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Control of Pesticides and Biocides 2017

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

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Christina Østerballe Pedersen
Eva Jacobsen
Sine Abraham Johannesen

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Preface

38 different types of products, covered by the pesticide and biocide regulation, were included in the Danish authority control in 2017. In this report, pesticides are defined as plant protection products (PPP).

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. Additionally, a co-formulant was quantified in 6 biocide products

Selected physical-chemical properties were tested for 9 pesticide products. The tests performed comprised the analysis of density, pH, persistent foam, emulsion stability and dilution stability. Additionally, density was measured for all liquid products.

Four pesticide products were screened by GC-MS to confirm the identity of the solvent used.

For the 2017 programme, 5 tested products (2 pesticides and 3 biocides) did not comply with the tolerance limits defined by the Danish Statutory Order on Pesticides No. 1574 of 12 December 2016 and by Regulation 1107/2009 concerning marketing of plant protection products.[1,2,3]

Sammenfatning og konklusion

Denne rapport beskriver den analytisk kemiske kontrol af pesticidprodukter (sprøjtemidler) og biocidprodukter på det danske marked, der er udført af Miljøstyrelsens Kemikalieinspektion i 2017.[4,5]

38 produkter fra udvalgte typer af bekæmpelsesmidler (24 pesticider og 14 biocider) 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. 1574 af 12 december 2016 og i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler.[1,2,3]

Seks biocidprodukter blev analyseret for co-formulanten piperonyl butoxid.

Densitet blev målt på alle flydende produkter. Herudover blev 9 pesticidprodukter udvalgt til analyse for pH, vedvarende skumdannelse, emulsionsstabilitet og fortyndingsstabilitet.

Der blev foretaget screening ved gaskromatografi med masse spektrometrisk detektion (GC-MS) af fire produkter for at bekræfte identiteten af det anvendte solvent.

Følgende typer af produkter blev analyseret, se Tabel 1:

- 14 insekticider (biocider) indeholdende pyrehtrin I+II
- 6 insekticider (pesticider) indeholdende cypermethrin, indoxacarb, pyrethrin I+II og thiacloprid
- 7 herbicider (pesticider) indeholdende mesotrion, metsulfuron-methyl, prosulfocarb og tribenuron-methyl
- 3 fungicider (pesticider) indeholdende azoxystrobin, fluazinam, and mandipropamid
- 8 vækstreguleringsmidler (pesticider) indeholdende ethephon, mepiquat-chlorid, metconazol (fungicid), prohexadion-calcium og trinexapac-ethyl.

Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold i 33 produkter, idet resultatet er indenfor tolerancen.

Det målte indhold af aktivstoffer var ikke i overensstemmelse med det deklarerede indhold i 5 produkter (2 pesticider and 3 biocider), idet resultatet er udenfor tolerancen. Produkter, hvor der ikke er overensstemmelse med det deklarerede indhold, udtages til analyse igen i 2018.

Alle produkter, som blev testet for fysisk-kemiske parametre og identificering af det anvendte solvent, var i overensstemmelse med produkternes specifikationer.

TABEL 1. Oversigt over antal analyserede produkter og konklusion.

Aktivstof	Antal analyserede produkter	Antal indenfor tolerance	Antal udenfor tolerance
Azoxystrobin	1	1	0
Cypermethrin	1	1	0
Fluazinam	1	1	0
Indoxacarb	1	1	0
Mandipropamid	1	1	0
Mepiquat-Chlorid & Ethephon	1	1	0
Mepiquat-Chlorid & Metconazol	1	1	0
Mepiquat-Chlorid & Prohexadione-Calcium	1	0	1
Mesotrion	2	2	0
Prosulfocarb	1	1	0
Pyrethrin I+II	16	12	4
Thiacloprid	2	2	0
Tribenuron-methyl	3	3	0
Tribenuron-methyl & Metsulfuron-methyl	1	1	0
Trinexpac-ethyl	5	5	0
Total	38	33	5

Summary and conclusion

This report describes the analytical chemical control of plant protection products (pesticide products) and biocide products on the Danish market that was carried out by the Danish Environmental Protection Agency (Danish EPA), Chemical Inspection Service, in 2017.[4,5]

38 products from selected types of pesticides (24) and biocides (14) 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.

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. 1574 of 12 December 2016 and in Regulation 1107/2009 concerning Marketing of Plant Protection Products.[1,2,3]

Six biocide products were analysed for the co-formulant piperonyl butoxide.

The density of all liquid products was measured. In addition, nine pesticide products were selected for analysis of pH, persistent foam, emulsion stability and dilution stability.

Screenings were carried out of four selected pesticide products by gas chromatography with mass spectrometric detection (GC-MS) to identify the solvent used.

The following type of products were analysed, see Table 2:

- 14 insecticides (biocides) containing pyrethrin I+II
- 6 insecticides (pesticides) containing cypermethrin, indoxacarb, pyrethrin I+II, and thiacloprid
- 7 herbicides (pesticides) containing mesotrione, metsulfuron-methyl, prosulfocarb and tribenuron-methyl
- 3 fungicides (pesticides) containing azoxystrobin, fluazinam, and mandipropamid
- 8 growth regulators (pesticides) containing ethephon, mepiquat-chloride, metconazole (fungicide), prohexadione-calcium and trinexapac-ethyl.

The measured content of active substances complied with the declared content in 33 products as the result was within the range of tolerance.

The measured content of active substances did not comply with the declared content in 5 products (2 pesticides and 3 biocides), as the result was outside the range of tolerance. Non-comply products will be collected for analysis again in 2018.

All products that were tested for physical-chemical parameters and identification of the solvent used complied with the specification of the products.

TABLE 2. Outline of total number of analysed products and conclusion.

Active substance	Number of analysed products	Number of products comply	Number of products non-comply
Azoxystrobin	1	1	0
Cypermethrin	1	1	0
Fluazinam	1	1	0
Indoxacarb	1	1	0
Mandipropamid	1	1	0
Mepiquat-Chloride & Ethephon	1	1	0
Mepiquat-Chloride & Metconazole	1	1	0
Mepiquat-Chloride & Prohexadione-Calcium	1	0	1
Mesotrione	2	2	0
Prosulfocarb	1	1	0
Pyrethrin I+II	16	12	4
Thiacloprid	2	2	0
Tribenuron-methyl	3	3	0
Tribenuron-methyl & Metsulfuron-methyl	1	1	0
Trinexpac-ethyl	5	5	0
Total	38	33	5

1. Control campaign in 2017

1.1 Selected active substances

The Danish control campaign conducted in 2017 covered 16 active substances in different combinations in 38 products, which resulted in 42 analyses for active substances. Overall, the area of application is divided into two types: 24 plant protection products (PPP, pesticides) and 14 biocide products (non-agricultural pesticides).
A summary of the selected active substances is given in following table:

TABLE 3. Outline of selected active substances in the 2017 control campaign.

Type	Active substance	CAS no.	Area of application
Biocide	Pyrethrin I+II	8003-34-7	Insecticide
Pesticide	Azoxystrobin	131860-33-8	Fungicide
	Cypermethrin	52315-07-8	Insecticide
	Ethephon	16672-87-0	Growth regulator
	Fluazinam	79622-59-6	Fungicide
	Indoxacarb	173584-44-6	Insecticide
	Mandipropamid	374726-62-2	Fungicide
	Mepiquat-Chloride	24307-26-4	Growth regulator
	Mesotrione	104206-82-8	Herbicide
	Metconazole	125116-23-6	Fungicide
	Metsulfuron-methyl	74223-64-6	Herbicide
	Prohexadione-Calcium	127277-53-6	Growth regulator
	Prosulfocarb	52888-80-9	Herbicide
	Pyrethrin I+II	8003-34-7	Insecticide
	Thiacloprid	111988-49-9	Insecticide
	Tribenuron-methyl	101200-48-0	Herbicide
	Trinexpac-ethyl	95266-40-3	Growth regulator

1.2 Collecting products

All products were collected by the Chemical Inspection Service of the Danish Environmental Protection Agency during the period from March to October 2017. The product samples were collected either from wholesale dealers/importers or at retailer outlets.

The collected product samples were stored at the Laboratory for Chemistry and Microbiology, Danish Technological Institute (DTI)[6], in the 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.

1.3 Tolerance for active substances

The Danish Statutory Order on Pesticides No. 1574 of 12 December 2016 and Regulation 1107/2009 concerning Marketing of Plant Protection Products specify the general tolerance of deviation from the declared content of active substances.[1,2] These tolerances are listed in Table 4.

TABLE 4. The tolerance of deviation from the declared content of active substances, 2017.

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 2017

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 is accredited for a flexible scope regarding parameters and performance of the methods within parts of the scope.

1.4.1 Analysing 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 chemical analyses were as far as possible performed as at least four freshly prepared samples of each product. If the average result is outside the tolerance interval, then the analysis is repeated with a minimum of four 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 the purity of the reference standard. The expanded analysis uncertainty is used to determine a 95% confidence interval for the analysis result.

1.4.1 Analysing additives

The additive piperonyl butoxide was analysed in 6 biocide samples. An analytical scheme equivalent to the one described in section 1.4.1 for the analysis of active substances was applied to the additive.

1.4.2 Physical-chemical testing

The density of all liquid products was measured. Additionally, nine pesticide products were selected for analysis of density, pH, persistent foam, emulsion stability and dilution stability and evaluated as comply/non-comply.

1.4.3 Screening of solvent

Screenings were carried out of selected products by gas chromatography with mass spectrometric detection (GC-MS) to identify the used solvent and compare it to the solvent specified for the formulation.

2. Biocides

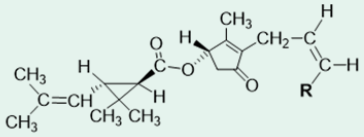
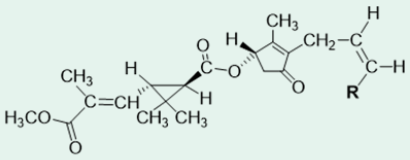
The objective of the active substances, contained in the biocidal products, is to protect humans, animals, materials or articles against harmful organisms such as pests or bacteria.

For the Danish Pesticide Control Campaign 2017, 14 biocide insecticides were selected. The selected active substances were pyrethrin I+II.

2.1 Insecticides (Biocides)

Fourteen insecticides containing pyrethrin I+II as active substance were selected for the 2017 control campaign. The active substances had not previously been selected for control by the Danish EPA.

TABLE 5. Insecticides (biocides) analysed in the 2017 control campaign.

Name	CAS no.	Molecular structure[8]
Pyrethrin I+II	8003-34-7	 Pyrethrins I (chrysanthemates) R = -CH=CH$_2$ (pyrethrin I) R = -CH$_3$ (cinerin I) R = -CH$_2$CH$_3$ (jasmolin I)  Pyrethrins II (pyrethrates) R = -CH=CH$_2$ (pyrethrin II) R = -CH$_3$ (cinerin II) R = -CH$_2$CH$_3$ (jasmolin II)

2.1.1 Analysis

Pyrethrin I+II was analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD) according to DTI's method OA-879. Details concerning the implementation of the analyses, the calculation of the result and expanded analysis uncertainty are described in section 1.4.

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. The 95% confidence interval is based on the calculated expanded measurement uncertainty described in section 1.4.1.

TABLE 6. Analysis results of insecticides (biocides), g/kg.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	95% confidence interval	Comply/ Non-comply
751811-18	Pyrethrin I+II	1.74	1.31-2.18	1.65	1.6	1.47-1.83	Comply
751811-20	Pyrethrin I+II	4.0	3.40-4.60	3.72	3.8	3.23-4.22	Comply
751811-22	Pyrethrin I+II	1.74	1.31-2.18	1.65	4.5	1.31-1.99	Comply
751811-23	Pyrethrin I+II	4.00	3.40-4.60	3.52	1.9	3.12-3.93	Comply
751811-32	Pyrethrin I+II	4.00	3.40-4.60	3.76	2.5	3.39-4.13	Comply
751811-36	Pyrethrin I+II	1.74	1.31-2.18	1.68	4.0	1.38-1.97	Comply
751811-37	Pyrethrin I+II	1.74	1.31-2.18	1.49	1.4	1.34-1.63	Comply

TABLE 7. Analysis results of insecticides (biocides), g/L.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	95% confidence interval	Comply/ Non-comply
751811-13	Pyrethrin I+II	30	27-33	49	1.0	45-53	Non-comply
751811-14	Pyrethrin I+II	2.49	2.12-2.86	2.29	2.4	2.13-2.45	Comply
751811-15	Pyrethrin I+II	2.10	1.79-2.42	2.12	2.3	1.95-2.29	Comply
751811-16	Pyrethrin I+II	2.5	2.13-2.88	3.09	4.4	2.69-3.49	Non-comply
751811-24	Pyrethrin I+II	2.49	2.12-2.86	2.71	3.9	2.37-3.05	Comply
751811-34	Pyrethrin I+II	4.00	3.40-4.60	3.06	3.4	2.64-3.47	Non-comply
751811-40	Pyrethrin I+II	4.00	3.40-4.60	3.51	3.7	3.10-3.93	Comply

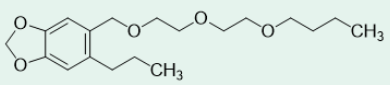
2.1.3 Conclusion

For the 14 products containing pyrethrin I+II as active substance, 11 comply with the declared content and with applicable Danish law. Of the three non-comply products, one (751811-34) had expired upon analysis and no further actions were made for this product.

2.2 Co-formulants

Six of the products containing pyrethrin I+II were co-formulated with the co-formulant piperonyl butoxide. This compound is not subject to the tolerances defined in Table 4.

TABLE 8. Additives analysed in the 2017 control campaign.

Name	CAS no.	Molecular structure[8]
Piperonyl butoxide	51-03-6	

2.2.1 Analysis

Piperonyl butoxide was analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD) according to DTI's method OA-879.

Details concerning the implementation of the analyses, the calculation of the result and expanded analysis uncertainty are described in section 1.4.

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. The 95% confidence interval is based on the calculated expanded measurement uncertainty described in section 1.4.1.

TABLE 9. Analysis results of additives in biocides, g/L.

DTI sample no.	Active substance	Label claim g/L	Analysis result g/L	RSD %	95% confidence interval
751811-13	Piperonyl butoxide	135	238	1.9	219-257
751811-14	Piperonyl butoxide	12.46	9.68	3.8	8.81-10.55
751811-23	Piperonyl butoxide	20.0	16.0	2.0	14.1-17.84
751811-24	Piperonyl butoxide	12.46	13.93	4.0	12.27-15.29
751811-34	Piperonyl butoxide	20.0	18.7	2.1	16.4-21.0
751811-40	Piperonyl butoxide	20.0	18.1	3.6	16.1-20.2

2.2.1 Conclusion

For products 751811-13, 751811-14 and 751811-23 the measured concentration deviates by more than 15% from the specified concentration. However, as co-formulants are not subject to the regulation applying to the active substances, the results cannot be evaluated as comply/non-comply.

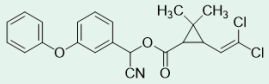
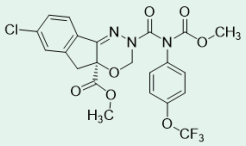
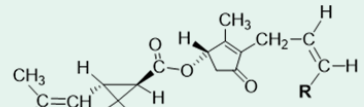
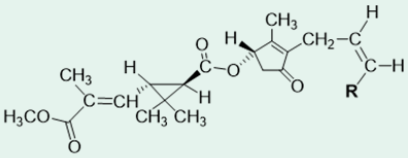
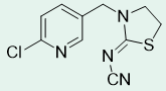
3. Pesticides

In this report, pesticides are defined as plant protection products (PPP). In the Danish Pesticide Control Campaign 2017, 24 pesticide products were selected: insecticides, herbicides, fungicides and growth regulators. The active substances in the selected pesticide products were azoxystrobin, cypermethrin, ethephon, fluazinam, indoxacarb, mandiproamid, mepiquat-chloride, mesotrion, metconazole, metsulfuron-methyl, prohexadione-calcium, prosulfocarb, pyrethrin I+II, thiacloprid, tribenuron-methyl and trinexapac-ethyl.

3.1 Insecticides (pesticides)

Six insecticides (one containing cypermethrin, one containing indoxacarb, two with pyrethrin I+II and two with thiacloprid as active substances) were selected for the 2017 control campaign. Table 10 states the previous years the active substances were selected for control.

TABLE 10. Insecticides (pesticides) included in the 2017 control campaign.

Name	CAS no.	Year selected for control	Molecular structure[8]
Cypermethrin	52315-07-8	2016, 2013, 2003	
Indoxacarb	173584-44-6	2016	
Pyrethrin I+II	8003-34-7	-	 Pyrethrins I (chrysanthemates) R = -CH=CH$_2$ (pyrethrin I) R = -CH$_3$ (cinerin I) R = -CH$_2$CH$_3$ (jasmolin I)  Pyrethrins II (pyrethrates) R = -CH=CH$_2$ (pyrethrin II) R = -CH$_3$ (cinerin II) R = -CH$_2$CH$_3$ (jasmolin II)
Thiacloprid	111988-49-9	-	

'-' Signifies that the compound has not previously been selected for control by the Danish EPA.

3.1.1 Analysis

Cypermethrin was analysed by gas chromatography coupled with tandem mass spectrometry (GC-MS/MS) according to DTI's method OA-825. The method is modified from CIPAC method alpha-cypermethrin 454.[9]

Indoxacarb was analysed by high-performance liquid chromatography with a chiral column combined with diode array detection (HPLC-DAD) according to DTI's method OA-883. The method is equivalent to the CIPAC method 612 indoxacarb.[9]

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

Thiacloprid was analysed by reversed phase HPLC-DAD according to DTI's method OA-876 and OA-884 (aerosols). Both methods are modified from the CIPAC method 631 thiacloprid.[9]

Details concerning the implementation of the analyses, the calculation of the result and expanded analysis uncertainty are described in section 1.4.

The methods for determination of thiacloprid are accredited.

3.1.2 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. The 95% confidence interval is based on the calculated expanded measurement uncertainty described in section 1.4.1.

TABLE 11. Analysis results of insecticides (pesticides), g/kg.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	95% confidence interval	Comply/ Non-comply
751811-17	Indoxacarb	300	285 - 315	304	1.1	279-329	Comply

TABLE 12. Analysis results of insecticides (pesticides), g/L.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	95% confidence interval	Comply/ Non-comply
751811-21	Thiacloprid	0.150	0.128-0.173	0.139	1.0	0.125-0.152	Comply
751811-29	Pyrethrin I+II	0.0459	0.0390-0.0528	0.0628	5.2	0.0493-0.0764	Non-comply
751811-30	Cypermethrin	0.020	0.017-0.023	0.023	1.8	0.022-0.024	Comply
751811-39	Pyrethrin I+II	4.59	3.90-5.28	3.86≈3.9	1.4	3.36-4.36	Comply
751811-41	Thiacloprid	240	226-254	236	1.7	222-250	Comply

3.1.3 Conclusion

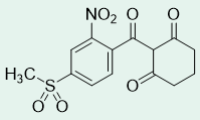
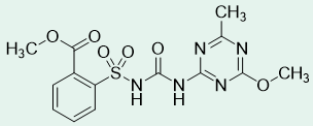
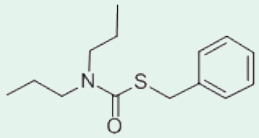
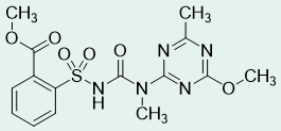
Two products containing pyrethrin I+II were analysed, and in one product the measured content of active substance does not comply with applicable Danish law as it is not within the tolerance interval.

The measured content of indoxacarb, thiacloprid and cypermethrin complies with the declared content for the 4 products and with applicable Danish law.

3.2 Herbicides (pesticides)

Seven herbicides containing mesotrione, prosulfocarb, metsulfuron-methyl and tribenuron-methyl as active substances were selected for the 2017 control campaign. Table 13 states the previous years the active substances were selected for control.

TABLE 13. Herbicides (pesticides) included in the 2017 control campaign.

Name	CAS no.	Year selected for control	Molecular structure[8]
Mesotrione	104206-82-8	2008	
Metsulfuron-methyl	74223-64-6	2012, 2005	
Prosulfocarb	52888-80-9	2016, 2009	
Tribenuron-methyl	101200-48-0	2005, 1994	

3.2.1 Analysis

Mesotrione, metsulfuron-methyl, prosulfocarb and tribenuron-methyl were analysed by reversed phase high-performance liquid chromatography combined with diode array detection, (HPLC-DAD). Mesotrion and prosulfocarb were analysed according to DTI's method OA-880. Metsulfuron-methyl and tribenuron-methyl were analysed according to DTI's method OA-885. The method used for analysis of metsulfuron-methyl and tribernuron-methyl is modified from CIPAC method 546 tribenuron-methyl.[9]

The method for determination of mesotrione and prosulfocarb is accredited.

3.2.2 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. The 95% confidence interval is based on the calculated expanded measurement uncertainty described in section 1.4.1.

TABLE 14. Analysis results of herbicides (pesticides), g/kg.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	95% confidence interval	Comply/ Non-comply
751811-42	Tribenuron-methyl	500	475-525	506	3.0	470-542	Comply
751811-43	Tribenuron-methyl	500	475-525	507	4.2	461-552	Comply
751811-44	Tribenuron-methyl	222	209-235	233	0.7	222-245	Comply
	Metsulfuron-methyl	111	104-117	107	1.3	103-110	Comply
751811-45	Tribenuron-methyl	750	725-775	772	2.0	734-809	Comply

TABLE 15. Analysis results of herbicides (pesticides), g/L.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	95% confidence interval	Comply/ Non-comply
751811-3	Mesotrione	100	90-110	103	0.8	97-109	Comply
751811-31	Prosulfocarb	800	775-825	810	1.1	770-850	Comply
751811-38	Mesotrione	100	90-110	106	1.6	100-112	Comply

3.2.3 Conclusion

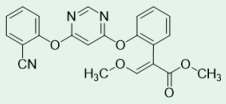
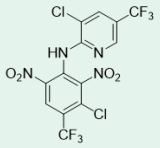
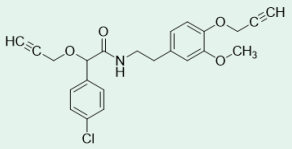
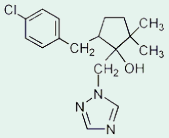
The measured content of tribenuron-methyl, metsulfuron-methyl, mesotrione and prosulfocarb in the 7 products complies with the declared content and with applicable Danish law.

3.3 Fungicides (pesticides)

Three fungicides containing azoxystrobin, fluazinam and mandipropamid as active substances were selected for the 2017 campaign. Table 16 states the previous years the active substances were selected for control.

One growth regulator containing the fungicide metconazole as a co-formulant was also selected.

TABLE 16. Fungicides (pesticides) included in the 2017 control campaign.

Name	CAS no.	Year selected for control	Molecular structure[8]
Azoxystrobin	131860-33-8	2006, 1999	
Fluazinam	79622-59-6	2008, 2000	
Mandipropamid	374726-62-2	2009	
Metconazole	125116-23-6	2015, 2014	

3.3.1 Analysis

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

Fluazinam, mandipropamid and metconazole were analysed by reversed phase high-performance liquid chromatography combined with diode array detection, (HPLC-DAD). Fluazinam and mandipropamid were analysed according to DTI's method OA-880. The method used for the analysis of metconazole is modified from CIPAC method 657 pyraclostrobin.[9]

Details concerning the implementation of the analyses, the calculation of the results and expanded analysis uncertainty are described in section 1.4.

The methods for fluazinam, mandipropamid and metconazole are accredited.

3.3.2 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. The 95% confidence interval is based on the calculated expanded measurement uncertainty described in section 1.4.1.

TABLE 17. Analysis results of fungicides (pesticides), g/L.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	95% confidence interval	Comply/ Non-comply
751811-1	Fluazinam	500	475-525	486	1.2	455-517	Comply
751811-2	Mandipropamid	250	235-265	246	2.4	230-262	Comply
751811-6	Azoxystrobin	250	235-265	257	0.9	241-273	Comply
751811-33	Metconazole*	30	27-33	28.5	1.0	28-29	Comply

*Co-formulated with mepiquat-chloride. See table 19 for mepiquat-chloride results.

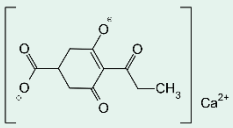
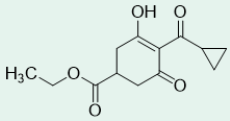
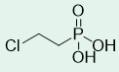
3.3.3 Conclusion

The measured contents of fluazinam, mandipropamid, azoxystrobin and metoconazole comply with the declared content and with applicable Danish law.

3.4 Growth regulators (pesticides)

Eight growth regulators containing mepiquat-chloride, prohexadione-calcium, trinexapac-ethyl and ethephon as active substances were selected for the 2017 control campaign. Table 18 states the previous years the active substances were selected for control.

TABLE 18. Fungicides (pesticides) included in the 2017 control campaign.

Name	CAS no.	Year selected for control	Molecular structure[8]
Mepiquat-chloride	**24307-26-4**	2006	
Prohexadione-calcium	**127277-53-6**	2013	
Trinexpac-ethyl	**95266-40-3**	2009, 1999	
Ethephon	**16672-87-0**	2006, 1996	

3.4.1 Analysis

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

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

Trinexapac-ethyl was analysed by reverse-phase HPLC-DAD according to DTI's method OA-880.

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

The methods for analysis of mepiquat-chloride, prohexadione-calcium and trinexapac-ethyl are accredited.

Details concerning the implementation of the analyses, the calculation of the results and expanded analysis uncertainty are described in section 1.4.

3.4.2 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. The 95% confidence interval is based on the calculated expanded measurement uncertainty described in section 1.4.1.

TABLE 19. Analysis results of growth regulators (pesticides), g/L.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	95% confidence interval	Comply/ Non-comply
751811-5	Trinexapac-ethyl	250	235-265	249	1.7	231-267	Comply
751811-8	Trinexapac-ethyl	250	235-265	252	1.6	234-270	Comply
751811-9	Mepiquat-Cl	305	290-320	306	0.6	291-321	Comply
	Ethephon	155	146-164	158	0.2	149-167	Comply
751811-11	Mepiquat-Cl	300	285-315	336	0.9	315-357	Non-comply
	Prohexadion-Ca	50	45-55	56	0.8	54-58	Non-comply
751811-26	Trinexapac-ethyl	175	165-186	183	1.8	171-194	Comply
751811-28	Trinexapac-ethyl	250	235-265	257	3.0	236-277	Comply
751811-33	Mepiquat-Cl*	210	197-223	217	0.7	200-233	Comply
751811-35	Trinexapac-ethyl	250	235-265	241	2.2	217-265	Comply

*Co-formulated with metconazole. See table 17 for metconazole results.

3.4.3 Conclusion

In one product that contains mepiquat-chloride as well as prohexadione-calcium, neither of the active substances comply with applicable Danish law as the results are outside the range of tolerance.
The measured content of trinexaxpac-ethyl and ethephon complies with the declared content and with applicable Danish law. The content of mepiquat-chloride and ethephon complies with the declared content and with applicable Danish law in two of the three products containing the active substance.

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4. Physical-chemical testing

The density of all liquid products was measured. Additionally, nine pesticide products were selected for analysis of density, pH, persistent foam, emulsion stability and dilution stability and evaluated as comply/non-comply.
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

4.1.1 Analysis

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

4.1.1.2 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.

4.1.1.3 pH
The pH for undiluted samples and for 1% solutions of the formulation was determined by potentiometric measuring according to DTI's 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.

4.1.1.4 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. One determination was performed unless the result deviated significantly from the specification.

4.1.1.5 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 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] Duplicate determination was performed.

4.1.1.6 Dilution stability
The test for dilution stability was performed according to DTI's method PCA 101 corresponding to the CIPAC method MT 41.1. The concentration tested was the maximum concentration prescribed for the product. If no concentration is specified, then 5 mL was used to dilute with 100 mL of Standard water. Standard CIPAC water C prepared according to CIPAC MT 18.1.4 was used unless otherwise specified for the product.[9] Any separated material was reported. Duplicate determination was performed.

4.1.2 Results

The tests performed on the 9 selected pesticides are summarized in Table 20.

TABLE 20. Physical-chemical tests performed on selected pesticide products. An 'X' signifies that the test was performed.

DTI sample no.	Active substance	Appearance	Persistent foam	Emulsion stability	Dilution stability	Density	pH
751811-41	Thiacloprid	X	X			X	X
751811-33	Mepiquat-chloride & Metconazol	X	X		X	X	X
751811-9	Mepiquat-chloride & ethephon	X	X		X	X	X
751811-8	Trinexapac-ethyl	X	X			X	X
751811-5	Trinexapac-ethyl	X	X	X		X	X
751811-39	Pyrethrin	X	X	X		X	X
751811-35	Trinexapac-ethyl	X	X	X		X	X
751811-26	Trinexapac-ethyl	X	X	X		X	X
751811-11	Mepiquat-chloride & prohexadion-Ca	X	X			X	X

4.1.3 Conclusion

The results of the physical-chemical testing complied with the specified values for all the products.

5. Screening of solvent

Screenings were carried out of selected products by gas chromatography with mass spectrometric detection (GC-MS) to identify the solvent used and compare it to the specified solvent.

The formulation of the product is subject to confidentiality, and only the general conclusions have been included in this report.

5.1 Screening of formulation solvents in selected pesticides

5.1.1 GC-MS Analysis

A subsample of the product was diluted with dichloromethane and analysed by gas chromatography with mass spectrometric detection (GC-MS), scan m/z 40 - 600. The resulting mass spectral data was compared to the NIST14 library to identify the formulation solvents.

TABLE 21. Selected products for screening of formulation solvents.

DTI sample no.	Active substance
751811-5	Trinexapac-ethyl
751811-8	Trinexapac-ethyl
751811-28	Trinexapac-ethyl
751811-38	Mesotrion

5.1.2 Results and conclusion

The specified solvents were identified in all four selected products. No additional solvents were identified.

References

1. Statutory Order on Pesticides. Statutory Order from the Ministry of the Environment, No. 1574 of 12 December 2015, Statutory Order is in Danish.

2. 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.

3. 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.

4. Ministry of Environment and Food of Denmark, Environmental Protection Agency (Danish EPA) site; http://eng.mst.dk/chemicals/ and http://mst.dk/kemi/pesticider/.

5. Danish EPA, 2017, approved Pesticides 2017 http://mst.dk/kemi/database-for-bekaempelsesmidler/bmd/ (Danish).

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.

9. CIPAC method no. 454, 546, 571, 612, 631, 657, MT 3, MT 18.1.4, MT 36.3, MT 41.1, MT 47.2 and MT 75.3. http://www.cipac.org/

[Tekst - Slet ikke efterfølgende linje, sektionsskifte]

Control of Pesticides and Biocides 2017

English
The analytical chemical authority control of pesticide and biocide products on the Danish market that was carried out in 2017 by the Danish Environmental Protection Agency (Danish EPA), Chemical Inspection Service, 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 complies with the product specification and the labelled content. A total of 38 different pesticide and biocide products were analysed. The content of active substance in two of the analysed pesticide products and three of the analysed biocide products was not within the accepted tolerance that is determined in the Danish Statutory Order on Pesticides.

Danish
Den analytisk kemiske kontrol af biocid- og pesticidprodukter på det danske marked, der er udført i 2017 af den danske Miljøstyrelses Kemikalieinspektion, 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 38 bekæmpelsesmidler. Indholdet af aktivstoffet i to af de analyserede pesticidprodukter og tre af de analyserede biocidprodukter var ikke inden for den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler.

The Danish Environmental
Protection Agency
Haraldsgade 53
DK-2100 København Ø

www.mst.dk