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Control of Pesticides 2022

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Sources must be acknowledged

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Preface

This report describes the control of pesticides on the Danish market that was carried out in 2022 by the Danish Chemical Inspection Service of the Danish Environmental Protection Agency. The Chemical control is part of the Danish National Strategy of Pesticides 2022-2026. Samples of pesticide products on the Danish market were collected and analysed to verify whether the content of active substances in the products complies with the product specifications supplied to the Danish Environmental Protection Agency from manufacturers.

According to the Danish National Strategy of Pesticides 2022 - 2026 also participates in activities against illegal and counterfeit pesticides. Therefore, the objective of the analyses was also to investigate the existence of illegal or counterfeit pesticides.

Abbreviations

a.s.: Active substance

CIPAC: Collaborative International Pesticides Analytical Council

DANAK: Danish Accreditation and Metrology Fund

DTI: Danish Technological Institute

FTIR: Fourier-transform infrared spectroscopy

GC-FID: Gas chromatography - flame ionization detection

GC-MS: Gas chromatography - mass spectrometry

HPLC-DAD: High-performance liquid chromatography - diode array detection

ICP-OES: Inductively coupled plasma - optical emission spectrometry

LC-MS: Liquid chromatography-mass spectrometry

MAM: Multi-active method

Plant protection products: Pesticide products

RSD: Relative standard deviation

STD: Standard deviation

U: Expanded uncertainty

Resume

Denne rapport beskriver den analytisk kemiske kontrol af pesticidprodukter (plantebeskyttelsesmidler) på det danske marked, der er udført af Miljøstyrelsens Kemikalieinspektion i 2022 (Ref. 1, 2).

Den planlagte kontrolkampagne dækkede over 25 aktivstoffer i forskellige kombinationer i 31 plantebeskyttelsesprodukter (pesticider). Produkterne blev analyseret for at verificere, om indholdet af de respektive aktivstoffer var 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. 1278 af 06/06/2021 (gældende bekendtgørelse nr. 1569 af 19/12/2022) og i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler (Ref. 3, 4).

Følgende typer af produkter blev analyseret i den planlagte kontrolkampagne (se tabel på næste side):

- 9 fungicider indeholdende aktivstofferne boscalid, cyazofamid, cymoxanil, difenoconazol, mandipropamid, mefentrifluconazol, pyraclostrobin og tebuconazol.
- 2 vækstreguleringsmidler indeholdende aktivstofferne ethephon, maleinhydrazid og mepiquat-chlorid.
- 14 herbicider indeholdende aktivstofferne clopyralid, diflufenican, fenoxaprop-p-ethyl, foramsulfuron, glyphosate, iodosulfuron-methyl-sodium, mesosulfuron-methyl, nonanoic acid, picloram, prosulfocarb og tribenuron-methyl.
- 4 insekticider indeholdende aktivstofferne flupyradifuron, lambda-cyhalothrin og tau-fluvalinat.

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

Der blev udført fysisk-kemiske test på alle 31 pesticidprodukter:

- Udseende blev vurderet for 31 produkter.
- Densitet blev målt på 24 produkter.
- Vedvarende skumdannelse blev bestemt for 29 produkter.
- Emulsionsstabilitet blev vurderet for 8 produkter.
- Suspensibilitet blev målt for 10 produkter.
- Opløsningsstabilitet blev målt på 1 produkt.

Tre af produkterne, som blev testet for fysisk-kemiske parametre, var ikke i overensstemmelse med produkternes specifikationer hvad angår vedvarende skumdannelse.

Oversigt over analyserede produkter og aktivstoffer i den planlagte kontrolkampagne:

Aktivstof	Antal analyserede produkter	Antal indenfor tolerance
Boscalid	1	1
Clopyralid	1	1
Cyazofamid	1	1
Cymoxanil	1	1
Difenoconazol	1	1
Diflufenican	1	1
Ethephon	1	1
Fenoxaprop-P-Ethyl	1	1
Flupyradifuron	1	1
Foramsulfuron	1	1
Glyphosat	8	8
Iodosulfuron-methyl-natrium	2	2
Lambda-cyhalothrin	2	2
Maleinhydrazid	1	1
Mandipropamid	2	2
Mefentrifluconazol	3	3
Mepiquat-chlorid	1	1
Mesosulfuron-methyl	1	1
Pelargonsyre	1	1
Picloram	1	1
Prosulfocarb	3	3
Pyraclostrobin	3	3
Tau-fluvalinat	1	1
Tebuconazol	1	1
Tribenuron-methyl	1	1
Total	41	41

Abstract

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), The Danish Chemical Inspection Service, in 2022 (Ref. 1, 2).

The planned control campaign covered 25 active substances in different combinations in 31 plant protection products (PPP, pesticides). The products were analysed to verify whether 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. 1278 of 06/06/2021 (applicable Danish Statutory Order 1569 of 19/12/2022) as well as in Regulation 1107/2009 concerning Marketing of Plant Protection Products (Ref. 3, 4).

The following products were analysed in the planned control campaign (see table on next page):

- 9 fungicides containing the active substances boscalid, cyazofamid, cymoxanil, difenoconazole, mandipropamid, mefentrifluconazole, pyraclostrobin, and tebuconazole.
- 2 growth regulators containing the active substances ethephon, maleic hydrazide, and mepiquat chloride.
- 14 herbicides containing the active substances clopyralid, diflufenican, fenoxaprop-p-ethyl, foramsulfuron, glyphosate, iodosulfuron-methyl-sodium, mesosulfuron-methyl, nonanoic acid, picloram, prosulfocarb, and tribenuron-methyl.
- 4 insecticides containing the active substances flupyradifurone, lambda-cyhalothrin, and tau-fluvalinate.

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.

Physico-chemical tests were performed on all 31 products:

- Appearance was assessed for 31 products.
- Density was measured on 24 products.
- Persistent foaming was performed on 29 products.
- Emulsion stability was performed on 8 products.
- Suspensibility was performed on 10 products.
- Solution stability was performed on 1 product.

Three products did not comply with the specified values of the products regarding persistent foaming.

Overview of analysed products and active substances in the planned control campaign:

Active substance	No. of analysed products	No. within tolerance
Boscalid	1	1
Clopyralid	1	1
Cyazofamid	1	1
Cymoxanil	1	1
Difenoconazole	1	1
Diflufenican	1	1
Ethephon	1	1
Fenoxaprop-P-Ethyl	1	1
Flupyradifurone	1	1
Foramsulfuron	1	1
Glyphosate	8	8
Iodosulfuron-methyl-sodium	2	2
Lambda-cyhalothrin	2	2
Maleic hydrazide	1	1
Mandipropamid	2	2
Mefentrifluconazole	3	3
Mepiquat chloride	1	1
Mesosulfuron-methyl	1	1
Nonanoic acid	1	1
Picloram	1	1
Prosulfocarb	3	3
Pyraclostrobin	3	3
Tau-fluvalinate	1	1
Tebuconazole	1	1
Tribenuron-methyl	1	1
Total	41	41

1. Control campaign 2022

1.1 Collecting products

The planned control campaign conducted in 2022 covered 25 active substances (a.s.) in different combinations in a total of 31 plant protection products (PPP, pesticides). The a.s. were selected according to their sales figures in the previous years, availability at retailers, and whether they had been part of previous campaigns. All products were collected by The Danish Chemical Inspection Service of the Danish Environmental Protection Agency during the period from April to June 2022. The products were collected from wholesale dealers/importers or at retail outlets. An overview of the selected active substances is given in TABLE 1.

TABLE 1. Overview of selected active substances, part of 2022 control campaign.

Area of application	Active substance	CAS no.
Fungicide	Boscalid	188425-85-6
	Cyazofamid	120116-88-3
	Cymoxanil	57966-95-7
	Difenoconazole	119446-68-3
	Mandipropamid	374726-62-2
	Mefentrifluconazole	1417782-03-6
	Pyraclostrobin	175013-18-0
Growth regulator	Tebuconazole	107534-96-3
	Ethephon	16672-87-0
	Maleic hydrazide	123-33-1
Herbicide	Mepiquat chloride	24307-26-4
	Clopyralid	1702-17-6
	Diflufenican	83164-33-4
	Fenoxaprop-P-Ethyl	71283-80-2
	Foramsulfuron	173159-57-4
	Glyphosate	1071-83-6
	Iodosulfuron-methyl-sodium	144550-36-7
	Mesosulfuron-methyl	208465-21-8
	Nonanoic acid	112-05-0
	Picloram	1918-02-01
	Prosulfocarb	52888-80-9
Insecticide	Tribenuron-methyl	101200-48-0
	Flupyradifurone	951659-40-8
	Lambda-cyhalothrin	91465-08-6
	Tau-fluvalinate	102851-06-9

The collected products were stored at the Laboratory for Chemistry and Microbiology, Danish Technological Institute (DTI) (Ref. 5), in their original packaging until the chemical analyses were initiated. The products were stored at ambient temperature and protected from light during the entire storage period.

1.2 Tolerance of active substance

The objective of the Danish EPA was to determine the content of a.s. in the products. The results of the quantitative analysis were subsequently compared to the specification of the product and the declared content on the label supplied by the authorization holder.

The Danish Statutory Order on Pesticides No. 1278 of 06/06/2021 (applicable Danish Statutory Order 1569 of 19/12/2022) and Regulation 1107/2009 concerning Marketing of Plant Protection Products specify the general tolerance of deviation from the declared content of active substances (Ref. 3, 4). These tolerances are listed in TABLE 2.

TABLE 2. The tolerance of deviation from the declared content of active substance.

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 Analytical program and executing party

The analyses of the products for a.s. were performed by Danish Technological Institute, Laboratory for Chemistry and Microbiology. DTI is a self-owned and not-for-profit Institute (Ref. 5).

The Laboratory for Chemistry and Microbiology is accredited by DANAK (Danish Accreditation and Metrology Fund), registration no. 90, according to DS/EN ISO/IEC 17025:2017 (Ref. 6). The laboratory has a flexible accreditation for determination of a.s. in pesticide products. The methods for determination of density and persistent foaming are accredited.

1.3.1 Quantification of active substances and methods

A total of 41 analyses for active substances were performed. Methods were adapted from existing reference methods, e.g., CIPAC.

The chemical quantification was performed on at least five freshly prepared samples of each product. If the average result was outside the tolerance interval, then the analysis was repeated with a minimum of five new and freshly prepared samples.

The methods were validated based on linearity, specificity, accuracy, and control tests at two levels. The validation of the methods was performed on at least eight freshly prepared samples of the product. The analyses were distributed over at least two days for each product. The mean value of the analyses and the standard deviation (STD) were calculated for each day and for all eight results. The recovery percentage was determined by adding a known amount of the relevant a.s. to a minimum of five samples of each product. The mean recovery and STD were calculated.

The expanded uncertainty ($k = 2$) for each method was calculated based on the spread of the analysis results, the recovery, and on the purity of the reference standard. The expanded uncertainty is used to determine a 95% confidence interval of the result. The expanded uncertainty varies between 1-12% depending on the analytical method, the product formulation, and the purity of available reference material.

1.3.2 Physico-chemical testing

A total of 104 physico-chemical tests were performed on the products. The tests performed varied with the product formulation. The analytical program was carried out in accordance with the reference document presenting best practices for formulation analysis on pesticide products. The results were compared to the values specified in the registration report from the authorization holder of the product.

The density of all liquid products (24 products) was measured, and the results were used to determine the content in g/L of the a.s. in the product. Additionally, the pesticide products were submitted for evaluation of appearance (31 products), determination of persistent foam (29 products), suspensibility (10 products), emulsion stability (9 products), and solution stability (1 product).

2. Analysis of active substances

In the planned Danish pesticide control campaign conducted in 2022, 31 pesticide products were selected for an analytical program. The pesticide types covered in the 2022 campaign were: Fungicides, growth regulators, herbicides, and insecticides.

2.1 Fungicides

Nine fungicide products containing the a.s. boscalid, cyazofamid, cymoxanil, difenoconazole, mandipropamid, mefentrifluconazole, pyraclostrobin or tebuconazole were part of the 2022 campaign. TABLE 5 gives an overview of the analytical methods and when the a.s. was part of a prior control campaign.

2.1.1 Results and conclusion

The results of the quantitative determination of a.s. in the fungicides are listed in TABLE 3 and TABLE 4. RSD% is the relative reproducibility percentage for the analysis of the product.

The concentration of a.s. complied with the declared content and with applicable Danish law in all nine products.

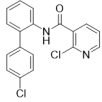
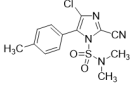
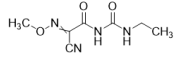
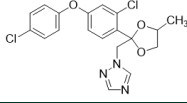
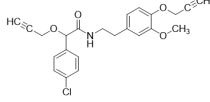
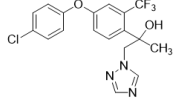
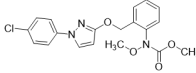
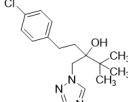
TABLE 3. Analysis results (g/L) for fungicide products.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD%	Comply/ Non-comply
133173-2	Mefentrifluconazole	100	90-110	100	1.1	Comply
	Pyraclostrobin	100	90-110	100	0.8	Comply
133173-3	Boscalid	500	475-525	512	0.9	Comply
133173-18	Mefentrifluconazole	100	90-110	102	0.8	Comply
	Pyraclostrobin	100	90-110	103	0.7	Comply
133173-19	Mefentrifluconazole	100	90-110	98	0.6	Comply
	Pyraclostrobin	100	90-110	100	0.8	Comply
133173-20	Mandipropamid	250	235-265	262	1.6	Comply
	Difenoconazole	250	235-265	260	1.5	Comply
133173-21	Mandipropamid	250	235-265	253	0.4	Comply
133173-22	Tebuconazole	200	188-212	206	0.4	Comply
133173-24	Cyazofamid	160	150-170	158	1.6	Comply

TABLE 4. Analysis results (g/kg) for fungicide products.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
133173-28	Cymoxanil	450	428-473	443	0.4	Comply

TABLE 5. Active substances categorized as fungicides in the 2022 control campaign.

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Boscalid	188425-85-6	2021, 2020, 2015, 2007	HPLC-DAD	OA-902	Yes	-	
Cyazofamid	120116-88-3	2021, 2020, 2008	HPLC-UV	OA-880	Yes	CIPAC MAM (Ref. 9)	
Cymoxanil	57966-95-7	2018	HPLC-DAD	OA-886	Yes	CIPAC 419 (Ref. 8)	
Difenoconazole	119446-68-3	2018, 2014	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 9)	
Mandipropamid	374726-62-2	2018, 2017, 2009	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 9)	
Mefentrifluconazole	1417782-03-6	-	HPLC-DAD	OA-887	Yes	-	
Pyraclostrobin	175013-18-0	2021, 2020, 2019, 2015, 2012, 2005	HPLC-DAD	OA-887	Yes	-	
Tebuconazole	107534-96-3	2021, 2018	HPLC-DAD	OA-887	Yes	-	

2.2 Growth regulators

Two growth regulator products containing the a.s. ethephon, maleic hydrazide, and mepiquat chloride were part of the 2022 campaign. TABLE 8 gives an overview of the analytical methods and when the a.s. was part of a prior control campaign.

2.2.1 Results and conclusion

The results of the quantitative determination of a.s. in the growth regulators are listed in TABLE 6 and TABLE 7. RSD% is the relative reproducibility percentage for the analysis of the product.

The concentration of a.s. complies with the declared content and with applicable Danish law in all nine products.



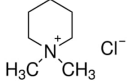
TABLE 6. Analysis results (g/L) for growth regulator products.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD%	Comply/ Non-comply
133173-25	Mepiquat chloride	305	290-320	310	0.5	Comply
	Ethephon	155	146-164	158	0.1	Comply

TABLE 7. Analysis results (g/kg) for growth regulator products.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
133173-1	Maleic hydrazide	600	575-625	598	2.1	Comply

TABLE 8. Active substances categorized as growth regulator in the 2022 control campaign.

Name	CAS no.	Year selected for control	Analytical method			Molecular structure (Ref. 7)	
			Principle	DTI method	Accreditation		Adapted from reference method
Ethephon	16672-87-0	2018, 2017, 2006, 1996	Titration	UA-244	No	-	
Maleic hydrazide	123-33-1	2014	HPLC-UV	OA-854	Yes	-	
Mepiquat chloride	24307-26-4	2021, 2018, 2017, 2006	LC-MS	OA-1200	Yes	-	

2.3 Herbicides

16 herbicides containing the a.s. clopyralid, diflufenican, fenoxaprop-p-ethyl, foramsulfuron, glyphosate, iodosulfuron-methyl-sodium, mesosulfuron-methyl, nonanoic acid, picloram, prosulfocarb or tribenuron-methyl were selected for the 2022 campaign. TABLE 11 states which previous years the a.s. were selected for control and outlines the analytical method applied for each a.s.

2.3.1 Results and conclusion

The results of quantitative determinations of a.s. in the herbicides are listed in TABLE 9 and TABLE 10. RSD% is the relative reproducibility percentage for the analysis of the product.

The concentration of a.s. complies with the declared content and with applicable Danish law in all 16 products.

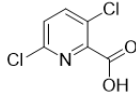
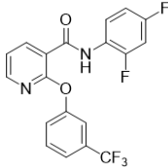
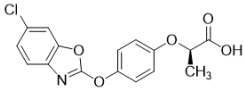
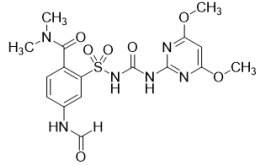
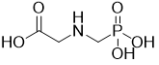
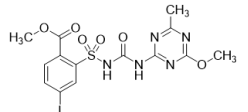
TABLE 9. Analysis results (g/L) for herbicide products.

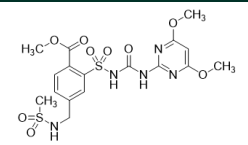
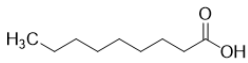
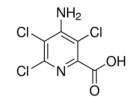
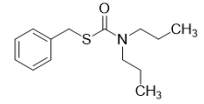
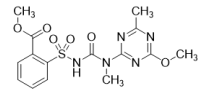
DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
133173-6	Clopyralid	267	254-280	258	0.2	Comply
	Picloram	67	60-74	62	0.3	Comply
133173-7	Glyphosate	360	342-378	359	0.3	Comply
133173-10	Glyphosate	360	342-378	367	0.2	Comply
133173-11	Glyphosate	490	466-515	488	0.2	Comply
133173-12	Glyphosate	360	342-378	355	0.2	Comply
133173-13	Prosulfocarb	800	775-825	806	1.0	Comply
133173-14	Prosulfocarb	800	775-825	816	0.8	Comply
133173-15	Glyphosate	480	456-504	488	0.2	Comply
133173-17	Diflufenican	40	36-44	43	0.3	Comply
	Glyphosate	250	235-265	259	0.3	Comply
133173-23	Fenoxaprop-P-Ethyl	69	62-76	65	1.4	Comply
133173-26	Iodosulfuron methyl sodium	50	45-55	54	2.8	Comply
	Mesosulfuron-methyl	7.5	6.4-8.6	8	1.5	Comply
133173-29	Glyphosate	7.2	6.1-8.3	8	1.6	Comply
	Nonanoic acid	10.2	8.7-11.7	10	0.6	Comply
133173-31	Foramsulfuron	300	285-315	303	1.4	Comply
	Iodosulfuron-methyl-sodium	10	8-13	11	2.6	Comply
133173-32	Prosulfocarb	800	775-825	804	0.7	Comply

TABLE 10. Analysis results (g/kg) for herbicide products.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
133173-5	Tribenuron-methyl	750	725-775	771	0.4	Comply
133173-9	Glyphosate	720	695-745	726	0.2	Comply

TABLE 11. Active substances categorized as herbicides in the 2022 control campaign.

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Clopyralid	1702-17-6	2020, 2016, 2009, 2000	HPLC-DAD	OA-857	Yes	CIPAC 174 (Ref. 10)	
Diflufenican	83164-33-4	2020, 2019, 2016, 2012, 2007	HPLC-DAD	OA-873	Yes	CIPAC 462 (Ref. 11)	
Fenoxaprop-P-ethyl	71283-80-2	2019, 2014, 2008, 1999	HPLC-DAD	OA-852	Yes	CIPAC 484 (Ref. 12)	
Foramsulfuron	173159-57-4	-	HPLC-DAD	OA-911	Yes	-	
Glyphosate	1071-83-6	2020, 2019, 2016, 2011, 2003	HPLC-UV	OA-811	Yes	CIPAC 284 (Ref. 13)	
Iodosulfuron-methyl-sodium	144550-36-7	2013, 2003	HPLC-DAD	OA-911	Yes	-	

Mesosulfuron-methyl	208465-21-8	2013	HPLC-DAD	OA-911	Yes	-	
Nonanoic acid	112-05-0	2019	HPLC-DAD	OA-910	Yes	-	
Picloram	1918-02-01	2019, 2014	HPLC-DAD	OA-857	Yes	CIPAC 174 (Ref. 10)	
Prosulfocarb	52888-80-9	2017, 2016	GC-FID	OA-826	Yes	-	
Tribenuron-methyl	101200-48-0	2017, 2006	HPLC-DAD	Modified CIPAC 546	No	CIPAC 546 (Ref. 14)	

2.4 Insecticides

Four insecticides contained one of the a.s. flupyradifurone, lambda-cyhalothrin, or tau-fluvalinate were selected for the 2022 campaign. TABLE 14 states which previous years the active substances were selected for control and outlines the analytical method applied for each a.s.

2.4.1 Results and conclusion

The results for quantitative determination of a.s. in the insecticides are listed in TABLE 12 and TABLE 13. RSD% is the relative reproducibility percentage for the analysis of the product.

The concentration of a.s. complies with the declared content and with applicable Danish law in all four products.

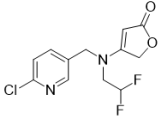
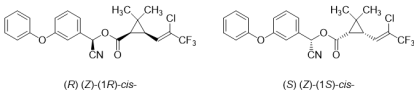
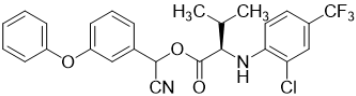
TABLE 12. Analysis results (g/L) for insecticide products.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
133173-16	Tau-fluvalinate	240	226-254	249	0.2	Comply
133173-27	Flupyradifurone	0.08	0.068-0.092	0.08	0.4	Comply

TABLE 13. Analysis results (g/kg) for insecticide products.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
133173-4	Lambda-cyhalothrin	25	21-29	26	2.3	Comply
133173-8	Lambda-cyhalothrin	25	21-29	24	2.2	Comply

TABLE 14. Active substances categorized as insecticides in the 2022 control campaign.

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Flupyradifurone	951659-40-8	2021	HPLC-DAD	OA-907	Yes	CIPAC MAM (Ref. 9)	
Lambda-cyhalothrin	91465-08-6	2021, 2016, 2003	GC-FID	OA-839	Yes	-	 (R) (Z)-(1R)-cis- (S) (Z)-(1S)-cis-
Tau-fluvalinate	102851-06-9	2021, 2019, 2016, 1998	HPLC-DAD	OA-872	Yes	-	

3. Physico-chemical testing

The collected pesticide products were submitted to a physico-chemical test program. A program depending on the formulation type and in accordance with the reference document presenting best practices for formulation analysis on pesticide products (Ref. 15). The tests included evaluation of appearance, determination of density, persistent foam, emulsion stability, suspensibility, and solution stability. The results were subsequently compared to the values specified in connection with the authorisation of the product.

The physico-chemical parameters are subject to confidentiality, and only the general conclusions have been included in this report.

3.1 Physico-chemical testing of selected pesticides

Details concerning the performed physico-chemical tests are provided below.

3.1.1 Appearance

The colour and physical state of the formulation were described after homogenization of the product according to DTI's method UA-407.

3.1.2 Density

The density of the formulations was determined according to DTI's analysis methods UA-202 or UA-312. The methods are equivalent to CIPAC MT 3 (Ref. 16). The density of the products was determined as the average of a triple determination carried out by measuring with a Densito 30 PX densitometer or by Pycnometer. The methods are accredited.

3.1.3 Persistent foaming

The test for persistent foaming was performed in accordance with DTI's method UA-400, equivalent to CIPAC method MT 47 (Ref. 17). The highest in-use concentrations prescribed for the products were tested. Standard CIPAC water D, prepared according to CIPAC MT 18, was used unless otherwise specified for the product (Ref. 18). The amount of foam present after 1 minute was reported. The test was performed in duplicate for each pesticide product. The method is accredited.

3.1.4 Emulsion stability

Emulsion stability was determined via DTI's method UA-406 equivalent to CIPAC method MT 36 (Ref. 19). The highest in-use concentrations prescribed for the products were tested. Standard CIPAC water D, prepared according to CIPAC MT 18, was used unless otherwise specified for the product (Ref. 18). The test was performed in duplicate for each pesticide product.

3.1.5 Suspensibility

Suspensibility of the pesticide products was determined by DTI's method UA-402. The method is equivalent to the CIPAC method MT 184 (Ref. 20). The highest in-use concentrations prescribed for the products were tested. Standard CIPAC water D, prepared according to CIPAC MT 18, was used unless otherwise specified for the product (Ref. 18).

3.1.6 Degree of dissolution and solution stability

The degree of dissolution and solution stability of the pesticide products was determined by DTI's method UA-421. The method is equivalent to the CIPAC method MT 179.1 (Ref. 21). The highest in-use concentrations prescribed for the products were tested.

3.1.7 Results

The tests conducted on the collected pesticides are summarized in TABLE 15.

TABLE 15. Physico-chemical tests performed on the collected pesticide products. 'X' signifies the test performed on the sample.

DTI sample no.	Appearance	Density	Persistent foam	Emulsion stability	Suspensibility	Solution stability
133173-1	X		X			X
133173-2	X	X	X	X		
133173-3	X	X	X		X	
133173-4	X		X		X	
133173-5	X		X			
133173-6	X	X	X			
133173-7	X	X	X			
133173-8	X		X		X	
133173-9	X		X			
133173-10	X	X	X			
133173-11	X	X	X			
133173-12	X	X	X			
133173-13	X	X	X	X		
133173-14	X	X	X	X		
133173-15	X	X	X			
133173-16	X	X	X	X		
133173-17	X	X	X		X	
133173-18	X	X	X	X		
133173-19	X	X	X	X		
133173-20	X	X	X		X	
133173-21	X	X	X		X	
133173-22	X	X	X	X		
133173-23	X	X	X	X		
133173-24	X	X	X		X	
133173-25	X	X	X			
133173-26	X	X	X		X	
133173-27	X	X				
133173-28	X		X		X	
133173-29	X	X				
133173-31	X		X			
133173-32	X	X	X	X		

3.1.8 Conclusion

Three products were non-comply for persistent foaming. The test results of all other physico-chemical tests were comparable with the specified values of the product or were within the legal requirements and tolerances.

4. Comparison of pesticide products

4.1 Comparison of pesticide products

Comparison of parallel imported pesticide products, imported from different countries.

4.2 Analysed products

The analysed products are listed in TABLE 16.

TABLE 16. Selected products.

DTI no.	Reg No.	Active substances
133173-18	623-8 A*	Mefentrifluconazole & Pyraclostrobin
133173-19	623-8 B*	

* 623-8 A and 623-8 B denoted the product Himalaya Pro reg. no. 623-8, imported from different countries.

4.3 GC-MS analysis

A sub-sample of the products was analysed according to DTI's method OA-843:

The sub-sample was diluted by methanol and analysed by gas chromatography coupled with mass spectrometry (GC-MS) in scan mode, and the resulting chromatograms were compared.

4.4 FTIR analysis

A sub-sample was analysed by fourier-transform infrared spectroscopy (FTIR) according to DTI's method UA-234: The sample was analysed with a Perkin Elmer Spectrum Two™ FTIR with ATR (Attenuated total reflection). The samples were measured directly with no preparation or cleaning. Resolution 4 cm⁻¹, 4 scan per sample.

4.5 Results and conclusion

The results of the comparison of the products are listed in TABLE 17. Based on the applied parameters no significant difference between the two products was identified.

TABLE 17. Comparison of the product 133173-19 with 133173-18.

DTI No.	Parameter	Compared to 133173-18
133173-19	Active substance concentration	Equivalent
	Appearance	Equivalent
	Density	Equivalent
	Persistent foaming	Equivalent
	Emulsion stability	Equivalent
	GC-MS screening	Equivalent
	FTIR screening	Equivalent

5. References

1. Ministry of Environment and Food of Denmark, Environmental Protection Agency (Danish EPA) site; <http://eng.mst.dk/chemicals/pesticides/> and <http://mst.dk/kemi/pesticider/>
2. Danish EPA, 2022, approved Pesticides 2021 <http://mst.dk/kemi/database-for-bekaempelsesmidler/bmd/> (Danish)
3. Statutory Order on Pesticides No. 1278 of 06/06/2021 (applicable Danish Statutory Order 1569 of 19/12/2022)
4. 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
5. Danish Technological Institute, Kongsvang Allé 29, DK-8000 Aarhus C, Denmark, <http://www.dti.dk/>
6. The Danish Accreditation and Metrology Fund – DANAK, <http://english.danak.dk/>
7. The e-Pesticide Manual, Eighteenth Edition, online version, 2021. British Crop Protection Council, United Kingdom
8. CIPAC method 419 Cymoxanil. <http://www.cipac.org/>
9. CIPAC Multi-active method for the analysis of active substances in formulated products to support quality control, <http://www.cipac.org/>
10. CIPAC method 174 Picloram. <http://www.cipac.org/>
11. CIPAC method 462 Diflufenican. <http://www.cipac.org/>
12. CIPAC method 484 Fenoxaprop-P. <http://www.cipac.org/>
13. CIPAC method 284 Glyphosate. <http://www.cipac.org/>
14. CIPAC method 546 Tribenuron. <http://www.cipac.org/>
15. Reference document illustrating best practices on analytical strategies and interpretation of results for the formulation analysis of plant protection products obtained during official market control. Version 1 from March 2019 - EU Working Group on Formulation Analysis.
16. CIPAC MT 3 Specific gravity, density, and weight per milliliter. <http://www.cipac.org/>
17. CIPAC MT 47 Persistent foaming. <http://www.cipac.org/>
18. CIPAC MT 18 Standard waters. <http://www.cipac.org/>

19. CIPAC MT 36 Emulsion characteristics of emulsifiable concentrates.
<http://www.cipac.org/>
20. CIPAC MT 184 Suspensibility of formulations forming suspensions on dilution with water. <http://www.cipac.org/>
21. CIPAC 179.1 Degree of Dissolution and Solution Stability. <http://www.cipac.org/>

Appendix 1: Pesticide products collected for the planned control campaign 2022

TABLE 18. Fungicide products.

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
133173-2	Mefentrifluconazole Pyraclostrobin	19-240	Balaya	BASF A/S
133173-3	Boscalid	19-246	Entargo	BASF A/S
133173-18	Mefentrifluconazole Pyraclostrobin	623-8 A*	Himalaya PRO	Vestjydsk Agro
133173-19	Mefentrifluconazole Pyraclostrobin	623-8 B*	Himalaya PRO	Vestjydsk Agro
133173-20	Mandipropamid Difenoconazole	1-289	Revus Top SC	Syngenta Nordics A/S
133173-21	Mandipropamid	623-6	Potato Super	Vestjydsk Agro
133173-22	Tebuconazole	347-57	Orius Gold	Nufarm Deutschland GmbH
133173-24	Cyazofamid	352-8	Ranman Top	ISK Biosciences Europe N.V.
133173-28	Cymoxanil	632-4	Cymbal 45	Belchim Crop Protection NV/SA

* 623-8 A and 623-8 B denoted the product Himalaya Pro reg. no. 623-8, imported from different countries.

TABLE 19. Growth regulator products.

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
133173-1	Maleic hydrazide	558-4	Antergon MH	Arysta LifeScience Great Britain Ltd.
133173-25	Mepiquat chloride Ethephon	19-4	Terpal	BASF A/S

TABLE 20. Herbicide products.

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
133173-5	Tribenuron-methyl	347-36	Nuance Max 75 WG	Nufarm Deutschland GmbH
133173-6	Clopyralid Picloram	318-176	LFS Clopyralid-Picloram	LFS Kemi A/S
133173-7	Glyphosate	357-4	Barclay Gallup Super 360	Barclay Chemicals Manufacturing Ltd.

133173-9	Glyphosate	48-47	Roundup PowerMax	Monsanto Crop Sciences Denmark A/S
133173-10	Glyphosate	48-16	Roundup Bio	Monsanto Crop Sciences Denmark A/S
133173-11	Glyphosate	357-3	Barclay Gallup Hi-Aktiv	Barclay Chemicals Manufacturing Ltd.
133173-12	Glyphosate	396-53	Glypper	ADAMA Registrations B.V.
133173-13	Prosulfocarb	1-211	Boxer	Syngenta Nordics A/S
133173-14	Prosulfocarb	613-3	Fidox EC	Globachem NV
133173-15	Glyphosate	48-43	Roundup Flex	Monsanto Crop Sciences Denmark A/S
133173-17	Diflufenican Glyphosate	19-241	Pistol ukrudtsmiddel	BASF A/S
133173-23	Fenoxaprop-P-Ethyl	11-31	Foxtrot	Cheminova A/S
133173-26	Iodosulfuron-methyl-sodium Mesosulfuron-methyl	18-569	Hussar Plus OD	Bayer A/S
133173-29	Glyphosate Nonanoic acid	724-16	Roundup WeedX Spray	Evergreen Garden Care Österreich GmbH
133173-31	Foramsulfuron Iodosulfuron-methyl-sodium	18-442	MaisTer	Bayer A/S
133173-32	Prosulfocarb	613-5	Roxy EC	Globachem NV

TABLE 21. Insecticide products.

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
133173-4	Lambda-cyhalothrin	396-77	Lamdex	ADAMA Registrations B.V.
133173-8	Lambda-cyhalothrin	1-252	Axiendo 2,5 WG	Syngenta Nordics A/S
133173-16	Tau-fluvalinate	396-82	Mavrik	ADAMA Registrations B.V.
133173-27	Flupyradifurone	579-9	Provanto Spray	SBM Développement SAS

Control of pesticides 2022

English

The analytical chemical authority control of pesticide products on the Danish market that was carried out in 2022 by the Danish Environmental Protection Agency (Danish EPA), Chemical Inspection Service, is described in this report. Samples of selected types of plant protection products (pesticides) were collected on the Danish market and analysed to verify whether the content of the active substances in the products in question complies with the product specification and the labelled content. 31 different pesticide products were analysed as part of the planned control program.

Danish

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked, der er udført i 2022 af den danske Miljøstyrelses Kemikalieinspektion, er beskrevet i denne rapport. Prøver fra udvalgte typer af bekæmpelsesmidler (pesticider) er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med det deklarerede indhold. I alt 31 bekæmpelsesmidler (pesticider) blev undersøgt som en del af den planlagte kontrolkampagne.



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