



Danish Ministry of the Environment
Environmental Protection Agency

Control of Pesticides and Biocides 2013

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

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Appendix 1:

Pesticide and biocide samples collected on the Danish market for authority control in 2013.

Foreword

26 different types of products, covered by the pesticide and biocide regulation, were included in the Danish authority control in 2013.

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.

For the 2013 programme, 2 tested products (1 biocides and 1 pesticide) did not comply with the tolerance limits defined by the Danish Statutory Order on pesticides No. 702 of 24 June 2011 incl. revisions, and in Regulation 1107/2009 concerning marketing of plant protection products¹⁺²⁺³.

Konklusion og sammenfatning

Denne rapport beskriver den analytisk kemiske kontrol af biocid- og pesticidprodukter på det danske marked, der er udført af Miljøstyrelsens Kemikalieinspektion i 2013.

26 produkter fra udvalgte typer af bekæmpelsesmidler 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. 702 af 24. juni 2011 inkl. revisioner og i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler¹⁺²⁺³.

26 forskellige produkter er inkluderet i den analytisk kemiske kontrol, der blev udført af myndighederne i 2013:

- 3 rodenticider indeholdende brodifacoum og flocoumafen
- 5 insekticider indeholdende cypermethrin og pymetrozin
- 12 herbicider indeholdende foramsulfuron, iodosulfuron, mesosulfuron og pendimethalin
- 4 fungicider indeholdende fludioxonil, fosetyl-aluminium og laminarin
- 1 vækstreguleringsmiddel indeholdende prohexadion-calcium.

Aktivstof	Antal analyserede produkter	Antal inden for tolerance	Antal uden for tolerance
Brodifacoum	3	2	1
Cypermethrin	4	3	1
Flocoumafen	1	1	0
Fludioxonil	1	1	0
Fosetyl-aluminium	2	2	0
Iodosulfuron, foramsulfuron, mesosulfuron	5	5	0
Laminarin	1	1	0
Pendimethalin	7	7	0
Prohexadione-calcium	1	1	0
Pymetrozine	1	1	0
Total	26	24	2

TABLE 1
OVERSIGT OVER ANTAL ANALYSEREDE PRODUKTER OG KONKLUSION

Det målte indhold af aktivstoffer er ikke i overensstemmelse med det deklarerede indhold i 2 produkter, og overholder således ikke gældende dansk lovgivning, idet der mangler overlap mellem interval for analyseresultat og tolerance.

Det målte indhold af aktivstoffer er i overensstemmelse med det deklarerede indhold in 24 produkter, og overholder således gældende dansk lovgivning, idet der er overlap mellem interval for analyseresultat og tolerance.

Conclusion and summary

This report describes the analytical chemical control of pesticide and biocide products on the Danish market that was carried out by the Danish Environmental Protection Agency (Danish EPA), Chemical Inspection Service, in 2013.

26 products from selected types of pesticides and biocides were collected and analysed to verify whether or not 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. 702 of 24 June 2011 incl. revisions, and in Regulation 1107/2009 concerning Marketing of Plant Protection Products¹⁺²⁺³.

26 different products are covered by the analytical chemical control that was carried out by the authorities in 2013:

- 4 rodenticides containing Brodifacoum and Flocoumafen
- 5 insecticides containing Cypermethrin and Pymetrozine
- 12 herbicides containing Foramsulfuron, Iodosulfuron, Mesosulfuron and Pendimethalin
- 4 fungicides containing Fludioxonil, Fosetyl-aluminium and Laminarin
- 1 plant growth regulator containing Prohexadion-calcium

Active substances	Number of analysed products	Number of products comply	Number of products non-comply
Brodifacoum	3	2	1
Cypermethrin	4	3	1
Flocoumafen	1	1	0
Fludioxonil	1	1	0
Fosetyl-aluminium	2	2	0
Iodosulfuron, Foramsulfuron, Mesosulfuron	5	5	0
Laminarin	1	1	0
Pendimethalin	7	7	0
Prohexadione-calcium	1	1	0
Pymetrozine	1	1	0
Total	26	24	2

TABLE 1
OUTLINE OF TOTAL OF ANALYSED PRODUCTS AND CONCLUSION

The measured content of active component did not comply with the declared content for 2 products and is not in compliance with applicable Danish law, because of the lack of overlap between the range of analysis results and tolerance.

The measured content of active compounds complies with the declared content for 24 products and is in compliance with applicable Danish law, because of the overlap between the range of analysis results and tolerance.

1. Control campaigns in 2013

1.1 Selected active substances

The control campaigns conducted in 2013 covered 12 active substances in pesticides. Overall, pesticides are distinguished in two types: plant protection products and biocides (non-agricultural pesticides).

An outline of the selected active substances is given in following table:

Type	Active substance	CAS no.	Area of application
Biocides	Brodifacoum	56073-10-0	Rodenticide
	Flocoumafen	90035-08-8	Rodenticide
Pesticides	Cypermethrin	52315-07-8	Insecticide
	Fludioxonil	131341-86-1	Fungicide
	Foramsulfuron	173159-57-4	Herbicide
	Fosetyl-aluminium	39148-24-8	Fungicide
	Iodosulfuron	144550-36-7	Herbicide
	Laminarin	9008-22-4	Fungicide
	Mesosulfuron	400852-66-6	Herbicide
	Pendimethalin	40487-42-1	Herbicide
	Prohexadione-calcium	127277-53-6	Plant Growth Regulator
	Pymetrozine	123312-89-0	Insecticide

TABLE 2
OUTLINE OF SELECTED ACTIVE SUBSTANCES IN CONTROL CAMPAIGNS IN 2013

1.2 Collecting products

Product samples of the various pesticide and biocide formulations from different manufacturers, covered in the 2013 control campaigns, were collected by the Chemical Inspection Service from the Danish Environmental Protection Agency, Chemical Inspection Service, during the period from April to August 2013. The product samples were collected from either wholesale dealers/importers or at retailer outlets.

A total of 26 products were collected. Among them, 4 were rodenticides, 12 were herbicides, 4 were fungicides, 5 were insecticides and 1 was a plant growth regulator.

The collected product samples were stored at Danish Technological Institute (DTI) 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. One product was stored in a refrigerator.

1.3 Tolerance for active substances

The Danish EPA aims to examine the content of active substances in the products and will compare the result of the chemical analysis with the content according to the specification of the products and the declared content on the label supplied by the authorisation holder.

The Danish Statutory Order on pesticides No. 702 of 24 June 2011 incl. revisions, and the Regulation 1107/2009 concerning Marketing of Plant Protection Products specify the general tolerance of deviation from the declared content¹⁺²⁺³. These tolerances are listed in the following table:

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

TABLE 3
THE TOLERANCE OF DEVIATION FROM THE DECLARED CONTENT OF ACTIVE SUBSTANCES 2013

1.4 Chemical analysis 2013

The analyses of the products for the active substances were performed by Danish Technological Institute, Laboratory for Chemistry and Microbiology. DTI is a self-owned and not-for-profit institute⁷.

The Laboratory for Chemistry and Microbiology is accredited by DANAK (Danish Accreditation and Metrology Fund), registration no. 90, according DS/EN ISO/IEC 17025⁸. The Laboratory also complies with the GMP regulation of the Danish Medicines Agency regarding analysis of medicinal products and intermediate products (§ 39).

1.4.1 Analysing active substances

The chemical analyses were performed as eight freshly prepared samples of each product. The analyses were distributed over two days (four samples each day), typically within the same week. The mean value of the eight analyses and the SD (standard deviation) were calculated for each day and for all eight results.

Validation of the applied analytical method was carried out. The method was validated with regard to linearity, specificity, accuracy and control tests at two levels spread over 2 days. Eight samples

were analysed from each product to which a known amount of the relevant active substance had been added in order to calculate the recovery.

The density of liquid products was determined by measuring with a densimeter called Densito 30 PX and as average of triple determination. The mean value and the SD were calculated.

The result in % (w/w) has been converted to g/L by using the measured density: $\text{Result (g/L)} = \text{Result (\% (w/w))} * \text{density (kg/L)} * 10$.

For each product, the expanded uncertainty ($k=2$) was calculated on the basis of the spread of the results of the eight analyses, the spread of the three density measurements (only included if the product is liquid), and bias was calculated on the basis of the eight recovery investigations. The expanded analysis uncertainty is used to determine a 95% confidence interval concerning the analysis result.

The results \pm the expanded uncertainty were compared with the tolerance of deviation calculated from the declared content of active substances.

2. Biocides

For the Danish 2013 Pesticide Control Campaign, 4 biocides were selected, all of them rodenticides. The selected active substances were Brodifacoum and Flocoumafen.

2.1 Rodenticides (Biocides)

Rodenticides containing Brodifacoum and Flocoumafen as active substances were selected for the control campaign for 2013. All products were examined for their content of active substances.

2.1.1 Brodifacoum

Brodifacoum is a rodenticide used in Denmark for control of rodents and moles. Chemically, it belongs to the group of hydroxycoumarines, and is an indirect anticoagulant. Brodifacoum inhibits the Vitamin K- dependent steps in synthesis of clotting factors.⁹⁺¹⁰ Products with Brodifacoum were previously selected in 2002 by the Danish EPA for control of content of active substances.

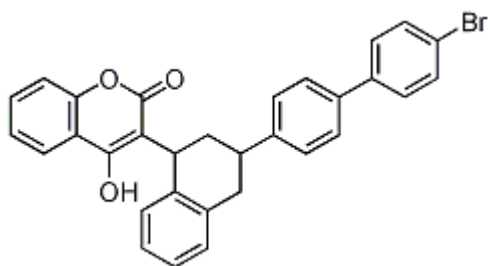


FIGURE 1 MOLECULE STRUCTURE OF BRODIFACOUM¹⁰, CAS NO. 56073-10-0

2.1.2 Flocoumafen

Flocoumafen is a rodenticide used in Denmark for control of rodents and moles. Chemically, it belongs to the group of hydroxycoumarines, and is a second generation indirect anticoagulant. Flocoumafen inhibits the metabolism of Vitamin K, and thereby blocks the formation of prothrombin.⁹⁺¹⁰ Products with Brodifacoum were previously selected in 1994 by the Danish EPA for control of content of active substances.

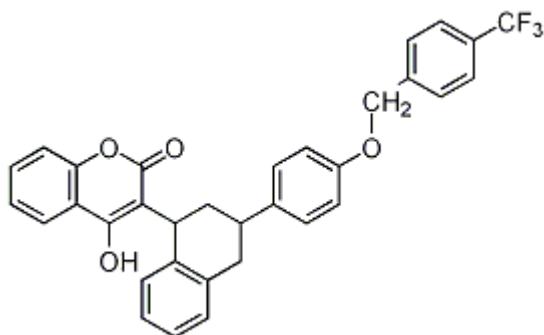


FIGURE 2 MOLECULE STRUCTURE OF FLOCOUMAFEN¹⁰, CAS NO. 90035-08-8

2.1.3 Analysis methods

Brodifacoum and Flocoumafen were analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved or diluted in methylene chloride and methanol and were ultrasound treated before the analysis. The method is a modified HPLC method according to AOAC-CIPAC method no. 370¹¹.

Details concerning the implementation of the analyses and the calculation of the result and expanded analysis uncertainty are described in chapter 1.4.1.

2.1.4 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following tables. % RSD is the percentage relative reproducibility of 8 determinations of the product. U_E is the calculated expanded measurement uncertainty described in section 1.4.1.

TI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	U_E g/kg	Analysis interval	Comply / Non-Comply
37504-29	Brodifacoum	0.05	0.038 – 0.063	0.027	11	0.0073	0.020 – 0.034	Non-Comply
37504-30	Brodifacoum	0.05	0.043 – 0.058	0,044	1,5	0,011	0,033 – 0,055	Comply
37504-31	Brodifacoum	0.05	0.038 – 0.063	0,040	3,6	0,007	0,033 – 0,047	Comply
37504-19	Flocoumafen	0.05	0.038 – 0.063	0.042	14.3	0.015	0.027 – 0.057	Comply

TABLE 4
ANALYSIS RESULTS OF RODENTICIDES (BIOCIDES), CONTENT IN G/KG

2.1.5 Conclusion

The measured content of Brodifacoum does not comply with the declared content for 1 product and is not in compliance with applicable Danish law, because of the lack of overlap between the range of analysis results and tolerance.

The measured content of Flocoumafen complies with the declared content for 1 product with applicable Danish law, because of the overlap between the range of analysis results and tolerance.

3. Pesticides

In the 2013 Danish Pesticide Control Campaign, a total of 22 pesticide products were selected: 12 herbicides, 4 fungicides, 5 insecticides and 1 plant growth regulator. The active substances in the selected pesticide products were Cypermethrin, Fludioxonil, Foramsulfuron, Fosetyl-Aluminium, Iodosulfuron, Laminarin, Mesosulfuron, Pendimethalin, Prohexadione-Calcium, and Pymetrozine. 4 herbicides were controlled for two active substances.

3.1 Herbicides (Pesticides)

Herbicides containing Foramsulfuron, Iodosulfuron, Mesosulfuron and Pedimethalin as active substances were selected for the control campaign for 2013. All products were examined for their content of selected active substances.

3.1.1 Foramsulfuron

Foramsulfuron is a herbicide used in Denmark for weed control in maize and Christmas trees etc. It is normally used in combination with other herbicides. Chemically, it belongs to the group of sulfonyleureas, and is a branched chain amino acid synthesis inhibitor. Foramsulfuron is particularly translocated to the meristematic regions, where it inhibits growth.⁹⁺¹⁰ Products with Foramsulfuron were previously selected in 2004 by the Danish EPA for control of content of active substances.

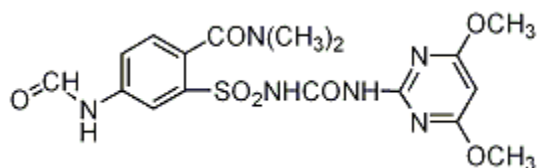


FIGURE 3 MOLECULE STRUCTURE OF FORAMSULFURON¹⁰, CAS NO. 173159-57-4

3.1.2 Iodosulfuron

Iodosulfuron is a herbicide used in Denmark for weed control in corn etc. It is often used in combination with other herbicides. Chemically, it belongs to the group of sulfonyleureas, and is a branched chain amino acid synthesis inhibitor. Iodosulfuron inhibits biosynthesis of two essential amino acids, hence stopping plant growth.⁹⁺¹⁰ Products with Iodosulfuron were previously selected in 2004 by the Danish EPA for control of content of active substances.

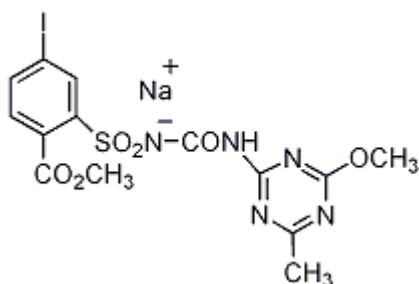


FIGURE 4 MOLECULE STRUCTURE OF IODOSULFURON¹⁰, CAS NO. 144550-36-7

3.1.3 Mesosulfuron

Mesosulfuron is a herbicide used in Denmark to control seed weeds in corn. It is normally used in combination with other herbicides. Chemically, it belongs to the group of sulfonylureas, and is a branched chain amino acid synthesis inhibitor. Mesosulfuron inhibits biosynthesis of two essential amino acids, hence stopping plant growth.⁹⁺¹⁰ Products with Mesosulfuron have not previously been selected by the Danish EPA for control of content of active substances.

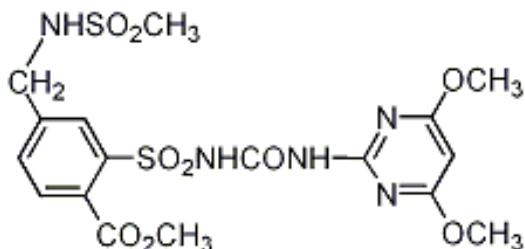


FIGURE 5 MOLECULE STRUCTURE OF MESOSULFURON¹⁰, CAS NO. 400852-66-6

3.1.4 Pendimethalin

Pendimethalin is a herbicide used in Denmark for weed control in, e.g., corn, grass, vegetables and bulbs. Chemically, it belongs to the group of dinitroanilines, and acts through microtubule assembly inhibition. Pendimethalin is a selective herbicide, absorbed by the roots and leaves.⁹⁺¹⁰ Products with Pendimethalin were previously selected in 2001 by the Danish EPA for control of content of active substances.

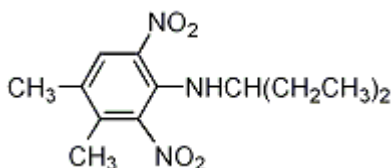


FIGURE 6 MOLECULE STRUCTURE OF PENDIMETHALIN¹⁰, CAS NO.40487-42-1

3.1.5 Analysis

Foramsulfuron, Iodosulfuron and Mesosulfuron were analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved in an acetonitrile/phosphoric acid buffer and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC method no. 411¹¹.

Pendimethalin was analysed by reversed phase high-performance liquid chromatography combined with UV detection. All samples were dissolved or diluted in acetonitrile or water/acetonitrile and were ultrasound treated before the analysis. The method is a modified HPLC method according to AOAC-CIPAC method no. 357¹¹.

Details concerning the implementation of the analyses and calculation of the result and expanded analysis uncertainty are described in chapter 1.4.1.

3.1.6 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following tables. % RSD is the percentage relative reproducibility of 8 determinations of the product. U_E is the calculated expanded measurement uncertainty described in section 1.4.1.

TI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	U _E g/kg	Analysis interval	Comply / Non-Comply
37504-13	Foram-sulfuron	300	285 - 315	306	2.3	18	288 - 324	Comply
37504-15	Foram-sulfuron	300	285 - 315	298	2.9	22	276 - 320	Comply
37504-13	Iodo-sulfuron	10	8.5 - 11.5	9,6	1.5	0,4	9,2-10,0	Comply
37504-15	Iodo-sulfuron	10	8.5 - 11.5	10	1.4	0,3	9,7 - 10,3	Comply
37504-20	Pendi-methalin	400	380-420	410	1.0	12	398 - 422	Comply

TABLE 5
ANALYSIS RESULTS OF HERBICIDES (PESTICIDES), CONTENT IN G/KG

TI sample no.	Active substance	Label claim g/l	Tolerance interval	Analysis result g/l	RSD %	U _E g/l	Analysis interval	Comply / Non-Comply
37504-5	Iodosulfuron-methyl-natrium	2.5	2.1 - 2.9	2.8	3.5	0.4	2.4 - 3.2	Comply
37504-6	Iodosulfuron-methyl-natrium	2.0	1.7 - 2.3	2.1	9.3	0.4	1.7 - 2.5	Comply
37504-8	Iodo-sulfuron	100	90 - 110	94	5.9	16.2	78 - 110	Comply
37504-5	Meso-sulfuron	7.5	6.8 - 8.6	7.7	9.0	2.0	5.7 - 9.7	Comply
37504-6	Meso-sulfuron	10	8.5 - 11.5	11.5	7.2	1.8	9.7 - 13.3	Comply
37504-2	Pendi-methalin	400	380-420	411	1.5	55	356 - 466	Comply
37504-3	Pendi-methalin	455	432 - 478	467	2.4	29	438 - 496	Comply
37504-4	Pendi-methalin	320	304 - 336	316	1.9	28	288 - 344	Comply
37504-10	Pendi-methalin	330	314 - 347	338	0.4	18	320 - 356	Comply
37504-17	Pendi-methalin	330	314 - 347	339	3.0	10	329 - 349	Comply

TI sample no.	Active substance	Label claim g/l	Tolerance interval	Analysis result g/l	RSD %	U _E g/l	Analysis interval	Comply / Non-Comply
37504-27	Pendimethalin	330	314 - 347	343	0.9	47	296 - 390	Comply

TABLE 6
ANALYSIS RESULTS OF HERBICIDES (PESTICIDES), CONTENT IN G/L

3.1.7 Conclusion

The measured content of Foramsulfuron, Iodosulfuron, Mesosulfuron and Pendimethalin complies with the declared content of all 12 products and is in compliance with applicable Danish law because of the overlap between the range of analysis results and tolerance.

3.2 Fungicides (Pesticides)

Fungicides containing Fludioxonil, Fosetyl-Aluminium and Laminarin as active substances were selected for the Danish Pesticide Control Campaign in 2013. All products were examined for their content of active substances.

3.2.1 Fludioxonil

Fludioxonil is a fungicide used in Denmark to control fungal diseases in corn. Chemically, it belongs to the group of phenylpyrroles and inhibits mitogen-activated protein kinase in osmotic signal transduction. Fludioxonil is a non-systemic fungicide with long residual activity. Uptake into the plant tissues and curative properties are generally limited.⁹⁺¹⁰ Products with Fludioxonil have not previously been selected by the Danish EPA for control of content of active substances.

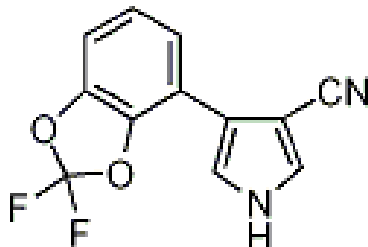


FIGURE 7 MOLECULE STRUCTURE OF FLUDIOXONIL¹⁰, CAS NO. 131341-86-1

3.2.2 Fosetyl-Aluminium

Fosetyl-Aluminium is a fungicide used in Denmark to control fungal diseases in, e.g., outdoor lettuce and strawberries, melon, vegetables on ornamental plants outdoor and in greenhouses. Chemically, it belongs to the group of phosphonates. Fosetyl-Aluminium is a systemic fungicide that possibly acts by inhibiting germination of spores or by blocking development of mycelium and sporulation. Fosetyl-Aluminium is rapidly absorbed through the plant leaves or roots, with translocation both acropetally and basipetally.⁹⁺¹⁰ Products containing Fosetyl-Aluminium have not previously been selected by the Danish EPA for control of content of active substances.

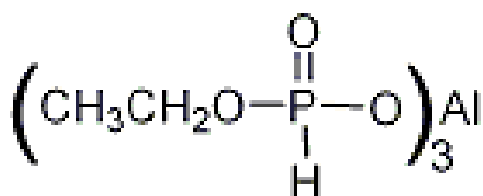


FIGURE 8 MOLECULE STRUCTURE OF F FOSETYL-ALUMINIUM¹⁰, CAS NO. 39148-24-8

3.2.3 Laminarin

Laminarin is a fungicide used in Denmark to control fungal diseases in strawberries. Laminarin induces host plant defence system by stimulating the plant's natural defence mechanisms.

Laminarin is reported to be a systemic acquired resistance inducer.⁹⁺¹⁰ The product containing Laminarin was approved by the Danish EPA in 2013 and has not previously been selected for control of content of active substances.

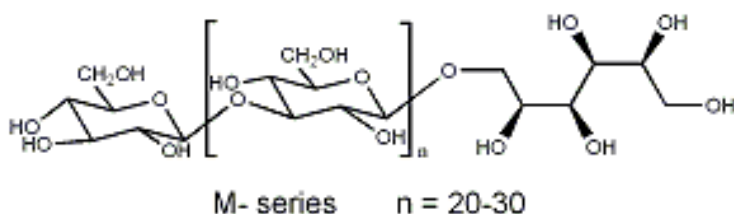


FIGURE 9 MOLECULE STRUCTURE OF LAMINARIN¹⁰, CAS. NO. 9008-22-4

3.2.4 Analysis

Fludioxonil was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved or diluted in methanol and were ultrasound treated before the analysis.

The content of aluminium in Fosetyl-Aluminium was analysed by atom absorption spectrometry in flame (AAS) according to DS 262:1982 Determination of aluminium in water, sludge and sediment by atomic absorption spectrophotometry in flame. To verify the identity of Fosetyl-Aluminium, the samples were analysed by ion chromatography. The samples were dissolved in water, diluted in a buffer and were ultrasound treated before the analysis. The method is a modified method according to CIPAC method no. 384¹¹.

Laminarin was analysed by high-performance liquid chromatography combined with refraction index detection, HPLC-RI, with a TSK-GEL® Gel Filtration Column. All samples were dissolved or diluted in water and methanol and were ultrasound treated before the analysis.

Details concerning the implementation of the analyses and calculation of the result and expanded analysis uncertainty are described in chapter 1.4.1.

3.2.5 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following tables. % RSD is the percentage relative reproducibility of 8 determinations of the product. U_E is the calculated expanded measurement uncertainty described in section 1.4.1.

TI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	U_E g/kg	Analysis interval	Comply / Non-Comply
37504-24	Fosetyl-Aluminium	800	775 - 825	794	2.3	54	740 - 849	Comply
37504-25	Fosetyl-Aluminium	800	775 - 825	790	1.1	27	764 - 817	Comply

TABLE 7
ANALYSIS RESULTS OF FUNGICIDES (PESTICIDES), CONTENT IN G/KG

TI sample no.	Active substance	Label claim g/l	Tolerance interval	Analysis result g/l	RSD %	U_E g/l	Analysis interval	Comply / Non-Comply
37504-23	Fludioxonil	100	90 - 110	97	3.4	12	85 - 109	Comply
37504-22	Laminarin	45	41 - 50	44	1.8	2.2	42 - 46	Comply

TABLE 8
ANALYSIS RESULTS OF FUNGICIDES (PESTICIDES), CONTENT IN G/L

3.2.6 Conclusion

The measured content of Fludioxonil, Fosetyl-Aluminium and Laminarin complies with the declared content of all 4 products, and is in compliance with applicable Danish law because of the overlap between the range of analysis results and tolerance.

3.3 Insecticides (Pesticides)

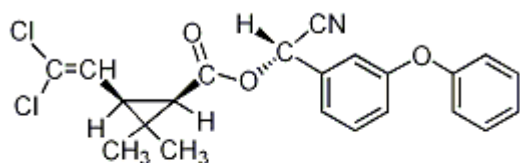
Insecticides containing Cypermethrin and Pymetrozine as active substances were selected for the 2013 control campaign. All products were examined for their content of active substances.

3.3.1 Cypermethrin

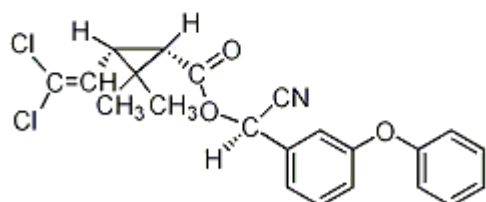
Cypermethrin is an insecticide used in Denmark to control insect pests in, e.g., corn, grass, vegetables including lettuce, cabbage and root crops plus tomatoes, cucumbers and aubergines in greenhouses and also timber and conifers.

Chemically, it belongs to the group of pyrethroides. Cypermethrin acts on the nervous system of the insect, and disturbs the function of neurons by interaction with the sodium channel. Cypermethrin acts as a non-systemic insecticide with contact and stomach action. Also exhibits anti-feeding action. Good residual activity on treated plants.⁹⁺¹⁰ Products containing Cypermethrin were previously selected in 2003 by the Danish EPA for control of content of active substances.

(S) (1*R*)-*cis*-



+



(R) (1*S*)-*cis*-

FIGURE 10 MOLECULE STRUCTURE OF CYPERMETHRIN[®], CAS NO. 52315-07-8

3.3.2 Pymetrozine

Pymetrozine is an insecticide used in Denmark to control insect pests in rape as well as ornamental plants, tomatoes, lettuce, cucumbers and peppers in greenhouses. It belongs to the group of selective feeding blockers. The biochemistry is novel and unidentified. Pymetrozine acts as a selective insecticide against Homoptera, causing them to stop feeding.⁹⁺¹⁰ Products containing Pymetrozine have not previously been selected by the Danish EPA for control of content of active substances.

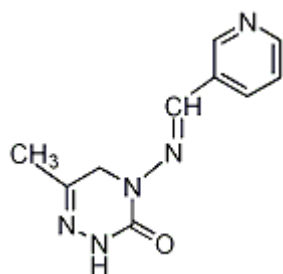


FIGURE 11 MOLECULE STRUCTURE OF PYMETROZINE[®], CAS NO. 123312-89-0

3.3.3 Analysis methods

Cypermethrin was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved in methanol and were ultrasound treated before the analysis. The method is a modified HPLC method according to CIPAC method no. 332¹¹.

Pymetrozine was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved in methanol and were ultrasound treated before the analysis.

Details concerning the implementation of the analyses and calculation of the result and expanded analysis uncertainty are described in chapter 1.4.1.

3.3.4 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following tables. % RSD is the percentage relative reproducibility of 8 determinations of the product. U_E is the calculated expanded measurement uncertainty described in section 1.4.1

TI sample no.	Active substance	Label claim g/kg	Tolerance interval	Analysis result g/kg	RSD %	U_E %	Analysis interval	Comply / Non-Comply
37504-9	Pymetrozin	500	475 - 525	513	1.0	26	476 – 527	Comply

TABLE 9
ANALYSIS RESULTS OF INSECTICIDES (PESTICIDES), CONTENT IN G/KG

TI sample no.	Active substance	Label claim mg/l	Tolerance interval	Analysis result g/l	RSD %	U_E g/l	Analysis interval	Comply / Non-Comply
37504-1	Cypermethrin	100	90 - 110	103	1.2	10	93 – 113	Comply
37504-7	Cypermethrin	100	90 - 110	98.9	0.88	9.3	89.6–108.2	Comply
37504-16	Cypermethrin	0.02	0.017-0.023	0.039	3.6	0.0078	0.031 – 0.047	Non-Comply
37504-28	Cypermethrin	500	475 - 525	520	2.5	109	411 – 629	Comply

TABLE 10
ANALYSIS RESULTS OF INSECTICIDES (PESTICIDES), CONTENT IN G/L

3.3.5 Conclusion

The measured content of Cypermethrin does not comply with the declared content in 1 product and is not in compliance with applicable Danish law, because of the lack of overlap between the range of analysis results and tolerance.

The measured content of Cypermethrin and Pymetrozine complies with the declared content for 4 products and is in compliance with applicable Danish law, because of the overlap between the range of analysis results and tolerance.

3.4 Plant Growth Regulator (Pesticide)

Plant Growth Regulator containing Prohexadione-Calcium as active substances was selected for the 2013 control campaign. The product was examined for its content of the selected active substance.

3.4.1 Prohexadione-Calcium

Prohexadione-Calcium is a plant growth regulator used in Denmark to control growth in corn etc. Prohexadione-Calcium inhibits 3β -hydroxylation of GA_{20} to GA_1 in gibberellin biosynthesis. The reduced level of gibberellins leads to growth retardation of plants. Foliar-applied and absorbed via green tissue: translocated basipetally, as well as acropetally, within plants. ⁹⁺¹⁰

The product containing Prohexadione-Calcium was approved by the Danish EPA in 2012 and has not previously been selected for control of content of active substances.

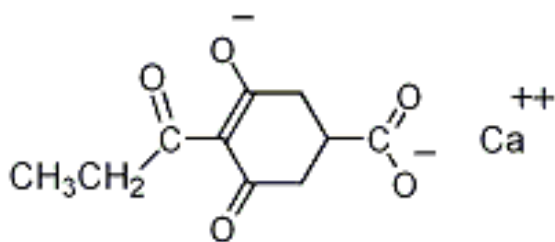


FIGURE 12 MOLECULE STRUCTURE OF PROHEXADIONE-CALCIUM¹⁰, CAS. NO. 127277-53-6

3.4.2 Analysis methods

Prohexadione-Calcium was analysed by reversed phase high-performance liquid chromatography combined with UV detection, HPLC-UV. All samples were dissolved in acetonitrile and phosphate buffer and were ultrasound treated before the analysis.

Details concerning the implementation of the analyses and calculation of the result and expanded analysis uncertainty are described in chapter 1.4.1.

3.4.3 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following tables. % RSD is the percentage relative reproducibility of 8 determinations of the product. U_E is the calculated expanded measurement uncertainty described in section 1.4.1

TI sample no.	Active substance	Label claim g/l	Tolerance interval	Analysis result g/l	RSD %	U_E g/l	Analysis interval	Comply / Non-Comply
37504-21	Prohexadione-Calcium	50	45 - 55	54	0,2	2,7	51 - 56	Comply

TABLE 11 ANALYSIS RESULTS OF PLANT GROWTH REGULATORS (PESTICIDES), CONTENT IN G/L

3.4.4 Conclusion

The measured content of Prohexadione-Calcium complies with the declared content for the product and is in compliance with applicable Danish law, because of the overlap between the range of analysis results and tolerance.

References

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7. Danish Technological Institute, <http://www.dti.dk/>
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10. The e-Pesticide Manual, fifteenth Edition, version 5.1 online, 2010-2011. British Crop Protection Council, United Kingdom.
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13. Danish Ministry of the Environment, Environmental Protection Agency, Control of Pesticides and Biocides 2011, Working Report No. 1, 2012.
14. Danish Ministry of the Environment, Environmental Protection Agency, Control of Pesticides and Biocides 2012, Working Report No. 7, 2013.

Appendix 1: Pesticide and biocide samples collected on the Danish market for authority control in 2013

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
37504-29	Brodifacoum	732-1	Klerat Voksblok	Syngenta Crop Protection AG
37504-30	Brodifacoum	2-83	Rentokil Brodifacoum pasta mod mus	Rentokil Initial A/S
37504-31	Brodifacoum	732-2	Klerat pellets	Syngenta Crop Protection AG
37504-19	Flocoumafen	19-128	Storm rotteblok	BASF A/S

TABLE 12
COLLECTED RODENTICIDES (BIOCIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
37504-13	Foramsulfuron, Iodosulfuron	18-442	MaisTer	Bayer A/S, Bayer CropScience
37504-15	Foramsulfuron, Iodosulfuron	18-484	Logo	Bayer A/S, Bayer CropScience
37504-5	Iodosulfuron-methyl-natrium, Mesosulfuron	18-520	Othello	Bayer A/S, Bayer CropScience
37504-6	Iodosulfuron-methyl-natrium, Mesosulfuron	18-505	Atlantis OD	Bayer A/S, Bayer CropScience
37504-8	Iodosulfuron	18-493	Hussar OD	Bayer A/S, Bayer CropScience
37504-2	Pendimethalin	19-138	Stomp	BASF A/S
37504-3	Pendimethalin	19-205	Stomp CS	BASF A/S
37504-4	Pendimethalin	19-172	Flight Xtra	BASF A/S
37504-10	Pendimethalin	19-142	Stomp Pentagon	BASF A/S
37504-17	Pendimethalin	653-11	Sharpen 33% EC	Sharda Europe b.v.b.a
37504-20	Pendimethalin	396-36	Activus 40 WG	Makhteshim-Agan Holland B.V.
37504-27	Pendimethalin	221-140	Inter-Pendimethalin 330	Inter Trade, Aalborg A/S

TABLE 13
COLLECTED HERBICIDES (PESTICIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
37504-23	Fludioxonil	650-97	Agros Fludioxonil 100	Syngenta
37504-24	Fosetyl-Aluminium	18-407	Aliette WG 80	Bayer A/S, Bayer CropScience
37504-25	Fosetyl-Aluminium	318-177	LFS Fosetyl	Bayer A/S, Bayer CropScience
37504-22	Laminarin	740-1	Vacciplant	GOËMAR

TABLE 14
COLLECTED FUNGICIDES (PESTICIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
37504-1	Cypermethrin	579-3	Cyperb-100 W	SBM Développement
37504-7	Cypermethrin	579-2	Cyperb 100	SBM Développement
37504-16	Cypermethrin	579-1	Maladan Insekt spray	SBM Développement
37504-28	Cypermethrin	361-14	CythrIn 500	Agriphar S.A.
37504-9	Pymetrozin	1-216	Plenum 50 WG	Syngenta Crop Protection A/S

TABLE 15
COLLECTED INSECTICIDES (PESTICIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
37504-21	Prohexadione-Calcium	19-201	Medax Top	BASF A/S

TABLE 16
COLLECTED PLANT GROWTH REGULATORS (PESTICIDES)

Control of Pesticides and Biocides 2013

English

The analytical chemical authority control of pesticide and biocide products on the Danish market that was carried out in 2013 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 complied with the product specification and the labelled content. A total of 26 different pesticide products were analysed. The content of active substance in 2 of the analysed 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 2013 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 26 bekæmpelsesmidler. Indholdet af aktivstoffet i 2 af de analyserede produkter var ikke indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler



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