam, aminopyralid & pyroxsulam	1
Mepiquat-chlorid & prohexadion-calcium	1
Metamitron	2
Paclobutrazol	1
Pendimethalin	1
Propamocarb	1
Propamocarb & cymoxanil	1
Propamocarb & fosetyl-aluminium	2
Propiconazol	1
Prothioconazol	1
Prothioconazol & fluopyram	1
Prothioconazol & spiroxamin	1
Prothioconazol & tebuconazol	3
Pyrethrin I+II	1
Tebuconazol	1
TOTAL	29

Summary and conclusion

This report describes the analytical chemical control of plant protection products (pesticide products) on the Danish market that was carried out by the Danish Environmental Protection Agency (Danish EPA), Chemical Inspection Service, in 2018.^{1,2}

29 products from selected types of pesticides were collected and analysed to verify whether the content of the active substances in the products in question complies with the product specification and the declared content. 47 analyses were carried out for active substances.

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. 1647 of 17 December 2017 and 815 18/06/2018 as well as in Regulation 1107/2009 concerning Marketing of Plant Protection Products.^{3,4,5}

The following products were analysed (see table on next page):

- 1 insecticide containing pyrethrin I+II
- 6 herbicides containing pendimethalin, 2,4-D-ethylhexyl, aminopyralid, florasulam, metamitron and pyroxsulam
- 19 fungicides containing azoxystrobin, cymoxanil, difenoconazole, fluopyram, fosetyl-aluminium, mandipropamid, propamocarb, propiconazole, prothioconazole, spiroxamine and tebuconazole
- 3 growth regulators containing ethephon, mepiquat-chloride, prohexadione-calcium and paclobutrazol

The measured content of active substances complied with the declared content in all the selected products as the results were within the range of tolerance.

In total, 103 physical-chemical tests were performed:

- Density was measured on 25 products
- Appearance was assessed for 23 products
- pH was determined for 23 products
- Persistent foaming was performed on 22 products
- Emulsion stability was performed on 7 products
- Suspensibility was performed on 3 products

Five products that were tested for physical-chemical parameters did not comply with the specified pH values. In addition, one product did not comply with legal requirements with respect to persistent foam.

Screening was performed on one parallel product and the corresponding original product to examine whether there was a difference between the formulation chemicals. No difference was found between the parallel and the original product.

Three of the pesticide products were analysed for known impurities. Two products were analysed for the content of polychlorinated dibenzodioxines (PCDD) and polychlorinated dibenzofurans (PCDF) and one product was analysed for N-nitrosopendimethalin.

Overview of the number of analysed products

Active substance	Number of analysed products
2,4-D-ethylhexyl & florasulam	1
2,4-D-ethylhexyl, florasulam & aminopyralid	1
Cymoxanil	2
Difenoconazole	1
Difenoconazole & azoxystrobin	2
Difenoconazole & mandipropamid	1
Difenoconazole & propiconazole	1
Ethephon	1
Florasulam, aminopyralid & pyroxsulam	1
Mepiquat-chloride & prohexadione-calcium	1
Metamitron	2
Paclobutrazol	1
Pendimethalin	1
Propamocarb	1
Propamocarb & cymoxanil	1
Propamocarb & fosetyl-aluminium	2
Propiconazole	1
Prothioconazole	1
Prothioconazole & fluopyram	1
Prothioconazole & spiroxamine	1
Prothioconazole & tebuconazole	3
Pyrethrin I+II	1
Tebuconazole	1
TOTAL	29

1. Control campaign in 2018

1.1 Collecting products

The Danish control campaign conducted in 2018 covered 22 active substances in different combinations in 29 plant protection products (PPP, pesticides). All products were collected by the Chemical Inspection Service of the Danish Environmental Protection Agency during the period from March to June 2018. The product samples were collected either from wholesale dealers/importers or at retailer outlets. A summary of the selected active substances is given in Table 1.

Table 1 Outline of selected active substances in the 2018 control campaign

Area of application	Active substance	CAS no.
Fungicide	Azoxystrobin	131860-33-8
	Cymoxanil	57966-95-7
	Difenoconazole	119446-68-3
	Fluopyram	658066-35-4
	Fosetyl-aluminium	39148-24-8
	Mandipropamid	374726-62-2
	Propamocarb	24579-73-5
	Propiconazole	60207-90-1
	Prothioconazole	178928-70-6
	Spiroxamine	118134-30-8
	Tebuconazole	107534-96-3
Growth regulator	Ethephon	16672-87-0
	Mepiquat-chloride	24307-26-4
	Paclobutrazol	76738-62-0
	Prohexadione-calcium	127277-53-6
Herbicide	2,4-D-ethylhexyl	94-75-7
	Aminopyralid	150114-71-9
	Florasulam	145701-23-1
	Metamitron	41394-05-2
	Pendimethalin	40487-42-1
	Pyroxsulam	422556-08-9
Insecticide	Pyrethrin I+ II	8003-34-7

The collected product samples were stored at the Laboratory for Chemistry and Microbiology, Danish Technological Institute (DTI)⁶, in their original packaging until the chemical analyses were initiated. The product samples were stored at ambient temperature and protected from light during the entire storage period.

1.2 Tolerance for active substances

The objective of the Danish EPA was to examine the content of active substances in the products. The results of the chemical analyses were subsequently compared to the specification of the product and the declared content on the label supplied by the authorisation holder.

The Danish Statutory Order on Pesticides of 1647 dated 17 December 2017 and 815 of 18/06/2018 and Regulation 1107/2009 concerning Marketing of Plant Protection Products specify the general tolerance of deviation from the declared content of active substances.^{3,4} These tolerances are listed in Table 2.

Table 2 The tolerance of deviation from the declared content of active substances, 2018

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

1.3 Analyses 2018

The analyses of the products for active substances were performed by Danish Technological Institute, Laboratory for Chemistry and Microbiology. DTI is a self-owned and not-for-profit Institute.⁶

The Laboratory for Chemistry and Microbiology is accredited by DANAK (Danish Accreditation and Metrology Fund), registration no. 90, according DS/EN ISO/IEC 17025.⁷ The laboratory has a flexible scope for determination of active substances in pesticides. In addition, the methods for determination of pH and density of pesticides are accredited.

1.3.1 Analysing active substances

A total of 47 analyses for active substances were performed. The chemical analyses were as far as possible performed as at least five freshly prepared samples of each product. If the average result is outside the tolerance interval, then the analysis is repeated with a minimum of three new and freshly prepared samples.

The methods were validated with regard to linearity, specificity, accuracy and control tests at two levels. The chemical analyses for validation were performed as at least eight freshly prepared samples of the product. The analyses were distributed over at least two days for each product formulation. The mean value of the analyses and the SD (standard deviation) were calculated for each day and for all eight results. Recovery was determined by adding a known amount of the relevant active substance to a minimum of four samples of each product. The mean recovery and SD were calculated.

The expanded uncertainty U_E ($k=2$) of each product was calculated on the basis of the spread of the analysis results, the recovery and on the purity of the reference standard. The expanded analysis uncertainty is used to determine a 95% confidence interval for the analysis result. The uncertainty varies between 2.6-16% depending on the analytical method, the product formulation and the available reference standards.

1.3.2 Analysing impurities

Three products were selected for analysis of known impurities. The results were evaluated in accordance with the specified maximum concentration of the impurities in the products.

1.3.3 Physical-chemical testing

A total of 103 physical-chemical tests were performed. The density of all liquid products was measured, and the results were used to determine the content in g/L of the active substance in the product. Additionally, a number of pesticide products were selected for evaluation of appearance, and determination of pH, persistent foam, suspensibility and emulsion stability. The tests performed vary with the product formulation. The results were compared to the values specified in connection with the authorisation of the product.

1.3.4 Screening by GC-MS

Screening of one parallel product and the associated original was carried out by gas chromatography with mass spectrometric detection (GC-MS) to compare the chemical profiles of the two products.

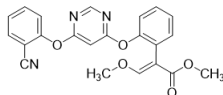
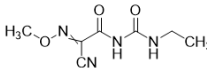
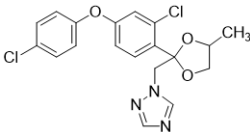
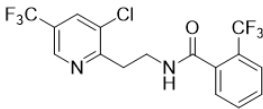
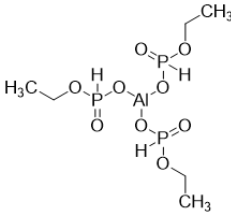
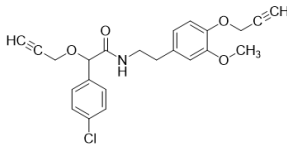
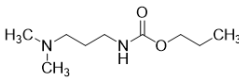
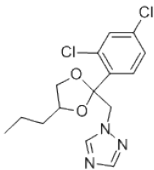
2. Analysis of active substances

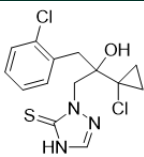
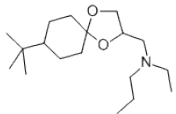
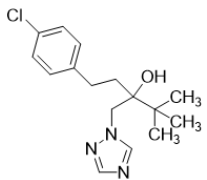
In this report, pesticides are defined as plant protection products (PPP). In the Danish Pesticide Control Campaign 2018, 29 pesticide products were selected: fungicides, growth regulators, herbicides and insecticides.

2.1 Fungicides

Fifteen fungicides containing azoxystrobin, cymoxanil, difenoconazole, fluopyram, fosetyl-aluminium, mandipropamid, propamocarb, propiconazole, prothioconazole, spiroxamine and tebuconazole as active substances were selected for the 2018 campaign. Table 3 states the previous years the active substances were selected for control.

Table 3. Fungicides included in the 2018 control campaign

Name	CAS no.	Year selected for control	Molecular structure ⁸
Azoxystrobin	131860-33-8	2017, 2006, 1999	
Cymoxanil	57966-95-7	-	
Difenoconazole	119446-68-3	2014	
Fluopyram	658066-35-4	-	
Fosetyl-Al	39148-24-8	2013	
Mandipropamid	374726-62-2	2017, 2009	
Propamocarb	24579-73-5	2011, 2007, 2001	
Propiconazole	60207-90-1	2010, 2006	

Name	CAS no.	Year selected for control	Molecular structure ⁸
Prothioconazole	178928-70-6	2010, 2008	
Spiroxamine	118134-30-8	-	
Tebuconazole	107534-96-3	2010, 2008, 2002, 1998	

-: Means not previously selected

2.1.1 Analysis

Azoxystrobin and spiroxamine were analysed by gas chromatography with flame ionization detector (GC-FID). Azoxystrobin was analysed according to DTI's method OA-827. The method has been adapted from CIPAC method 571 azoxystrobin.⁹ Spiroxamine was analysed according to DTI's method OA-829.

Cymoxanil, difenoconazole, fluopyram, mandipropamid, propamocarb, propiconazole, prothioconazole and tebuconazole were analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD).

Cymoxanil was analysed according to DTI's method OA-886. The method has been adapted from CIPAC method 419 cymoxanil.⁹ Difenoconazole, fluopyram, mandipropamid, propiconazole, prothioconazole and tebuconazole were analysed according to DTI's method OA-880, OA-887 or OA-889. Propamocarb was analysed according to DTI's method OA-807. The method has been adapted from CIPAC method 399 propamocarb hydrochloride.⁹

Fosetyl-Al was analysed by reversed phase liquid chromatography combined with mass spectrometry (LC-MS) according to DTI's method OA-1202.

The methods for azoxystrobin, cymoxanil, difenoconazole, mandipropamid, propamocarb, propiconazole, prothioconazole and tebuconazole are accredited.

2.1.2 Results

The results from the performed measurements are listed in the following tables. % RSD is the percentage relative reproducibility of the determinations of the product.

Table 4. Analysis results of fungicides, g/kg

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	Comply/ Non-comply
798071-1	Cymoxanil	600	575-625	593	1.1	Comply
798071-10	Cymoxanil	450	428-473	442	1.2	Comply

Table 5. Analysis results of fungicides, g/L

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	Comply/ Non-comply
798071-2	Prothioconazol	125	118-133	119	1.1	Comply
	Fluopyram	125	118-133	123	1.5	Comply
798071-3	Propiconazol	250	235-265	259	0.9	Comply
798071-4	Prothioconazol	125	118-133	129	0.6	Comply
	Tebuconazol	125	118-133	126	1.4	Comply
798071-5	Prothioconazol	250	235-265	254	1.1	Comply
798071-6	Prothioconazol	160	150-170	164	0.4	Comply
	Tebuconazol	80	72-88	82	1.3	Comply
798071-7	Propamocarb	334	317-350	321	0.7	Comply
	Cymoxanil	50	45-55	52	2.2	Comply
798071-11	Propiconazol	150	141-159	151	1.9	Comply
	Difenoconazole	150	141-159	154	2.2	Comply
798071-12	Prothioconazol	80	72-88	82	0.5	Comply
	Tebuconazol	160	150-170	161	0.8	Comply
798071-14	Tebuconazol	200	188-212	202	0.9	Comply
798071-17	Prothioconazol	160	150-170	164	0.5	Comply
	Spiroxamin	300	285-315	300	1.6	Comply
798071-19	Azoxystrobin	200	188-212	199	0.8	Comply
	Difenoconazole	125	118-133	128	1.9	Comply
798071-20	Propamocarb	530	505-555	527	0.6	Comply
	Fosetyl-Al	310	295-326	316	1.5	Comply
798071-21	Propamocarb	530	505-555	531	0.9	Comply
	Fosetyl-Al	310	295-326	324	2.4	Comply
798071-22	Propamocarb	605	580-630	606	0.4	Comply
798071-26	Mandipropamid	250	235-265	259	1.9	Comply
	Difenoconazol	250	235-265	255	1.5	Comply
798071-27	Azoxystrobin	125	118-133	121	1.4	Comply
	Difenoconazol	125	118-133	126	1.4	Comply
798071-28	Difenoconazol	250	235-265	263	0.9	Comply

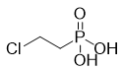
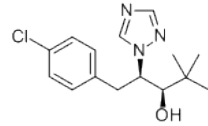
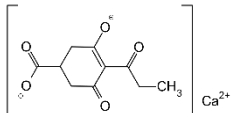
2.1.3 Conclusion

The measured contents of azoxystrobin, cymoxanil, difenoconazole, fluopyram, fosetyl-Al, mandipropamid, propamocarb, propiconazole, prothioconazole, spiroxamine and tebuconazole comply with the declared content and with applicable Danish law.

2.2 Growth regulators

Three growth regulators containing mepiquat-chloride, prohexadione-calcium, paclobutrazol and ethephon as active substances were selected for the 2018 control campaign. Table 6 states the previous years the active substances were selected for control.

Table 6. Growth regulators included in the 2018 control campaign

Name	CAS no.	Year selected for control	Molecular structure ⁸
Ethephon	16672-87-0	2017, 2006, 1996	
Mepiquat-chloride	24307-26-4	2017, 2006	
Paclobutrazol	76738-62-0	2008	
Prohexadione-calcium	127277-53-6	2017, 2013	

2.2.1 Analysis

Ethephon was determined by acid-base titration according to DTI's method UA-244.

Mepiquat-chloride was analysed by hydrophilic interaction chromatography combined with mass spectrometry (LC-MS) according to DTI's method OA-1200.

Paclobutrazol and prohexadione-calcium were analysed by reversed phase high-performance liquid chromatography combined with diode array detection, (HPLC-DAD). Paclobutrazol was analysed according to DTI's method OA-880. Prohexadion-calcium was analysed according to DTI's method OA-882.

The methods for analysis of prohexadione-calcium and paclobutrazol are accredited.

2.2.2 Results

The results from the performed measurements are listed in the following table. % RSD is the percentage relative reproducibility of the determinations of the product.

Table 7. Analysis results of growth regulators, g/L

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	Comply/ Non-comply
798071-15	Ethephon	480	456-504	491	1.1	Comply
798071-16	Mepiquat-Cl	300	285-315	315	4.3	Comply
	Prohexadione-Ca	50	45-55	48	0.0	Comply
798071-29	Paclobutrazol	4.0	3.4-4.6	4.1	0.5	Comply

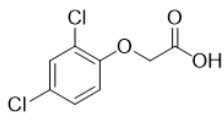
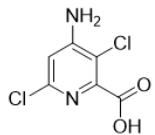
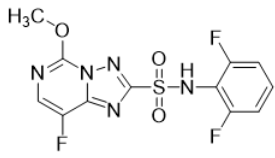
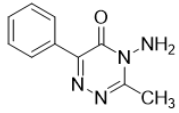
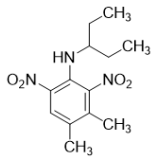
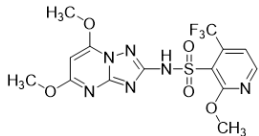
2.2.3 Conclusion

The measured content of ethephon, mepiquat-chloride, prohexadione-calcium and paclobutrazol in the 3 products complies with the declared content and with applicable Danish law.

2.3 Herbicides

Six herbicides containing 2,4-D-ethylhexyl, aminopyralid, florasulam, metamiltron, pendimethalin and pyroxsulam as active substances were selected for the 2018 control campaign. Table 8 states the previous years the active substances were selected for control.

Table 8. Herbicides included in the 2018 control campaign

Name	CAS no.	Year selected for control	Molecular structure ⁸
2,4-D-ethylhexyl	94-75-7	2014	
Aminopyralid	150114-71-9	-	
Florasulam	145701-23-1	2016, 2005	
Metamiltron	41394-05-2	2012, 2006, 1999	
Pendimethalin	40487-42-1	2015, 2013, 2001	
Pyroxsulam	422556-08-9	-	

-: Means not previously selected

2.3.1 Analysis

Products containing 2,4-D-ethylhexyl, aminopyralid, florasulam metamiltron, pendimethalin and pyroxsulam were analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD).

2,4-D-ethylhexyl were analysed according to DTI's method R38247-6, aminopyralid was analysed according to DTI's method OA-893, florasulam and pyroxsulam were analysed according to DTI's method OA-890, metamiltron was analysed according to DTI's method OA-891 and pendimethalin was analysed according to DTI's method OA-888.

The methods for determination of florasulam, metamiltron and pendimethalin are accredited.

2.3.2 Results

The results from the performed measurements are listed in the following tables. % RSD is the percentage relative reproducibility of the determinations of the product.

Table 9. Analysis results of herbicides, g/kg

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	Comply/ Non-comply
798071-18	Metamitron	700	675-725	698	0.8	Comply
	Florasulam	25	19-31	25	1.6	Comply
798071-23	Aminopyralid	50	45-55	45	0.9	Comply
	Pyroxsulam	50	45-55	50	2.1	Comply

Table 10. Analysis results of herbicides, g/L

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	Comply/ Non-comply
798071-8	Pendimethalin	455	432-478	462	0.9	Comply
	2,4-D-ethylhexyl	271.5	258-285	277	3.3	Comply
798071-9	Florasulam	5.0	4.3-5.8	4.9	0.5	Comply
	Aminopyralid	10	8.50-11.5	9.76	2.4	Comply
	2,4-D-ethylhexyl	453.5	430-475	432	1.2	Comply
798071-13	Florasulam	6.25	5.3-7.2	6.9	1.2	Comply
798071-25	Metamitron	700	675-725	702	1.6	Comply

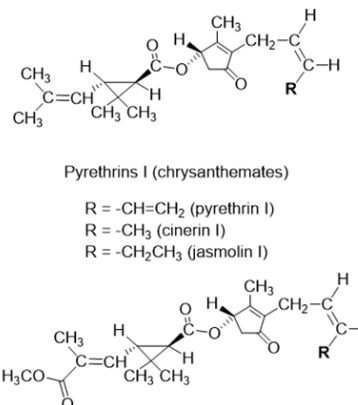
2.3.3 Conclusion

The measured content of 2,4-D-ethylhexyl, aminopyralid, florasulam metamitron, pendimethalin and pyroxsulam in the 6 products complies with the declared content and with applicable Danish law.

2.4 Insecticides

One insecticide containing pyrethrin I+II as active substances was selected for the 2018 control campaign. Table 11 states the previous years the active substances were selected for control

Table 11. Insecticides included in the 2018 control campaign

Name	CAS no.	Year selected for control	Molecular structure ⁸
Pyrethrin I+II	8003-34-7	2017	 Pyrethrins I (chrysanthemates) R = -CH=CH₂ (pyrethrin I) R = -CH₃ (cinerin I) R = -CH₂CH₃ (jasmolin I) Pyrethrins II (pyrethrates) R = -CH=CH₂ (pyrethrin II) R = -CH₃ (cinerin II) R = -CH₂CH₃ (jasmolin II)

2.4.1 Analysis

Pyrethrin I+II was analysed by reversed phase HPLC-DAD according to DTI's method OA-879.

2.4.2 Results

The results from the performed measurements are listed in the following table. % RSD is the percentage relative reproducibility of the determinations of the product.

Table 12. Analysis results of insecticides, g/L

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	Comply/ Non-comply
798071-30	Pyrethrin I+II	0.0459	0.0390-0.0528	0.0463	4.9	Comply

2.4.3 Conclusion

The measured content of pyrethrin I+II complies with the declared content and with applicable Danish law.

3. Analysis of impurities

3.1 Dioxins and furans

Two products containing 2,4-D-ethylhexyl as active substance were analysed for the content of polychlorinated dibenzodioxines (PCDD) and polychlorinated dibenzofurans (PCDF).

3.1.1 Analysis

The analysis was performed by gas chromatography coupled with a high-resolution mass spectrometer (GC/HRMS).

3.1.2 Results

The results from the performed measurements are listed in the following Table 13. The results represent a sum of 7 PCDD and 10 PCDF.

Table 13. Analysis results for polychlorinated dibenzodioxines (PCDD) and polychlorinated dibenzofurans (PCDF), ng/kg

DTI sample no.	Active substance	Max. content ΣPCDD+PCDF ng/kg	Analysis result ΣPCDD+PCDF ng/kg
798071-9	2,4-D-ethylhexyl	1899	166
798071-13	2,4-D-ethylhexyl	3207	299

3.1.3 Conclusion

For both products, the concentration of dioxins and furans were below the allowed maximum concentration.

3.2 N-Nitrosopendimethalin

One product containing pendimethalin as active substance was analysed for the content of the impurity N-nitrosopendimethalin.

3.2.1 Analysis

The analysis was performed by reversed phase liquid chromatography combined with mass spectrometry (LC-MS) according to the manufacturer's method.

3.2.2 Results

The results from the performed measurements are listed in the following Table 14.

Table 14. Analysis results for N-nitrosopendimethalin, g/kg

DTI sample no.	Active substance	Max. content g/kg	Analysis result g/kg
798071-8	Pendimethalin	1.0	0.004

3.2.3 Conclusion

The product is currently in the process of being re-approved. The measured concentration was below the currently allowed maximum concentration.

4. Physical-chemical testing

The density of all liquid products was measured. Additionally, a number of pesticide products were submitted to a test programme depending on the formulation type. The tests include determination of density, pH, persistent foam, emulsion stability and suspensibility. The results were subsequently compared to the values specified in connection with the authorisation of the product. In total, 103 physical-chemical tests were performed.

As the physical-chemical parameters are subject to confidentiality, only the general conclusions have been included in this report.

4.1 Physical-chemical testing of selected pesticides

Details concerning performed physical-chemical test are provided below.

4.1.1 Appearance

The colour and physical state of the formulation was described after homogenization of the product.

4.1.2 Density

The density of the formulations was determined according to DTI's analysis method UA-312. The method is based on CIPAC MT 3.⁹ The density of the product is determined as the average of a triple determination carried out by measuring with a Densito 30 PX densimeter.

4.1.3 pH

The pH for undiluted samples and for 1% solutions of the formulation was determined by potentiometric measuring according to DTI's accredited analysis method UA-310. The method is based on CIPAC MT 75.3.⁹ The pH was determined for products with specified pH values and the analysis was performed in triplicate.

4.1.4 Persistent foaming

The test for persistent foaming was performed with DTI's method PCA 100 according to the CIPAC method MT 47.2.⁹ The concentration tested was the maximum concentration prescribed for the product. Standard CIPAC water D prepared according to CIPAC MT 18.1.4 was used unless otherwise specified for the product.⁹ The amount of foam was reported at the times prescribed for the product. The test was performed in duplicate for each pesticide product.

4.1.5 Emulsion stability

The test for emulsion stability was performed according to DTI's method PCA 106 corresponding to the CIPAC method MT 36.3.⁹ Highest and lowest in-use concentrations prescribed for the product were tested. Standard CIPAC water D, prepared according to CIPAC MT 18.1.4, was used unless otherwise specified for the product.⁹ The test was performed in duplicate for each pesticide product.

4.1.6 Suspensibility

The test for suspensibility was performed according to DTI's method PCA 102 corresponding to the CIPAC method MT 161.⁹ Highest and lowest in-use concentrations prescribed for the product were tested. Standard CIPAC water D, prepared according to CIPAC MT 18.1.4, was used unless otherwise specified for the product.⁹

4.1.7 Results

The tests performed on selected pesticides are summarized in Table 15.

Table 15. Physical-chemical tests performed on selected pesticide products. An 'X' signifies that the test was performed

DTI sample no.	Appearance	Density	pH	Persistent foam	Emulsion stability	Suspensibility
798071-1	X		X			
798071-2	X	X	X	X		
798071-3	X	X	X	X	X	
798071-4	X	X	X	X		
798071-5		X				
798071-6	X	X	X	X	X	
798071-7		X				
798071-8	X	X	X	X		X
798071-9	X	X	X	X		
798071-10	X		X	X		
798071-11	X	X	X	X	X	
798071-12	X	X	X	X	X	
798071-13		X				
798071-14	X	X	X	X	X	
798071-15		X				
798071-16		X				
798071-17	X	X	X	X	X	
798071-18	X		X	X		X
798071-19	X	X	X	X		
798071-20	X	X	X	X		
798071-21	X	X	X	X		
798071-22	X	X	X	X		
798071-23	X		X	X		
798071-25	X	X	X	X		X
798071-26	X	X	X	X		
798071-27	X	X	X	X		
798071-28	X	X	X	X	X	
798071-29	X	X	X	X		
798071-30		X				
Total no. of tests	23	25	23	22	7	3

4.1.8 Conclusion

In most cases, the test results are comparable with specified values of the product or are within the legal requirements and tolerances. For five products, the measured pH was not comparable with the specified values taking into account the expanded uncertainty of the method. In addition, the test results for determination of persistent foam for one product were comparable with test results stated within the specification of the product. However, these results do not comply with the legal requirements.

5. Parallel products

One product under a parallel trade permit were compared by gas chromatography with mass spectrometric detection (GC-MS) to investigate if it contains the same solvents and additives as the original product. Furthermore, active substance concentration and physical-chemical properties were compared

5.1 Regulation in Denmark

The requirements for parallel trade permits are described in detail in Article 52 of Regulation No. 1107/2009.²

5.1.1 Parallel trade permits

A parallel trade permit is an authorisation for the import of a plant protection product that is identical with a product already authorised in Denmark. A parallel trade permit is valid only for Denmark. It is not valid in the rest of the North zone. For each country, an application must be made to obtain the permit.

A plant protection product under a parallel trade permit may only be placed on the market and used in accordance with the authorisation of the original product. The parallel trade permit will expire at the same time as the authorisation of the original product. If the authorisation of the original product is withdrawn for reasons other than safety, the parallel trade permit will be similarly affected.

5.1.2 Identical products

A plant protection product is identical with a product already authorised in Denmark only if:

- a) It is produced by the same company or an associated company or under licence according to the same method of manufacture as that of the authorised product.
- b) It has the same specification, that is, contains the same active substance, safeners and synergists. The plant protection product is of the same formulation type; and the contents of the co-formulants and the packaging are the same or equivalent.

The packaging and co-formulants must not have more negative effects on health or the environment than the original product.

5.2 Analysed products

The analysed products are listed in Table 16.

Table 16. Parallel and original product analysed in the 2018 control campaign

DTI sample no.	Permit	Active substances
798071-20	Parallel	Propamocarb & fosetyl-Al
798071-21	Original	

5.3 GC-MS analysis

Subsamples of both the parallel product and the original product were dissolved or extracted with methanol, acetone and dichloromethane, respectively. The extracts were analysed by gas chromatography with mass spectrometric detection (GC-MS) in scan mode and the resulting chromatograms were compared.

5.4 Results and conclusion

The results of the comparison of the parallel product and the original product are listed in Table 17. There was no difference between the parallel product and the original products based on the applied parameters.

Table 17. Comparison of the parallel product with DTI sample no. 798071-20 and the original product with DTI sample no. 798071-21

Parameter	Parallel product vs. original product
Propamocarb, concentration	Equivalent
Fosetyl-Al, concentration	Equivalent
Appearance	Equivalent
Density	Equivalent
GC-MS, screening, methanol extraction	Equivalent
GC-MS, screening, acetone extraction	Equivalent
GC-MS, screening, dichloromethane extraction	Equivalent

References

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2. Danish EPA, 2018, approved Pesticides 2018 <http://mst.dk/kemi/database-for-bekaempelsesmidler/bmd/> (Danish)
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4. REGULATION (EC) No. 1107/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC
5. The regulation of the European Commission (EU) No. 546/2011 of 10 June 2011 concerning the implementation of the regulation of the European Parliament and the European Council (EF) No. 1107/2009 concerning uniform principles for evaluation and approval of crop protection agents
6. Danish Technological Institute, Kongsvang Allé 29, DK-8000 Aarhus, Denmark, <http://www.dti.dk/>
7. The Danish Accreditation and Metrology Fund – DANAK, <http://english.danak.dk/>
8. The e-Pesticide Manual, seventeenth Edition, online version, 2016. British Crop Protection Council, United Kingdom
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Control of Pesticides 2018

English

This report describes the analytical chemical control of pesticides on the Danish market, which was carried out in 2018 by the Chemical Inspection Service of the Danish Environmental Protection Agency. The control is part of the Danish National Plan of Pesticides 2017-2020. Samples of selected types of pesticides on the Danish market were collected and analysed to verify whether or not the content of active substances in the pesticides complies with the product specifications, the labelled content and the information given to the Danish Environmental Protection Agency. The Danish National Plan of Pesticides 2017-2020 is also engaged to act against illegal and counterfeit pesticides. Therefore, the objective of the analyses was also to investigate the existence of illegal or counterfeit pesticides.

A total of 29 different pesticides products were analysed.

The measured amount of active substances was consistent with the declared amount in all products, the results being within the tolerant limit.

Five products that were tested for physical and chemical parameters did not meet the product requirements for pH-value. A single product did not meet the applicable limit values for sustained foam formation.

Danish

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked, der er udført i 2018 af den danske Miljøstyrelses Kemikalieinspektion, er beskrevet i denne rapport. Der er udvalgt og indsamlet 29 pesticidprodukter. Produkterne blev analyseret for at verificere, om indholdet af de respektive aktivstoffer var i overensstemmelse med produktspecifikationen og det deklarerede indhold. Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold i alle produkter, idet resultaterne er indenfor tolerancen. Fem produkter, som blev testet for fysisk-kemiske parameter, var ikke i overensstemmelse med produkternes specifikationer for pH. Et enkelt produkt overholdt ikke gældende grænseværdier for vedvarende skumdannelse.



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