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Environmental
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Control of Biocides 2018

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Preface

This report describes the analytical chemical control of biocides on the Danish market, which was carried out in 2018 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 2018.^{1,2}

22 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. 1647 af 17/12/2017 og nr. 815 af 18/06/2018.^{3,4}

Følgende typer af produkter blev analyseret, se tabel nedenfor:

- 2 insekticider indeholdende pyrethrin I+II.
- 20 træbeskyttelsesprodukter indeholdende fungiciderne 3-iodo-2-propynyl butylcarbammat (IPBC), propiconazol, tebuconazol og insekticidet permethrin.

Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold i 18 produkter, idet resultatet var indenfor tolerancen.

Det målte indhold af aktivstoffer var ikke i overensstemmelse med det deklarerede indhold i 4 produkter. Produkter, hvor der ikke er overensstemmelse med det deklarerede indhold, udtages til analyse igen i 2019.

Densitet blev målt på alle produkter, og for et enkelt produkt blev co-formulanten piperonyl butoxid analyseret.

Oversigt over antal analyserede produkter og konklusion.

Aktivstof	Antal analyserede produkter	Antal indenfor tolerance	Antal udenfor tolerance
IPBC & propiconazol	13	10	3
IPBC, propiconazol & tebuconazol	4	4	0
IPBC, propiconazol, tebuconazol & permethrin	1	1	0
Propiconazol	1	1	0
Pyrethrin I+II	2	1	1
Tebuconazol	1	1	0
Total	22	18	4

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 2018.^{1,2}

22 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. 1647 dated 17/12/2017 and no. 815 dated 18/06/2018.^{3,4}

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

- 2 insecticides containing pyrethrin I+II.
- 20 wood protection products containing the fungicides 3-iodo-2-propynyl butylcarbamate (IPBC), propiconazole, tebuconazole, and the insecticide permethrin.

The measured content of active substances complied with the declared content in 18 products as the result was within the range of tolerance.

The measured content of active substances did not comply with the declared content in 4 products. Non-comply products will be collected for analysis again in 2019.

The density was measured for all products and for one product the co-formulant piperonyl butoxide was analysed.

Outline of total number of analysed products and conclusion.

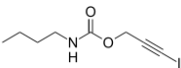
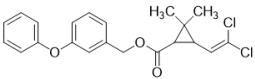
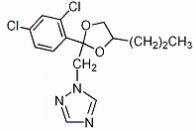
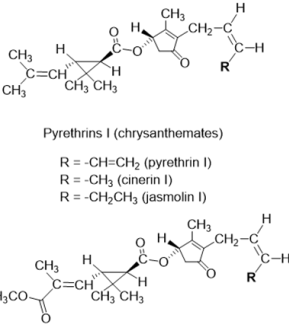
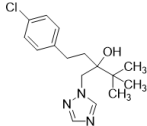
Active substance	No. of analysed products	No. within tolerance	No. outside tolerance
IPBC & propiconazole	13	10	3
IPBC, propiconazole & tebuconazole	4	4	0
IPBC, propiconazole, tebuconazole & permethrin	1	1	0
Propiconazole	1	1	0
Pyrethrin I+II	2	1	1
Tebuconazole	1	1	0
Total	22	18	4

1. Control campaign in 2018

1.1 Collecting products

The Danish 2018 biocide control campaign covered 5 active substances in different combinations in 22 products. The Danish Chemical Inspection Service of Danish EPA collected all products during the period from June to November 2018. The product samples were collected either from wholesale dealers/importers or at retailer outlets. A summary of the selected active substances is given in following table.

TABLE 1. Outline of selected active substances in the 2018 control campaign.

Active substance	CAS no.	Area of application	Year selected for control	Molecular structure ⁸
3-iodo-2-propynyl butyl-carbamate (IPBC)	55406-53-6	Wood protection, fungicide	2010	
Permethrin	52645-53-1	Wood protection, insecticide	2014, 2008	
Propiconazole	60207-90-1	Wood protection, fungicide	2010, 2006	
Pyrethrin I+II	8003-34-7	Insecticide	2017	 <p>Pyrethrins I (chrysanthemates)</p> <p>R = -CH=CH₂ (pyrethrin I) R = -CH₃ (cinerin I) R = -CH₂CH₃ (jasmolin I)</p> <p>Pyrethrins II (pyrethrates)</p> <p>R = -CH=CH₂ (pyrethrin II) R = -CH₃ (cinerin II) R = -CH₂CH₃ (jasmolin II)</p>
Tebuconazole	107534-96-3	Wood protection, fungicide	2010, 2008, 2002, 1998	

The collected product samples were stored at the Laboratory for Chemistry and Microbiology, Danish Technological Institute (DTI)⁵, 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. 1647 dated 17/12/2017 and no. 815 dated 18/06/2018 specify the general tolerance of deviation from the declared content of active substances.^{3,4} These tolerances are listed in table 2.

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

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

1.3 Analyses 2018

The analyses of the products for active substances were performed by DTI, Laboratory for Chemistry and Microbiology. DTI is a self-owned and not-for-profit Institute.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 17025.⁷ The laboratory has a flexible scope for determination of active substances in pesticides. 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 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. The uncertainty varies from 2-16% 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.

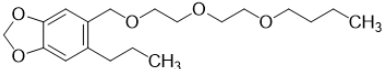
TABLE 3. Summary of applied analytical methods.

Active substance	CAS no.	Principle	DTI method	Accreditation
IPBC	55406-53-6	HPLC-DAD	OA-892	Yes
Permethrin	52645-53-1	HPLC-DAD	OA-892	Yes
		HPLC-DAD	OA-892	Yes
Propiconazole	60207-90-1	GC-FID	OA-830	No
		LC-MS	OA-1201	Yes
		HPLC-DAD	OA-879	No
Pyrethrin I+II	8003-34-7	HPLC-DAD	OA-879	No
Tebuconazole	107534-96-3	HPLC-DAD	OA-892	Yes

1.3.2 Analysing co-formulants

The co-formulant piperonyl butoxide was analysed in one sample containing pyrethrin I+II as active substance. An analytical scheme equivalent to the one described in section 1.4.1 for the analysis of active substances was applied to the co-formulant. 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.

TABLE 4. Co-formulants analysed in the 2018 control campaign.

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

1.3.3 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 3.⁸ 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. For one sample (DTI sample no. 818845-4), a pycnometer was used for the determination of density.

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

1.4 Insecticides

Two insecticides containing pyrethrin I+II were selected for the 2018 control campaign.

1.4.1 Results

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

TABLE 5. Analysis results of insecticides.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval	Analysis result g/L	RSD %	Comply/ Non-comply
818845-11	Pyrethrin I+II	2.5	2.1-2.9	1.6	3.5	Non-comply
818845-25	Pyrethrin I+II	30	27.0-33.0	28.2	0.6	Comply

1.4.2 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.

1.5 Wood protection products

Twenty wood protection products containing IPBC, propiconazole, tebuconazole and permethrin were selected for the 2018 control campaign.

1.5.1 Results

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

TABLE 6. Analysis results of wood protection products.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
818845-1	Propiconazole	9.0	7.7-10.4	9.4	1.9	Comply
	Tebuconazole	3.0	2.6-3.5	2.9	0.4	Comply
	IPBC	3.0	2.6-3.5	2.8	0.5	Comply
818845-2	Propiconazole	9.0	7.7-10.4	8.9	0.4	Comply
	Tebuconazole	3.0	2.6-3.5	2.9	0.6	Comply
	IPBC	3.0	2.6-3.5	2.9	0.7	Comply
818845-3	Propiconazole	1.9	1.6-2.2	2.0	1.4	Comply
	IPBC	6.1	5.2-7.0	5.7	1.4	Comply
818845-4	Tebuconazole	6.0	5.1-6.9	5.3	3.6	Comply
818845-5	Propiconazole	4.8	4.1-5.6	5.1	2.4	Comply
	Tebuconazole	1.6	1.4-1.8	1.7	0.4	Comply
	IPBC	1.6	1.4-1.8	1.4	1.4	Comply
	Permethrin	1.6	1.4-1.8	1.7	1.2	Comply
818845-6	Propiconazole	1.9	1.6-2.2	2.0	2.6	Comply
	IPBC	6.1	5.2-7.0	5.9	0.3	Comply
818845-7	Propiconazole	9.0	7.7-10.4	8.8	2.0	Comply
	Tebuconazole	3.0	2.6-3.5	2.9	0.4	Comply
	IPBC	3.0	2.6-3.5	2.9	1.2	Comply
818845-8	Propiconazole	1.9	1.6-2.2	2.0	2.5	Comply
	IPBC	6.1	5.2-7.0	5.9	0.4	Comply
818845-9	Propiconazole	2.4	2.0-2.8	2.6	1.3	Comply
	IPBC	7.6	6.5-8.7	7.3	1.1	Comply
818845-10	Propiconazole	2.4	2.0-2.8	2.3	2.3	Comply

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
	IPBC	7.5	6.4-8.6	5.9	0.1	Comply
818845-12	Propiconazole	2.4	2.0-2.8	2.5	0.9	Comply
	IPBC	7.6	6.5-7.7	7.2	1.3	Comply
818845-13*	Propiconazole	9.0	7.7-10.4	5.6	2.9	Non-comply
	IPBC	3.0	2.6-3.5	1.6	1.3	Non-comply
818845-14	Propiconazole	9.9	8.4-11.4	9.8	1.1	Comply
818845-15	Propiconazole	2.4	2.0-2.8	2.5	0.2	Comply
	IPBC	7.5	6.4-8.6	7.4	0.2	Comply
818845-16	Propiconazole	1.9	1.6-2.2	2.2	2.5	Comply
	IPBC	6.1	5.2-7.0	6.4	0.7	Comply
818845-17	Propiconazole	3.0	2.6-3.5	2.8	1.7	Non-comply
	IPBC	9.0	7.7-10.4	6.8	1.9	Non-comply
818845-18	Propiconazole	9.0	7.7-10.4	8.7	0.5	Comply
	IPBC	3.0	2.6-3.5	2.8	0.3	Comply
818845-19	Propiconazole	9.0	7.7-10.4	9.2	2.4	Comply
	Tebuconazole	3.0	2.6-3.5	3.0	2.0	Comply
	IPBC	3.0	2.6-3.5	2.8	2.5	Comply
818845-26*	Propiconazol	9.0	7.7-10.4	8.0	1.5	Comply
	IPBC	3.0	2.6-3.5	2.4	1.9	Non-comply
818845-31*	Propiconazol	9.0	7.7-10.4	8.6	0.7	Comply
	IPBC	3.0	2.6-3.5	2.8	0.5	Comply

*Sample 818845-13, -26 and -31 are samples of the same product. Sample 818845-13 and 818845-26 are subsamples from the same batch. Sample 818845-31 is from another batch. Subsamples of the product were provided by the manufacturer. Due to the non-comply conclusions of the submitted subsamples, a total of three subsamples was requested.

1.5.2 Conclusion

The measured content of IPBC, propiconazole, tebuconazole and permethrin complies with the declared content and with applicable Danish law in 18 of the 22 collected products. In two products, the measured concentration of both active substances (propiconazole and IPBC) did not comply with the declared content. For one product only, the measured concentration of the active substance IPBC did not comply with the declared content, whereas the other active substance propiconazole did comply.

1.6 Co-formulants

The co-formulant piperonyl butoxide was quantified in one biocide product containing pyrethrin I+II as active substance.

1.6.1 Results

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

TABLE 7. Analysis results of co-formulants in biocides.

DTI sample no.	Substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %
818845-25	Piperonyl butoxide	135	127-143	137	0.48

1.6.2 Conclusions

The measured content of piperonyl butoxide is comparable to the specified content. Because co-formulants are not subject to the regulation applying to the active substances, the results cannot be evaluated as comply/non-comply.

References

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Control of Biocides 2018

English

This report describes the analytical chemical authority control of biocide products on the Danish market that was carried out in 2018 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. A total of 22 different biocide products were analysed.

Danish

Den analytisk kemiske kontrol af biocidprodukter på det danske marked, der er udført i 2018 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 22 biocidprodukter blev undersøgt.



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