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Control of Biocides 2022

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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 that was carried out in 2022 by the Danish Chemical Inspection Service of the Danish Environmental Protection Agency. The control is part of the “Danish Political Agreement on biocidal initiatives 2022-2025, Control on Biocides”. Biocide products available on the Danish market were collected and analysed to verify whether the content of active substances in the product complies with the labelled content and the information supplied to the Danish Environmental Protection Agency. Additionally, a range of biocide samples were collected for ad hoc rodenticide analysis.

Abbreviations

a.s.: Active substance

DTI: Danish Technological Institute

DDAC: Didecyltrimethylammonium chloride (CAS no. 7173-51-5)

DANAK: Danish Accreditation and Metrology Fund

STD: Standard deviation

Resume

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

Den planlagte kontrolkampagne dækkede over to aktivstoffer som forefindes i seks udvalgte biocidprodukter. De indsamlede produkter er listet i tabellen nedenfor. Produkterne blev analyseret for at verificere, om indholdet af de respektive aktivstoffer var i overensstemmelse med produktspecifikationen og det deklarerede indhold. Grænsen for en accepteret afvigelse i indholdet af aktivstof i forhold til det deklarerede indhold er fastsat i bekendtgørelsen om bekæmpelsesmidler nr. 1278 af 06/06/2021 (gældende bekendtgørelse nr. 1569 af 19/12/2022, Ref. 2).

Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold for 5 ud af 6 produkter, idet resultatet var indenfor toleranceintervallet.

Overblik over analyserede produkter og aktivstoffer, som er en del af kontrolkampagnen 2022.

Aktiv stof	Antal af analyserede produkter	Antal indenfor toleranceinterval	Antal udenfor toleranceinterval
Nonanoic acid	4	3	1
DDAC	2	2	0
Total	6	5	1

Derudover blev der indsamlet en række prøver til ad hoc-analyse:

- Ni prøver blev indsamlet, hvor der var mistanke om uautoriseret anvendelse af rodenticider. Der blev påvist rodenticide aktivstoffer i alle ni prøver.

Abstract

This report documents the analytical chemical control of selected biocidal products on the Danish market. These tests are part of the Danish Environmental Protection Agency's Chemicals Inspection in 2022 (Ref. 1).

The planned control campaign covered two active substances found in six biocide products. The collected products are listed in the table below. The products were analysed to verify whether the content of the active substances in the products in question complied with the product specification and the declared content. The tolerance interval of an active substance is specified in the Danish Statutory Order on Pesticides No. 1278 of 06/06/2021 (applicable Danish Statutory Order 1569 of 19/12/2022) (Ref. 2).

The measured content of active substances was in accordance with the declared content for 5 out of 6 products, as the results were within the tolerance interval.

Overview of analysed products and active substances in the control campaign 2022.

Active substance	No. of analysed products	No. within tolerance	No. outside tolerance
Nonanoic acid	4	3	1
DDAC	2	2	0
Total	6	5	1

Additionally, a range of potential rodenticides samples were collected for ad hoc analysis:

- Nine ad hoc samples were collected. They were suspected of being rodenticides used without authorization. Rodenticides were identified in all nine samples.

1. Control of biocides 2022

The control of biocides 2022 was divided into two main activities:

- The planned control campaign of 2022.
- The ad hoc control of rodenticides utilized without permit.

1.1 The planned control campaign 2022

The planned control campaign conducted in 2022, covered two active substances (a.s.). The two a.s. were present in six commercial products found on the Danish market. The a.s. are presented in TABLE 1. The a.s. were selected according to their sales figures in the previous years, availability at retailers, and whether they had been part of previous campaigns. Products were collected by the Chemical Inspection Service of the Danish Environmental Protection Agency in April 2022. The products were collected from wholesale dealers/importers or at retailers.

TABLE 1. Overview of selected active substances in the 2022 control campaign.

Area of application	Active substance	CAS no.
Algaecides	Nonanoic acid	112-05-0
Algaecides	Didecyldimethylammonium chloride (DDAC)	7173-51-5

The collected products were stored at the Laboratory for Chemistry and Microbiology, Danish Technological Institute (DTI) (Ref. 4), in their original packaging until the chemical analyses were initiated. The products were stored at ambient temperature and protected from light during the entire storage period.

1.2 Ad hoc rodenticides

According to Statutory Order no. 2307 of 06/12/2021 (Ref. 3), the application of anticoagulant rodenticides is restricted to authorized exterminators only. Upon suspicion of unauthorized use of rodenticides, samples were collected by the municipalities in Denmark, and submitted for analysis of anticoagulant rodenticides.

1.3 Analysis

The analyses of the products and samples were performed by DTI, 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 Danish Accreditation and Metrology Fund (DANAK), registration no. 90, according to DS/EN ISO/IEC 17025:2017 (Ref. 5).

2. Control campaign 2022

2.1 Collected products

A total of six biocide products were collected by the Chemical Inspection Service of the Danish Environmental Protection Agency. All products are categorised as algaecides. The algaecides contained Nonanoic acid or Didecyldimethylammonium (DDAC) as a.s.

2.2 Tolerances on active substance concentration

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

The Danish Statutory Order on Pesticides No. 1278 of 06/06/2021 (applicable Danish Statutory Order 1569 of 19/12/2022) specifies the general tolerance of deviation from the declared content of active substances (Ref. 2). These tolerances are listed in TABLE 2.

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

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

2.3 Analysis

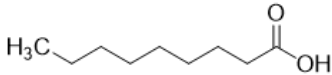
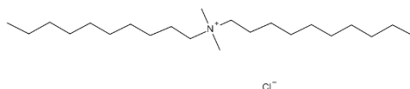
2.3.1 Analysis of active substances

The quantitative analyses were performed on a homogenous sub-sample prepared from each product. Five independent quantitative measurements were conducted for each product. If the average result was outside the tolerance interval, then the analysis was repeated with a minimum of five new and freshly prepared samples. The methods used for quantification were validated with regards to linearity, specificity, accuracy, and by using control reference material.

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

The expanded uncertainty ($k = 2$) for each method was calculated according to the spread of the analysis results, the recovery, and to the purity of the reference standard. The expanded uncertainty is used to determine a 95% confidence interval of the result. The expanded uncertainty varies from 8-35% for the analytical methods depending on the method, the product formulation, and the purity of available reference standards.

TABLE 3. Biocides in the 2022 control campaign.

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 6)
			Principle	DTI method	Accreditation	Adapted from reference method	
Nonanoic acid	112-05-0	-	HPLC-DAD, GC-FID*	OA-841, OA-910*	Yes	-	
DDAC	7173-51-5	-	LC-MS	OA-1204	Yes	-	

*Analytical method depends on product formulation

2.3.2 Relative density

The density of all liquid products was measured. The results were used to calculate the a.s. in g/L for each product. The density was determined according to DTI's analysis method UA-312. The method is based on CIPAC MT 3 (Ref. 8) and is accredited. The density of the product is determined as the average of a triple determination carried out by measuring with a Densito 30 PX densitometer.

2.4 Results and conclusions

The results of the quantification analysis of a.s. are presented in TABLE 4.

TABLE 4. Analysis results (g/L) in algaecides.

DTI sample no.	Active Substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
133174-1	Nonanoic acid	500	475-525	477	1.3	Comply
133174-2	Nonanoic acid	187	176-198	184	3.0	Comply
133174-3	Nonanoic acid	187	176-198	180	1.6	Comply
133174-4	DDAC	4.98	4.23-5.73	5.33	2.0	Comply
133174-5	Nonanoic acid	33	30-36	15	2.1	Non-comply
133174-6	DDAC	5	4.3-5.8	5	2.5	Comply

3. Ad hoc rodenticide samples

3.1 Collected products

A total of nine samples were submitted for identification and quantification of rodenticides as part of the ad hoc program. The physical condition of the samples varied from pristine to weathered, and the samples were in some cases mixed with other debris, e.g., soil or grain. The collected samples are listed in TABLE 6.

3.2 Analysis

The ad hoc samples were analysed for eight anticoagulant rodenticides according to DTI's method OA-1108 (TABLE 5). The method relies on screening by liquid chromatography with mass spectrometric detection (LC-MS) to determine the a.s. in the product. This analysis is followed by reversed phase liquid chromatography with diode array detection (HPLC-DAD) to both verify and quantify the content of the a.s. The HPLC method is modified from CIPAC method 370 brodifacoum (Ref. 7). The quantitative analysis was performed as a minimum with two replicates.

TABLE 5. Rodenticides included in screening program.

Active substance	CAS no.
Bromadiolone	28772-56-7
Difenacoum	56073-07-5
Difethialone	104653-34-1
Brodifacoum	56073-10-0
Flocoumafen	90035-08-8
Chlorophacinone	3691-35-8
Coumatetralyl	5836-29-3
Warfarin	81-81-2

3.3 Results and conclusions

The results of the analyses of the ad hoc rodenticide samples are listed in TABLE 6. RSD% is the percentage relative reproducibility of the determinations of the product. Rodenticides were identified in all nine samples.

TABLE 6. Analysis results of rodenticides in ad hoc samples.

EPA no.	DTI no.	Sample type	Identified a.s.	Analysis result g/kg	RSD%
2020-59553	119071-1	Blue powder	Coumatetralyl	< 0.01	-
2022-6214	120801-1	Blue/green grains	Difenacoum	0.058	1.0
2022-49807	146790-1	Blue grains	Bromadiolon	0.040	1.8
2022-49807	146790-2	Red grains	Bromadiolon	0.032	0.036
2022-45335	152401-1	Blue block	Brodifacoum	0.023	0.038
2022-78579	160667-1	Blue powder	Coumatetralyl	0.027	0.14
2022-78573	160669-1	Red block	Bromadiolon	0.044	0.43

2022-80538	161598-1	Red grains	Brodifacoum	0.034	8.6
2022-4511	161599-1	Red powder	Brodifacoum	0.030	0.77

a.s.: active substance

4. References

1. The Danish Environmental Agency, www.mst.dk, <https://mst.dk/kemi/biocider/> (in Danish) or <https://eng.mst.dk/chemicals/biocides/>
2. Statutory Order on Pesticides No. 1278 of 06/06/2021 (applicable Danish Statutory Order 1569 of 19/12/2022)
3. Statutory Order no. 2307 of 06/12/2021 Bekendtgørelse om forebyggelse og bekæmpelse af rotter (Statutory Order on prevention and control of rodents)
4. Danish Technological Institute, Kongsvang Allé 29, DK-8000 Aarhus C, Denmark, www.teknologisk.dk (in Danish), <http://www.dti.dk/>
5. The Danish Accreditation and Metrology Fund – DANAK, www.danak.dk (in Danish), <http://english.danak.dk/>
6. The e-Pesticide Manual, Eighteenth Edition, online version, 2021. British Crop Protection Council, United Kingdom
7. CIPAC method Brodifacoum 370, <http://www.cipac.org/>
8. CIPAC MT 3 Specific gravity, density, and weight per millilitre. <http://www.cipac.org/>

Appendix 1

Biocide products collected for the planned control campaign 2022

TABLE 7. Algaecides products.

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
133174-1	Nonanoic acid	632-12	AlgeVæk	Belchim Crop Protection NV/SA
133174-2	Nonanoic acid	364-74	Flügger Facade Algefjerner	W. Neudorff GmbH KG
133174-3	Nonanoic acid	364-16	AlgeFri _N Koncentrat	W. Neudorff GmbH KG
133174-4	DDAC	542-10	Protox Algefjerner	Protox ApS
133174-5	Nonanoic acid	364-17	AlgeFri _N	W. Neudorff GmbH KG
133174-6	DDAC	777-9	Neutralon – Klar til brug	Nowocoat Industrial A/S

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English

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Danish

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