



**Ministry of Environment  
and Food of Denmark**

Environmental  
Protection Agency

# Control of Biocides 2019

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Sources must be acknowledged.

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# Preface

This report describes the analytical chemical control of biocides on the Danish market, which was carried out in 2019 by the Danish Chemical Inspection Service of the Danish Environmental Protection Agency. The control is part of the “Danish Political Agreement on new joint chemicals initiatives 2018-2021”. Samples of selected types of biocides on the Danish market were collected and analysed to verify whether or not the content of active substances in the biocides complies with the product specifications, the labelled content and the information given to the Danish Environmental Protection Agency.

# Sammenfatning og konklusion

Denne rapport beskriver den analytisk kemiske kontrol af biocidprodukter på det danske marked, der er udført af Miljøstyrelsens Kemikalieinspektion i 2019 (Ref. 1, 2).

14 produkter fra udvalgte typer af 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. 815 af 22 Juni 2018 (Ref. 3).

Følgende typer af produkter blev analyseret, se tabel nedenfor:

- 6 insekticider indeholdende cyromazin, imidacloprid, muscalure og pyrethrin I+II
- 4 afskrækningsmidler indeholdende icaridin
- 3 rodenticider indeholdende chlorophacinon
- 1 træbeskyttelsesprodukt indeholdende fungiciderne 3-iodo-2-propynyl butylcarbammat (IPBC) og propiconazol.

Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold i alle 14 produkter, idet resultatet var indenfor tolerancen.

Densitet blev målt på alle flydende produkter.

Oversigt over antal analyserede produkter og konklusion.

Aktivstof	Antal analyserede produkter	Antal indenfor tolerance	Antal udenfor tolerance
Chlorophacinon	3	3	0
Cyromazin	2	2	0
Icaridin	4	4	0
Imidacloprid	2	2	0
Imidacloprid & muscalure	1	1	0
IPBC & propiconazol	1	1	0
Pyrethrin I+II	1	1	0
TOTAL	14	14	0

# Summary and conclusion

This report describes the analytical chemical control of biocide products on the Danish market that was carried out by the Danish Environmental Protection Agency (Danish EPA), Danish Chemical Inspection Service, in 2019 (Ref. 1, 2).

14 products 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. 815 of 22 June 2018 (Ref. 3).

The following type of products were analysed, see table below:

- 6 insecticides containing cyromazine, imidacloprid, muscalure and pyrethrin I+II.
- 4 repellents containing icaridin.
- 3 rodenticides containing chlorophacinone.
- 1 wood protection product containing the fungicides 3-iodo-2-propynyl butylcarbamate (IPBC) and propiconazole.

The measured content of active substances complied with the declared content in all 14 products as the result was within the range of tolerance.

The density was measured for all liquid products.

Outline of the total number of analysed products and conclusion.

Aktivstof	Antal analyserede produkter	Antal indenfor tolerance	Antal udenfor tolerance
Chlorophacinon	3	3	0
Cyromazin	2	2	0
Icaridin	4	4	0
Imidacloprid	2	2	0
Imidacloprid & muscalure	1	1	0
IPBC & propiconazol	1	1	0
Pyrethrin I+II	1	1	0
TOTAL	14	14	0

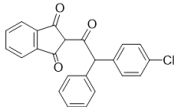
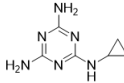
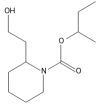
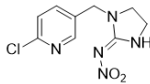
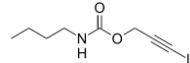

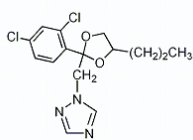
# 1. Control campaign in 2019

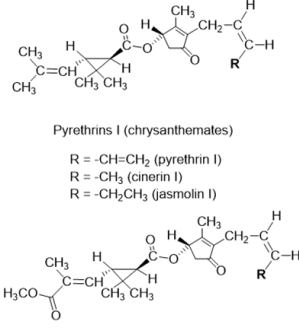
## 1.1 Collecting products

The Danish 2019 biocide control campaign covered 8 active substances in different combinations in 14 products. The active substances were selected according to the amount of active substance sold in previous years as well as to when the active substances lately were included in the control campaign. All products were collected by The Danish Chemical Inspection Service of the Danish EPA during the period from March to September 2019. The product samples were collected either from wholesale dealers/importers or at retailer outlets.

A list of the selected active substances is given in TABLE 1.

**TABLE 1.** List of selected active substances in the 2019 control campaign.

Active substance	CAS no.	Area of application	Year selected for control	Molecular structure <sup>6</sup>
Chlorophacinone	3691-35-8	Rodenticide	-	
Cyromazine	66215-27-8	Insecticide	2003	
Icaridin	119515-38-7	Repellent	2007	
Imidacloprid	138261-41-3	Insecticide	2012, 2004	
IPBC	55406-53-6	Wood protection, fungicide	2018, 2010	
Muscalure	27519-02-4	Insecticide	-	
Propiconazole	60207-90-1	Wood protection, fungicide	2018, 2010, 2006	

Active substance	CAS no.	Area of application	Year selected for control	Molecular structure <sup>6</sup>
Pyrethrin I+II	8003-34-7	Insecticide	2018, 2017	 <p>Pyrethrins I (chrysanthemates)</p> <p>R = -CH=CH<sub>2</sub> (pyrethrin I)  R = -CH<sub>3</sub> (cinerin I)  R = -CH<sub>2</sub>CH<sub>3</sub> (jasmolin I)</p> <p>Pyrethrins II (pyrethrates)</p> <p>R = -CH=CH<sub>2</sub> (pyrethrin II)  R = -CH<sub>3</sub> (cinerin II)  R = -CH<sub>2</sub>CH<sub>3</sub> (jasmolin II)</p>

<sup>6</sup> - means not previously selected for control

The collected product samples were stored at the Laboratory for Chemistry and Microbiology, Danish Technological Institute (DTI) (Ref. 4), 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.

## 1.2 Tolerance of 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 with the specification of the product and the declared content on the label supplied by the authorisation holder.

The Danish Statutory Order on Pesticides no. 815 of 22 June 2018 specifies the general tolerance of deviation from the declared content of active substances (Ref. 3). The tolerances are listed in TABLE 2.

**TABLE 2.** The tolerance of deviation from the declared content of active substance, 2019.

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 2019

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 (Ref. 4).

The Laboratory for Chemistry and Microbiology is accredited by DANAK (Danish Accreditation and Metrology Fund), registration no. 90, according DS/EN ISO/IEC 17025:2005 (Ref. 5). The laboratory has a flexible scope for determination of active substances in pesticides and biocides. In addition, the method for determination of density of biocides is accredited.



### 1.3.1 Analysing active substances

As far as possible, the chemical analyses were 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 five samples of each product. The mean recovery and SD were calculated.

The expanded uncertainty UE ( $k=2$ ) 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. The expanded uncertainty varies from 2-17% depending on the analytical method, the product formulation and the available reference standards.

Samples were analysed by reversed phase high-performance liquid chromatography combined with diode array detection, (HPLC-DAD), gas chromatography with flame ionization detection (GF-FID) or liquid chromatography with mass spectrometric detection (LC-MS). TABLE 3 summarizes the applied method of analysis of the individual active substances.

**TABLE 3.** Summary of applied analytical methods.

Active substance	CAS no.	Principle	DTI method	Accreditation
Chlorophacinone	3691-35-8	HPLC-DAD	OO-859	Yes
		LC-MS	OA-1203	Yes
Cyromazine	66215-27-8	HPLC-DAD	OA-898	Yes
Icaridin	119515-38-7	GC-FID	OA-833	No
Imidacloprid	138261-41-3	HPLC-DAD	OA-812	Yes
IPBC	55406-53-6	HPLC-DAD	OA-892	Yes
Muscalure	27519-02-4	GC-FID	OA-834	No
Propiconazole	60207-90-1	HPLC-DAD	OA-892	Yes

### 1.3.2 Physical-chemical testing

The density of the formulations was determined according to DTI's analysis method UA-312. The method is based on CIPAC MT 3 (Ref. 7). The density of the product is determined as the average of a triple determination carried out by measuring with a densimeter. The method is accredited.

The results were used to determine the g/L content of the active substance in the products.

## 1.4 Insecticides

Six insecticides containing cyromazine, imidacloprid, muscalure and pyrethrin I+II were selected for the 2019 control campaign.

### 1.4.1 Results

The results of the performed measurements are listed in TABLE 4. RSD % is the percentage relative reproducibility of the determinations of the product.

**TABLE 4.** Analysis results (g/kg) of insecticides.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
862539-1	Imidacloprid	0.3	0.23-0.38	0.31	1.4	Comply
862539-2	Imidacloprid	0.3	0.23-0.38	0.31	1.8	Comply
862539-4	Imidacloprid	5.0	3.8-6.3	4.84	0.1	Comply
	Muscalure	1.01	0.76-1.26	1.08	0.2	Comply
862539-10	Cyromazin	20	15.0-25.0	22.3	3.9	Comply
862539-12	Cyromazin	20	15.0-25.0	17.3	1.7	Comply

**TABLE 5.** Analysis results (g/L) of insecticides.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
862539-13	Pyrethrin I+II	2.5	2.1-2.9	2.13	1.7	Comply

## 1.4.2 Conclusion

In all collected products, the measured content of cyromazine, imidacloprid, muscalure and pyrethrin I+II complies with the declared content and with applicable Danish law.

## 1.5 Repellents

Four repellents containing icaridin were selected for the 2019 control campaign.

### 1.5.1 Results

The results of the performed measurements are listed in TABLE 6. RSD % is the percentage relative reproducibility of the determinations of the product.

**TABLE 6.** Analysis results (% w/w) of repellents

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis results g/kg	RSD %	Comply/ Non-comply
862539-3	Icaridin	100	90-110	97.9	1.5	Comply

**TABLE 7.** Analysis results (g/L) of repellents

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis results g/L	RSD %	Comply/ Non-comply
862539-5	Icaridin	137	129-145	138	1.3	Comply
862539-6	Icaridin	140	131-148	147	2.3	Comply
862539-7	Icaridin	200	188-212	206	0.9	Comply

## 1.6 Rodenticides

Three rodenticides containing chlorophacinone were selected for the 2019 control campaign.

### 1.6.1 Results

The results of the performed measurements are listed in TABLE 8. RSD % is the percentage relative reproducibility of the determinations of the product.

**TABLE 8.** Analysis results (g/kg) of rodenticides.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis results g/kg	RSD %	Comply/ Non-comply
862539-8	Chlorophacinone	0.050	0.038-0.063	0.054	4.5	Comply
862539-9	Chlorophacinone	0.050	0.038-0.063	0.050	1.1	Comply
862539-11	Chlorophacinone	0.050	0.038-0.063	0.051	3.0	Comply

### 1.6.2 Conclusion

In all collected products, the measured content of chlorophacinone complies with the declared content and with applicable Danish law.

## 1.7 Wood protection products

One wood protection product containing the fungicides propiconazole and IPBC was selected for the 2019 control campaign.

### 1.7.1 Results

The results of the performed measurements are listed in TABLE 9. RSD % is the percentage relative reproducibility of the determinations of the product.

**TABLE 9.** Analysis results (g/L) of wood protection product.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis results g/L	RSD %	Comply/ Non-comply
862539-14	Propiconazol	9.01	7.66-10.4	9.03	0.3	Comply
	IPBC	3.01	2.56-3.46	2.56	0.8	Comply

### 1.7.2 Conclusion

In all collected products, the measured content of propiconazole and IPBC complies with the declared content and with applicable Danish law.

# References

1. Ministry of Environment and Food of Denmark, Environmental Protection Agency (Danish EPA) site; <https://eng.mst.dk/chemicals/biocides/> and <https://mst.dk/kemi/biocider/>
2. Danish EPA, 2019, approved Pesticides 2019 <http://mst.dk/kemi/database-for-bekaempelsesmidler/bmd/> (Danish).
3. Statutory Order on Pesticides. Statutory Order from the Ministry of the Environment, No. 815 of 22 June 2018, Statutory Order is in Danish.
4. Danish Technological Institute, Kongsvang Allé 29, DK-8000 Aarhus C, Denmark, <http://www.dti.dk/>
5. The Danish Accreditation and Metrology Fund – DANAK, <http://english.danak.dk/>
6. The e-Pesticide Manual, seventeenth Edition, online version, 2016. British Crop Protection Council, United Kingdom.
7. CIPAC method no. MT 3, <http://www.cipac.org/>

## Control of Biocides 2019

### English

This report describes the analytical chemical authority control of biocide products on the Danish market that was carried out in 2019 by the Danish Environmental Protection Agency (Danish EPA), Danish Chemical Inspection Service. Samples of selected types of biocides 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. 14 different biocide products were analysed. The measured content of active substances complied with the declared content in all 14 products as the result was within the range of tolerance.

### Danish

Den analytisk kemiske kontrol af biocidprodukter på det danske marked, der er udført i 2019 af den danske Miljøstyrelses Kemikalieinspektion, er beskrevet i denne rapport. Prøver fra udvalgte typer af biocidprodukter er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med det deklarerede indhold. I alt 14 biocidprodukter blev undersøgt. Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold i alle 14 produkter, idet resultatet var indenfor tolerancen.



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