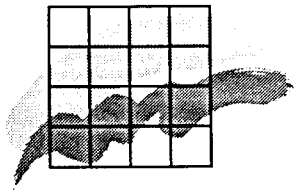

Chemical substances and chemical preparations

Control of pesticides 1994

NERI Technical Report No. 136
1995

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Ministry of Environment and Energy
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Contents

Summary

The analytical chemical authority control performed in 1994 on pesticide products on the Danish market is reported. Samples of selected groups of pesticides have been collected from the market and analysed to check whether the actual content of active ingredient agreed with the label claimed content. The tolerated limits of deviation of active ingredient content from label claim content are set by Danish pesticide regulations.

Three different groups of products covered by the pesticide regulations have been included in the authority control: 1) herbicides of the sulfonylurea type, 2) plant growth regulators containing chlormequat chloride as active ingredient and 3) various rodenticides containing coumarin-derived active ingredients.

Satisfactory results were found among products belonging to groups 1 and 2: The four examined samples of sulfonylurea herbicides containing the active ingredients chlorsulfuron, metsulfuron-methyl, thifensulfuron-methyl and tribenuron-methyl, respectively, all complied with the tolerated limits of active ingredient content. The same was found for all ten examined samples of products containing chlormequat chloride as active ingredient.

Unsatisfactory results were found among products belonging to group 3. Samples of products containing difenacoum, brodifacoum, flocoumafen or difethialone as active ingredient were examined. Four out of eight examined samples did not comply with the tolerated limits for content of active ingredient.

1 Introduction

In Denmark the Danish Environmental Protection Agency (DEPA) is responsible for evaluation and approval of all pesticides before they are introduced on the Danish market. Legal regulations for pesticides are given in a Statutory Order from the Ministry of the Environment *(Miljøministeriet, 1994)*, which also states that DEPA is responsible for control in relation to pesticides.

In practice authority control activities of pesticides on the market are organized in a way, that the Chemicals Inspection Service, DEPA conducts non-laboratory control and the National Environmental Research Institute conducts the laboratory control of pesticides as an assistance to DEPA. The present report describes only the part of the authority control of pesticides involving laboratory control.

Laboratory control of pesticides covers analytical chemical examination of technical pesticides or pesticide formulations in order to control whether the products comply with regulations as well as with the specification of contents supplied in connection with application for approval of the pesticide product.

Analytical chemical control can involve check of content of active ingredient as well as content of auxiliary matters or levels of impurities.
Laboratory control work covers two types of projects: 1) Ordinary control in the form of planned campaigns, where all products with a common characteristic, e.g. the same active ingredient, are collected from the market and examined, and 2) *ad hoc* projects, which consist of laboratory control needed in connection with administrative work at the regulatory authorities, e.g. complaints from users concerning a specific product, suspicion of a product not complying with regulations/specifications, etc.

Only the first type of control, campaigns, is covered by this report, which describes the laboratory control performed in 1994.

2 Control campaigns in 1994

Control campaigns conducted in 1994 have covered pesticides belonging to three different groups of pesticides: herbicides, plant growth regulators and rodenticides. All analytical chemical control has aimed at examining the content of active ingredient compared to the stated content on the label. Regulation in Denmark *(Miljøministeriet, 1994)* specifies generally tolerated limits of deviation from declared content. These are given in Table 1.

Samples of the various pesticides covered in the 1994 control campaigns have been collected by the Chemical Inspection Service, DEPA during the months March - May 1994 either at wholesale dealers/importers or at retailers. Usually only one sample of each product have been collected, but in a few cases, depending on availability on the market, more samples representing different production batches of the product have been collected.
Samples have been stored at NERI in the unopened containers until the time of analysis.

Tabel 1. Tolerated limits of deviations from declared content of active ingredients in pesticides.

Content of a.i., %, w/w	Tolerated limits
> 50	± 2.5 % (abs.)
50 - 25	± 5 % (rel.)
25 - 10	± 6 % (rel.)
10 - 2.5	± 10 % (rel.)
< 2.5	± 15 % (rel.)

2.1 Herbicides

2.1.1 Introduction

Among the various groups of herbicides used in Denmark herbicides with active ingredients belonging to the sulfonylurea group were selected for a general control of content of active ingredient. In 1994 four different sulfonylureas were on the Danish market as active ingredients in herbicide products *(Miljøstyrelsen, 1994)*: chlorsulfuron, metsulfuron-methyl, thifensulfuron-methyl and tribenuron-methyl.

Sulfonylureas are used to control most broad-leaved weeds and some annual grasses in grains and have become increasingly used since the introduction in 1983 of the first sulfonylurea, chlorsulfuron. The reason for treating the four different active ingredients as a common group becomes obvious by comparing the chemical structures, which are rather similar. Chemical structures of the four compounds are shown in Figure 1.

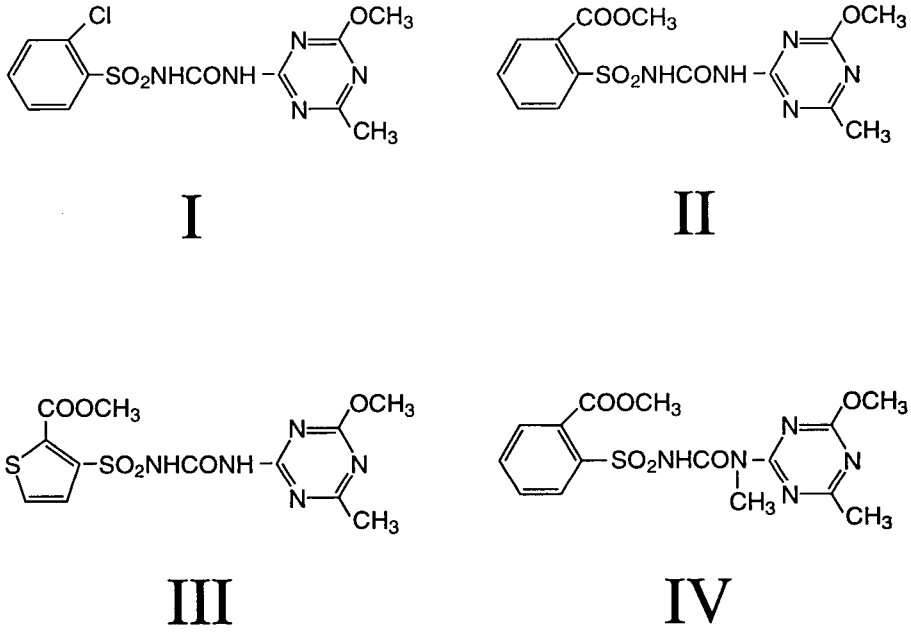


Figure 1. Chemical structure of the sulfonylureas chlorsulfuron (I), metsulfuron-methyl (II), thifensulfuron-methyl (III) and tribenuron-methyl (IV).

Table 2. Samples of sulfonylurea pesticides collected from the Danish market for control of content of active ingredient.

Product	Active ingredient	Formulation type	Company	NERI sample no.
Harmony	thifensulfuron-methyl	granules	DuPont de Nemeours	4-0379
Express	tribenuron-methyl	tablets	DuPont de Nemeours	4-0380
Ally 20 DF	metsulfuron-methyl	granules	DuPont de Nemeours	4-0381
Glean 20 DF	chlorsulfuron	granules	DuPont de Nemeours	4-0390

2.1.2 Samples

At the time of sample collection for the control campaign (March - May 1994) four different sulfonylurea pesticides were approved for use in Denmark *(Miljøstyrelsen, 1994)*. One sample of each pesticide product was collected. A list of the samples is shown in Table 2.
All samples were analysed at NERI in the period October - November 1994.

2.1.3 Results and discussion

All four samples were analysed using reversed phase high pressure liquid chromatography (RP-HPLC) with a method *(Køppen, 1994a)* based on information from the manufacturer company on methods of analysis.
Results from the analyses are shown in Table 3.
As apparent from the Table there were good agreement between declared and found contents. Hence, all four samples complied with the tolerated limits for content of active ingredient.

Table 3. Content of active ingredient in samples of sulfonylurea pesticides.

NERI sample no.	Active ingredient	Content, %		
		Label claim	Analysis[1)]	Tolerance[2)]
4-0379	thifensulfuron-methyl	75	76.2 ± 0.2	72.5 - 77.5
4-0380	tribenuron-methyl	50	51.9 ± 0.2	47.5 - 52.5
4-0381	metsulfuron-methyl	20	20.7 ± 0.1	19.8 - 21.2
4-0390	chlorsulfuron	20	20.5 ± 0.1	19.8 - 21.2

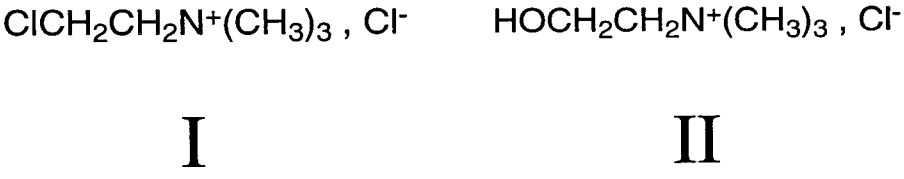
1) Mean (minimum triplicate determinations) ± 95 % confidence limits.
2) Tolerated limits for content of active ingredients according to Danish regulations in force *(Miljøministeriet, 1994)*.

2.2 Plant growth regulators

2.2.1 Introduction

Plant growth regulators are widely used in agriculture and gardening. Among the various plant growth regulators used in Denmark, products with the compound chlormequat chloride as active ingredient are by far the most used type of products. In 1993 325 tons of chlormequat chloride were used *(Miljøministeriet, 1995)*, which corresponds to 95 % of the total amount of active ingredients used as plant growth regulators in Denmark in that year. Chlormequat chloride acts by shortening and strengthening the stem, hereby facilitating harvest and increasing resistance to lodging. Chlormequat chloride also promotes flowering and fruit setting in several flowers and fruit trees.
Chlormequat chloride (Figure 2, **I**) is in some products formulated in combination with a structurally related compound choline chloride (Figure 2, **II**), which reduces the toxicity of the chlormequat chloride formulation.

Plant growth regulators are covered by the same legislation as traditional pesticides, which means that products must be approved by the Danish authorities (DEPA) before they are introduced on the market. This also means that plant growth regulation products already on the market are covered by the control campaigns performed on pesticides. The present control campaign has involved control of active ingredient content in order to examine the agreement between label claimed content and actual content.



I II

Figure 2. Chemical structures of chlormequat chloride (I) and choline chloride (II).

2.2.2 Samples

At the time of sample collection for the control campaign (March - May 1994) 11 different chlormequat plant growth regulation products were approved for use in Denmark *(Miljøstyrelsen, 1994)*. 7 of these 11 products were available on the market during the period of sample collection. In total 10 samples were collected representing these 7 products. A list of the samples is shown in Table 4.
All samples were analysed at NERI in the period June - July 1994.

Table 4. Samples of chlormequat containing plant growth regulation products collected from the Danish market for control of content of active ingredient.

Product	Active ingredient[1)]	Formulation type	Company	NERI sample no.
Stabilan extra	chlormequat	solution	Cyanamid Danmark	4-0373
Tricorta 750	chlormequat	solution	KVK Agro	4-0374
Tricorta	chlormequat	solution	KVK Agro	4-0375
Cycocel 750	chlormequat	solution	BASF Danmark	4-0384
Cycocel extra	chlormequat + cholin	solution	BASF Danmark	4-0385
Trece 700	chlormequat	solution	DK Petrokemi	4-0386
CCC 700	chlormequat	solution	DK Petrokemi	4-0387
CCC 700	chlormequat	solution	DK Petrokemi	4-0388
Cycocel 750	chlormequat	solution	BASF Danmark	4-0389
Cycocel extra	chlormequat + cholin	solution	BASF Danmark	4-0422

1) Active ingredients are formulated as chlorides.

2.2.3 Results and discussion

All samples were analysed using HPLC with a method *(Køppen, 1994b)* based on information from the manufacturer company on methods of analysis. The method allowed simultaneous determination of chlormequat chloride and choline chloride in samples containing both due to chromatographic separation of the two compounds.
Results from the analyses are shown in Table 5.
As apparent from the table there were reasonably good agreement between declared and found contents. Hence, all ten samples complied with the accepted tolerance for content of active ingredient.

Table 5. Content of active ingredient(s) in samples of chlormequat containing pesticides.

NERI sample no.	Active ingredient	Content, g/l		
		Label claim	Analysis[1)]	Tolerance[2)]
4-0373	chlormequat chloride	750	747 ± 8 (~ 65.5 %)	725 - 775
4-0374	chlormequat chloride	750	729 ± 8 (~ 64.3 %)	725 - 775
4-0375	chlormequat chloride	460	462 ± 5 (~ 42.6 %)	437 - 483
4-0384	chlormequat chloride	750	770 ± 8 (~ 67.5 %)	725 - 775
4-0385	chlormequat chloride choline chloride	460 320	458 ± 5 (~ 40.8 %) 311 ± 11 (~ 27.7%)	437 - 483 304 - 336
4-0386	chlormequat chloride	700	704 ± 8 (~ 62.5 %)	675 - 725
4-0387	chlormequat chloride	700	703 ± 8 (~ 62.3 %)	675 - 725
4-0388	chlormequat chloride	700	681 ± 7 (~ 60.6 %)	675 - 725
4-0389	chlormequat chloride	750	773 ± 9 (~ 67.8 %)	725 - 775
4-0422	chlormequat chloride choline chloride	460 320	459 ± 5 (~ 40.8 %) 313 ± 11 (~ 27.8 %)	437 - 483 304 - 336

1) Mean (minimum duplicate determinations) ± 95 % confidence limits.

2) Tolerated limits for content of active ingredients according to Danish regulations in force *Miljøministeriet, 1994).*

2.3 Rodenticides

2.3.1 Introduction

Rodenticides are pesticides used to control various rodent pests, most frequently rats and mice. Some rodenticides are products used as fumigants containing a toxic active ingredient, which can be applied as a gas, but most of the rodenticides used are products containing an active ingredient, which is toxic following ingestion. These rodenticides are formulated with the aim to make them appear like food or drinking water to the rodents. Typically products consist of food that has been added the toxic compound (e.g. impregnated grains) or as products intended for mixing with water before use. Among the active ingredients used in rodenticides applied as eating or drinking poison, compounds being derivatives of coumarin are the most widely used. The toxic effect of these compounds is expressed as bleeding of the animal, as the compounds interfere with and hamper blood coagulation.

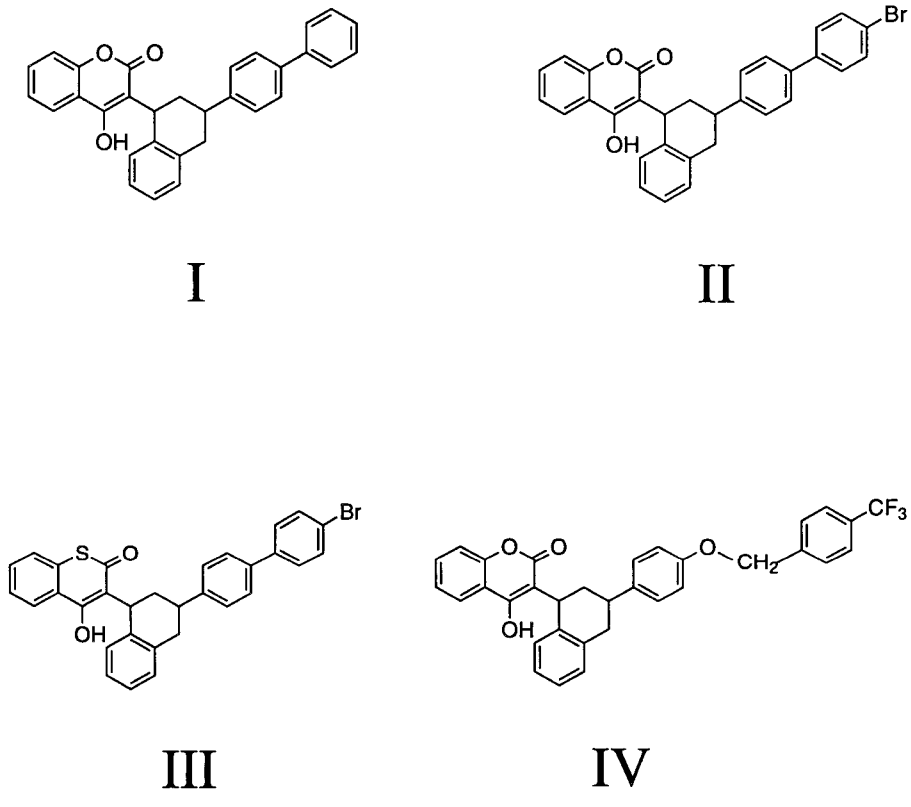


Figure 3. Chemical structures of the four rodenticide active ingredients difenacoum (I), brodifacoum (II), difethialone (III) and flocoumafen (IV).

In 1994 six different coumarin-derived active ingredients were used in rodenticides in Denmark *(Miljøstyrelsen, 1994)*. Four of these brodifacoum, difenacoum, difethialone and flocoumafen are included in the present analytical chemical authority control of rodenticides. Chemical structures of the four compounds are shown in Figure 3. A similar analytical chemical authority control of rodenticides was also performed in Denmark in 1988 *(Køppen, 1988a,b)*. However, none of the four present active ingredients were included in that latest control.
The present control campaign has only involved control of active ingredient content in order to examine the agreement between label claimed content and actual content.

2.3.2 Samples

At the time of sample collection for the control campaign (March - May 1994) 11 different rodenticide products containing one of the four active ingredients were approved for use in Denmark *(Miljøstyrelsen, 1994)*. Six of these 11 products were available on the market during the period of sample collection. In total eight samples were collected representing these six products. A list of the samples is shown in Table 6.
All samples were analysed at NERI in the period December 1994 - March 1995.

Table 6. Samples of rodenticide products collected from the Danish market for control of content of active ingredient.

Product	Active ingredient	Formulation type	Company	NERI sample no.
Ratak musekorn	difenacoum	impregn. grains	Zeneca Agro	4-0376
Ratak rottekorn	difenacoum	impregn. grains	Zeneca Agro	4-0377
Klerat pellets	brodifacoum	pellets	Zeneca Agro	4-0378
Klerat voksblok	brodifacoum	wax block	Zeneca Agro	4-0391
Klerat pellets	brodifacoum	pellets	Zeneca Agro	4-0392
Klerat voksblok	brodifacoum	wax block	Zeneca Agro	4-0699
Dita rottegift	difethialone	impregn. grains	Mortalin Prod.	4-0700
Storm rotteblok	flocoumafen	wax block	Cyanamid Danmark	4-0775

2.3.3 Results and discussion

All samples were analysed using HPLC with a method *(Køppen, 1995)* based on information from the manufacturer company on methods of analysis.
Results from the analyses are shown in Table 7.
Four of the eight analysed samples complied with the tolerated limits for content of active ingredient. One sample deviated to a minor extent from the tolerated limits, but three samples contained only half of the declared content or less. The fact that four out of eight analysed samples did not comply with the tolerances, is an unusually high frequency compared to what is usually found in pesticide control. A certain explanation could not be found from manufacturer companies information regarding history of the actual samples. One of the difenacoum samples found to have too low content of active ingredient originated from 1988, according to company information. This means that the sample was six - seven years old when it was analysed. For the second sample of a difenacoum product no explanation for the low content of active ingredient was found.
Although difenacoum is considered a relatively stable compound *(Tomlin, 1994)*, the inherent susceptibility to degradation of these coumarin-derived compounds when exposed to light is expected to give the product a limited stability.

Table 7. Content of active ingredient in samples of various rodenticides.

NERI sample no.	Active ingredient	Content, %		
		Label claim	Analysis[1)]	Tolerance[2)]
4-0376	difenacoum	0.005	0.0012 ± 0.0001	0.0042 - 0.0058
4-0377	difenacoum	0.005	0.0015 ± 0.0001	0.0042 - 0.0058
4-0378	brodifacoum	0.005	0.0042 ± 0.0001	0.0042 - 0.0058
4-0391	brodifacoum	0.005	0.0042 ± 0.0003	0.0042 - 0.0058
4-0392	brodifacoum	0.005	0.0040 ± 0.0001	0.0042 - 0.0058
4-0699	brodifacoum	0.005	0.0046 ± 0.0004	0.0042 - 0.0058
4-0700	difethialone	0.0025	0.0012 ± 0.0004	0.0021 - 0.0029
4-0775	flocoumafen	0.005	0.0047 ± 0.0002	0.0042 - 0.0058

1) Mean (minimum duplicate determinations) ± 95 % confidence limits.
2) Tolerated limits for content of active ingredients according to Danish regulations in force *(Miljøministeriet, 1994)*.

According to subsequent information from the Danish manufacturer company of the difethialone product *(Kildemoes, 1995)* problems with stability of the active ingredient have been observed and have been related to interaction with the added color substance. A stock concentrate solution of difethialone mixed with the color substance is used for impregnating grains, and the company has discovered problems with stability of difethialone in this solution as well.
Actions have subsequently been taken to avoid mixing of active ingredient with the color substance until production of the impregnated grains. Furthermore, the company will look into possibilities of replacing the color substance with a compound more compatible with difethialone.

However, it is worth noticing that all the three samples found to have far too low content of active ingredient were formulations consisting of impregnated grains.

Although the control includes a very limited number of samples, there seem to be problems for the manufacturer companies to secure a sufficient high quality of these impregnated grains formulations. In the latest similar control of rodenticides covering products consisting of impregnated grains *(Køppen, 1988a)* problems with too low content of active ingredient were found to be related to inhomogeneity of the formulation. In some cases the surface of the grains was not sufficiently resistant to attrition as a result of physical handling of the formulation package, and the active ingredient initially deposited on the surface of the grains was concentrated in the fine powder found on the bottom of the package.
No visible sign of lack of homogeneity was observed in the samples found to have far too low content of active in the present control analysis. Furthermore, repetitive sampling of subsamples from the formulation packages could be made and reproducible analysis results were found. These observations indicate that lack of homogeneity was not a problem - at least not on the level of the amount of formulation contained in the sample package.
More likely, the problem is in this case related to a limited chemical stability of the active ingredient when used in formulations consisting of impregnated grains compared to formulations like pellets or wax blocks, where the active ingredient is incorporated into the matrix.

In any case the results are unsatisfactory from an authority control point of view, considering that rodenticides with too low content of active ingredient increases the risk of development of resistance among target animal populations. None of the examined samples were labeled with a given limited storage stability. This is, however, not required at the moment according to Danish regulations, but it could seem to be an appropiate improvement of the labeling of these products.

3 Conclusions

Three different groups of products covered by the pesticide regulations have been included in the 1994 analytical chemical authority control: 1) herbicides of the sulfonylurea type, 2) plant growth regulators containing chlormequat chloride as active ingredient and 3) various rodenticides containing coumarin-derived active ingredients.

Satisfactory results were found among products belonging to groups 1 and 2. All four examined samples of sulfonylurea herbicides and all ten examined samples of chlormequat chloride containing plant growth regulators complied with the accepted tolerances with respect to content of active ingredient set by the Danish regulation of pesticides.

Unsatisfactory results were found among products belonging to group 3. Four out of eight examined samples (~ 50 %) did not comply with the tolerated limits for content of active ingredient. Three of these four samples contained only half or less of the declared content. The results may indicate problems with sufficient stability of these active ingredients, when formulated as impregnated grains. None of the samples were labeled with a given limited storage stability.

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National Environmental Research Institute

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