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Control of Pesticides 2000

Chemical Substances and Chemical Preparations

NERI Technical Report No. 371

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Data sheet

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Abstract: Three different groups of products covered by the pesticide regulation have been included in the 2000 analytical chemical authority control: 1) herbicides containing aclonifen, clopyralid, dicamba, quinoclamine, bromoxynil, ioxynil, simazine, and terbuthylazine. 2) Fungicides containing fenpropidin, fluazinam, and kresoxim-methyl. 3) Insecticides containing buprofezin and fenazaquin. All products were examined for content of active ingredient. Satisfactory results were found among herbicides containing aclonifen, dicamba, quinoclamine, bromoxynil, and simazine, among fungicides containing fenpropidin, fluazinam, and kresoxim-methyl, and among insecticides containing fenazaquin. Thus, all the eighteen analysed samples of these pesticides complied with the accepted tolerances with respect to content of active ingredients set by the Danish regulation of pesticides. The only product containing buprofezin, one of four samples containing terbuthylazine, one of eleven samples containing clopyralid, and one of four samples containing ioxynil did not comply with the accepted limits of content of active ingredient.

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Summary

The analytical chemical authority control on pesticide products on the Danish market performed in 2000 is reported. Samples of selected groups of pesticides have been collected from the market and analysed to verify whether the actual content of active ingredient agreed with the label-claimed content. The tolerance of deviation of active ingredient content from label-claimed content is set by the Danish pesticide regulation.

Three different groups of products covered by the pesticide regulation have been included in the 2000 analytical chemical authority control: 1) herbicides containing aclonifen, clopyralid, dicamba, quinoclamine, bromoxynil, ioxynil, simazine, and terbuthylazine. 2) Fungicides containing fenpropidin, fluazinam, and kresoxim-methyl. 3) Insecticides containing buprofezin and fenazaquin. All products were examined for content of active ingredient.

Satisfactory results were found among herbicides containing aclonifen, dicamba, quinoclamine, bromoxynil, and simazine, among fungicides containing fenpropidin, fluazinam, and kresoxim-methyl, and among insecticides containing fenazaquin. Thus, all the eighteen analysed samples of these pesticides complied with the accepted tolerances with respect to content of active ingredients set by the Danish regulation of pesticides.

The only product on the market containing buprofezin did not comply with the accepted limits of content of active ingredient. The content was found to be too high. According to the importer of the buprofezin-product, the product is imported in drums and decanted to 0,5 L bottles. The product is an inhomogeneous suspension concentrate, so the high content is probably due to insufficiently mixing of the product before decanting.

One of the four samples containing terbuthylazine did not comply with the accepted limits of content of active ingredient. The content was found to be too low. Subsequently the manufacturer had documented that the batch complied with the limits when it was produced.

One of eleven samples containing clopyralid and one of four samples containing ioxynil did not comply with the accepted limits of content of active ingredient due to incorrect labels. There were divergences between the contents declared in % and in g/l.

Resumé

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked udført i 2000 af de danske myndigheder er her afrapporteret. Prøver af udvalgte grupper af bekæmpelsesmidler er blevet samlet fra markedet og analyseret for at verificere om det aktuelle indhold af aktivstof er i overensstemmelse med det deklarerede indhold. Grænsen for en accepteret afvigelse af indholdet af aktivstof fra det deklarerede indhold er fastsat i bekendtgørelsen om bekæmpelsesmidler.

Tre forskellige grupper af produkter er inkluderet i den analytisk-kemiske kontrol udført af myndighederne i 2000: 1) herbicider indeholdende aclonifen, clopyralid, dicamba, quinoclamin, bromoxynil, ioxynil, simazin og terbutylazin 2) fungicider indeholdende fenpropidin, fluazinam og kresoxim-methyl 3) insekticider indeholdende buprofezin og fenazaquin.

Der blev opnået tilfredsstillende resultater blandt herbicider indeholdende aclonifen, dicamba, quinoclamin, bromoxynil og simazin, blandt fungicider indeholdende fenpropidin, fluazinam og kresoxim-methyl og blandt insekticider indeholdende fenazaquin. Indholdet af aktivstof i alle de atten analyserede prøver af disse bekæmpelsesmidler var indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler.

Det eneste produkt på markedet indeholdende buprofezin var ikke indenfor den accepterede tolerance for indhold af aktivstof. Indholdet var for højt. Ifølge importøren af buprofezin-produktet bliver produktet importeret i tromler og omhældt til 0,5 liters flasker. Produktet er et uhomogent suspensionskoncentrat , så det høje indhold af aktivt stof skyldes formentlig utilstrækkelig opblanding af produktet inden omhældningen.

En ud af fire prøver indeholdende terbutylazin var ikke indenfor den accepterede tolerance for indhold af aktivstof. Indholdet var for lavt. Efterfølgende har producenten dokumenteret at batchen var inden for tolerancen da det blev produceret.

En ud af elleve prøver indeholdende clopyralid og en ud af fire prøver indeholdende terbutylazin var ikke inden for den accepterede tolerance for indhold af aktivstof grundet ukorrekte etiketter. Der var divergens mellem det deklarerede indhold i % og i g/l.

1 Introduction

In Denmark the Danish Environmental Protection Agency (DEPA) is responsible for evaluation and authorisation of all pesticides before introduction on the Danish market. Legal regulations for pesticides are given in a Statutory Order from the Ministry of the Environment and Energy *(Miljø- og Energiministeriet, 2000)*, which also states that DEPA is responsible for control in relation to pesticides.

In practice authority control activities of pesticides on the market are organised in a way that the Chemicals Inspection Service at 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 regulation as well as with the specification of contents stated in connection with application for approval of the pesticide product.

Analytical chemical control can involve verification 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 i.e., campaigns, is covered by this report, which describes the laboratory control performed in 2000.

2 Control Campaigns in 2000

Control campaigns conducted in 2000 have covered pesticides belonging to three different groups of pesticides: Herbicides, fungicides and insecticides. All analytical chemical control has aimed at examining the content of active ingredient compared to that stated on the label. Regulation in Denmark *(Miljø- og Energiministeriet, 2000)* specifies general tolerance of deviations from declared content. These are given in Table 2.1.

Samples of the various pesticides covered in the 2000 control campaigns have been collected by the Chemical Inspection Service at DEPA during the months February – August 2000 either at whole sale dealers/-importers or at retailers. One sample of each product has been collected

Samples have been stored at NERI in the unopened containers until the time of analysis. The samples have been stored at ambient temperature (app. 20°C) protected from light.

Table 2.1 Tolerance of deviations from declared content of active ingredients (a.i.) in pesticides.

Declared content of a.i., %, w/w	**Tolerance, %**	
conc. ≥ 50	± 2.5%	(abs.)
25 < conc. ≤ 50	± 5%	(rel.)
10 < conc. ≤ 25	± 6%	(rel.)
2.5 < conc. ≤ 10	± 10%	(rel.)
conc. ≤ 2.5	± 15%	(rel.)

2.1 Herbicides

2.1.1 Introduction

Among the nearly 50 different herbicides available on the Danish market herbicides containing aclonifen, clopyralid, dicamba, quinoclamine, bromoxynil, ioxynil, simazine and terbuthylazine as active ingredients were selected for control in 2000. All products were examined for content of active ingredient.

Aclonifen (Figure 1,a) is a diphenyl ether herbicide, which in Denmark is used for control of grass and broad-leaved weeds in potatoes, parsnip, Hamburg parsley, different peas except sugar peas, carrot, onion set, shallot and celeriac. The herbicide formulation containing aclonifen is new on the Danish market (included in the Danish register of approved pesticides in 1999) and aclonifen therefore have not previously been selected for authority control.

Clopyralid (Figure 1,b) is a chlorinated pyridinecarboxylic acid herbicide, which is used for control of annual and perennial broad-leaved weeds in cereals, grass seed, rape, beet, beetroot, cabbage crop, cabbage seed, maize, caraway, strawberry, and blackcurrant and for control of broad-leaved weeds in meadows, pastures, lawns, and other grass covered areas. Herbicide formulations containing clopyralid have not previously been selected for authority control.

Dicamba (Figure 1,c) is a benzoic acid herbicide, which is used only for control of annual and perennial broad-leaved weeds in spring barley and oats and in meadows, pastures, lawns and other grass covered areas. Herbicide formulations containing dicamba have not previously been selected for authority control.

Quinoclamine (Figure 1,d) is a naphtoquinone herbicide, which in Denmark is used only for control of algae, moss and liverwort in nursery-grown plants. Herbicide formulations containing fluazifop-p-butyl have not previously been selected for authority control. The herbicide formulation containing quinoclamine is new on the Danish market (included in the Danish register of approved pesticides in 1999) and quinoclamine therefore have not previously been selected for authority control.

Bromoxynil (Figure 1,e) is a hydroxybenzonitrile, which is used only for control of annual broad-leaved weeds in cereals and grass seed and clover, alfalfa, beet seed, medick etc. Herbicide formulations containing bromoxynil have not previously been selected for authority control.

Ioxynil (Figure 1,f) is a hydroxybenzonitrile too, which is used only for control of annual broad-leaved weeds in cereals, grass seed, leek and onion and clover, alfalfa, beet seed, medick etc. Herbicide formulations containing ioxynil have not previously been selected for authority control.

Simazine (Figure 1,g) is a 1,3,5-triazine herbicide, which is used only for occupational control of germinating annual grasses and broad-leaved weeds in asparagus, fruit trees and bushes, shrubbery and hedges, and in

nurseries and forestry. The herbicide formulation containing simazine has not previously been selected for authority control.

Terbuthylazine (Figure 1,h) is a 1,3,5-triazine herbicide too, which is used only for occupational control of weeds in grass seed, clover, maize, fruit trees and bushes, shrubbery and hedges, and in nurseries and forestry. Herbicide formulations containing terbuthylazine have not previously been selected for authority control.

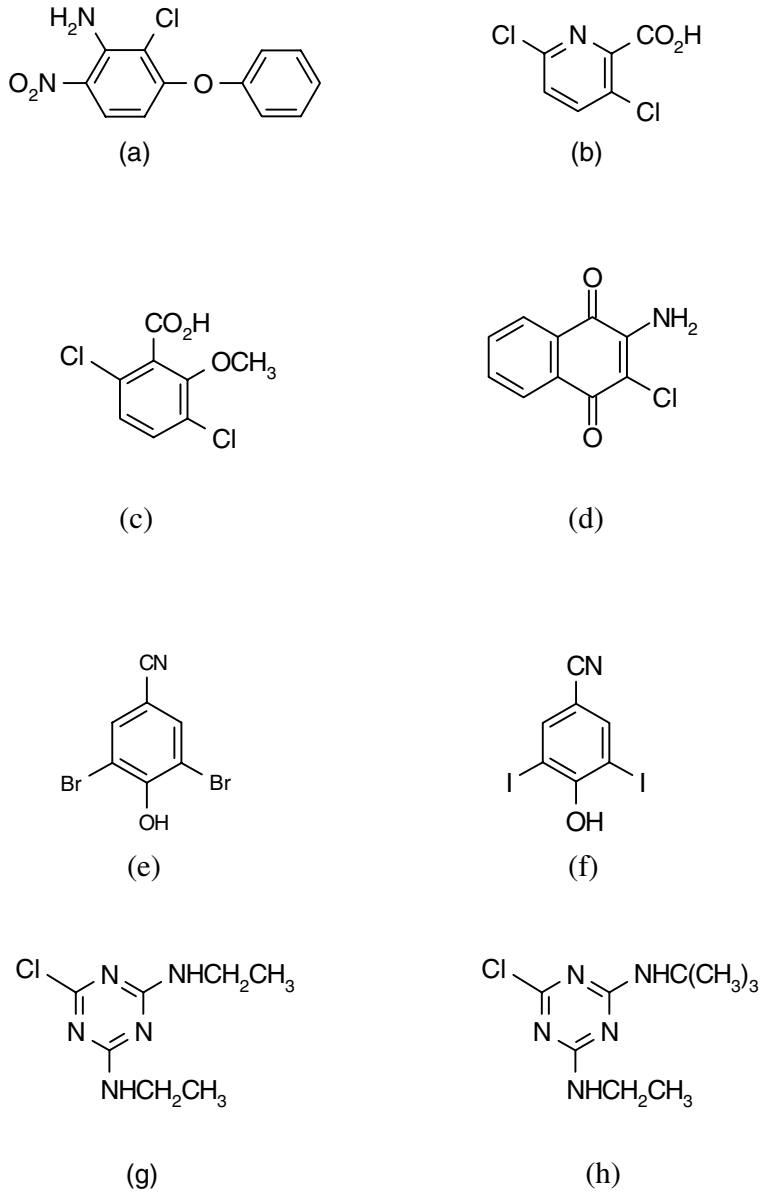


Figure 1
Chemical structures of the herbicide active ingredients: aclonifen (a), clopyralid (b), dicamba (c), quinoclamine (d), bromoxynil (e), ioxynil (f), simazine (g), and terbuthylazine (h).

2.1.2 Samples

At the time of sampling for the control campaign (February - August 2000) only one product of each of the herbicide aclonifen, simazin and quinoclamine were approved for use in Denmark. All three products were available on the market during the period of the sample collection. The two approved products containing bromoxynil, the four approved products containing ioxynil and the four approved products containing terbuthylazine were all available on the market. Six out of nine approved products containing dicamba and eleven out of fourteen approved products containing clopyralid (*Miljøstyrelsen, 2000*) were available on the market during the period of the sampling. One sample of each pesticide product was collected except for one of the dicamba-products, which was collected in triple. A list of the samples is given in Appendix I.

The sample containing quinoclamine was analysed at NERI in June 2000, aclonifen was analysed in July-August, dicamba in September-December, simazine in October-November and clopyralid in November-December 2000. The samples containing ioxynil, bromoxynil and terbuthylazine were analysed in October 2000-February 2001.

2.1.3 Results and Discussion

The content of aclonifen was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2000a)*. As no CIPAC method on aclonifen exists, the method is developed based on information from the manufacturer.

The contents of clopyralid were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2000b)*. As no CIPAC method on aclonifen either exists, the method is developed based on information from the manufacturer too.

The contents of dicamba were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2000c)*. A CIPAC method on dicamba exists but it is based on IR-spectrophotometry. In the laboratory we prefer to use GC- or HPLC-based methods if possibly. The method used is developed based on information from the manufacturer.

The content of quinoclamine was determined using gas chromatography and FID-detector (GC-FID) *(Krongaard, 2000d)*. We developed a new method in the laboratory as no CIPAC method on quinoclamine exists, and as the method provided from the manufacturer was based on packed GC-columns, which we don't have in the laboratory. The method can be used for determination of kresoxim-methyl and buprofezin too.

The contents of ioxynil and bromoxynil were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2001)*. The method used is a revised CIPAC method on ioxynil. Due to chemical similarity between ioxynil and bromoxynil the method was used for determination of bromoxynil too.

The contents of simazine and terbutylazine were determined using capillary gas chromatography and FID-detector too (GC-FID) *(Krongaard, 2000e)*. The method used is developed on basis of two CIPAC methods on simazine and terbuthylazine using packed columns. The new method can be used for determination of both active ingredients.

As apparent from Table 2.2 good agreement between declared and determined content was found for all the samples containing aclonifen, bromoxynil, dicamba, quinoclamine, and simazine. Hence, all the samples complied with the tolerated limits for content of active ingredient.

One of the four samples containing terbuthylazine did not comply with the accepted limits of content of active ingredient. The content was found to be too low. The sample was first analysed twice with our own method, with the content found to be 22,51% and 22,59%, and to confirm that, it was analysed twice with the method submitted by the company, with the content found to be 22,22% and 22,25%. All samples were analysed in double. Subsequent contact to the Manufactory Company revealed an incorrect label. The declared content was 25,8%, whereas it correctly should have been 24,5%. The label will accordingly be corrected. But still the content is too low. The accepted tolerance is 6% relatively, therefore the content must be within the range 23,0-26,0%. Subsequently, the manufacturer had documented that the batch complied with the limits of content when it was produced.

One sample containing clopyralid and one sample containing ioxynil did not comply with the accepted limits of content of active ingredient due to incorrect labels. There are divergences between the contents declared in % and in g/l. The content in clopyralid-product is incorrectly declared to be 100 g/l (12,5%). Subsequent contact to the Manufacturer Company revealed that it correctly should have been 100 g/l (9,56%). The content in the ioxynil-product is incorrectly declared to be 120 g/l (15,39%). Subsequent contact to the Manufacturer Company revealed that it correctly should have been 120 g/l (11,47%). The companies will accordingly correct the labels.

Table 2.2 Content of active ingredient in samples of herbicides.

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Aclonifen	49,6%	(600 g/l)	49,6 ± 0,1%	47,1 - 52,1%	0-0052
Bromoxynil	20,5%	(240 g/l)	19,5 ± 0,1%	19,3 - 21,7%	0-0047
Bromoxynil	22,4%	(300 g/l)	22,6% ± 0,1%	21,1 - 23,8%	0-0968
Clopyralid	2%	(21,5 g/l)	1,71 ± 0,01%	1,7 - 2,3%	0-0040
Clopyralid	9,56%	(100 g/l)	9,52 ± 0,02%	8,6 - 10,5%	0-0048
Clopyralid	1,82%	(20 g/l)	1,80 ± 0,01%	1,6 - 2,1%	0-0050
Clopyralid	1,8%	(20 g/l)	1,75 ± 0,01%	1,6 - 2,1%	0-0051
Clopyralid	9,5%	(100 g/l)	9,40 ± 0,02%	8,5 - 10,5%	0-0197
Clopyralid	1,3%	(15 g/l)	1,2 ± 0,01%	1,1 - 1,5%	0-0198
Clopyralid	1,82%	(20 g/l)	1,75 ± 0,01%	1,6 - 2,1%	0-0762
Clopyralid	3,5%	(40 g/l)	3,44 ± 0,01%	3,2 - 3,9%	0-0781
Clopyralid	2,87%	(30 g/l)	2,86 ± 0,01%	2,6 - 3,2%	0-0782
Clopyralid	12,5%	(100 g/l)	9,65 ± 0,02%	11,8 - 13,3%	0-0969[**)]
Clopyralid	9,56%	(100 g/l)	9,57 ± 0,02%	8,6 - 10,5%	0-0970
Dicamba	1,0%	(12 g/l)	1,045 ± 0,002%	0,85 - 1,15%	0-0049
Dicamba	1,4%	(17 g/l)	1,485 ± 0,002%	1,19 - 1,61	0-0198
Dicamba	1,0%	(12 g/l)	1,039 ± 0,002%	0,85 - 1,15%	0-0258
Dicamba	0,5%	(4,5 g/l)	0,471 ± 0,001%	0,43 - 0,58%	0-0259
Dicamba		(0,32 g/l)[3)]	0,350 ± 0,001 g/l	0,27 - 0,37 g/l[4)]	0-0260
Dicamba	1,0%	(12 g/l)	1,057 ± 0,002%	0,85 - 1,15%	0-0261
Dicamba		(0,32 g/l)[3)]	0,300 ± 0,001 g/l	0,27 - 0,37 g/l[4)]	0-0760
Dicamba	4,3%	(50 g/l)	4,363 ± 0,007%	3,65 - 4,95%	0-0781
Ioxynil		(225 g/l)[3)]	218,9 ± 1,2 g/l	212 - 239 g/l[4)]	0-0042
Ioxynil	13,7%	(160 g/l)	13,4 ± 0,1%	12,9 - 14,5%	0-0047
Ioxynil	15,39%	(120 g/l)	11,4 ± 0,1%	14,5 - 16,3%	0-0782[**)]
Ioxynil	14,9%	(200 g/l)	14,5 ± 0,1%	14,0 - 15,8%	0-0968
Quinoclamine	25%		25,9 ± 0,2%	23,5 - 26,5%	0-0262

Continues....

Table 2.2 Continued

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Simazine	43,9 %	(500 g/l)	43,8 ± 0,2%	41,7 - 46,1%	0-0780
Terbuthylazine		(500 g/l)[3)]	496,5 ± 2,1 g/l	475 - 525 g/l[4)]	0-0053
Terbuthylazine	14,7%	200 g/l	17,65 ± 0,07%	16,61 - 18,69%	0-0054
Terbuthylazine	25,8 %	250 g/l	22,55 ± 0,09%	24,5 - 26,1%	0-0055[*)]
Terbuthylazine	45%	500 g/l	46,25 ± 0,19%	42,75 - 47,25%	0-0056
Simazine	43,9 %	(500 g/l)	43,8 ± 0,2%	41,7 - 46,1%	0-0780
Terbuthylazine		(500 g/l)[3)]	496,5 ± 2,1 g/l	475 - 525 g/l[4)]	0-0053
Terbuthylazine	14,7%	200 g/l	17,65 ± 0,07%	16,61 - 18,69%	0-0054
Terbuthylazine	25,8 %	250 g/l	22,55 ± 0,09%	24,5 - 26,1%	0-0055[*)]
Terbuthylazine	45%	500 g/l	46,25 ± 0,19%	42,75 - 47,25%	0-0056

1) Mean ± 95% confidence limits.
2) Tolerated limits for content of active ingredients according to Danish regulations *(Miljø- og Energiministeriet, 2000)*.
3) Content (expressed as %) not declared.
4) Calculated on basis of declared content in g/l.
*) Found content is outside the accepted tolerance.
**) Divergence between the content declared in % and in g/l.

2.2 Fungicides

2.2.1 Introduction

In 2000 around 35 different fungicide active ingredients were approved in Denmark *(Miljøstyrelsen, 2000)*. Among these active ingredients products containing fenpropidin, fluazinam, and kresoxim-methyl were selected for control in 2000. They were all examined for content of active ingredient.

Fenpropidin (Figure 2,a) is a morpholine type of fungicide, which in Denmark is used only for control of powdery mildew and rust etc. on wheat. The fungicide formulation containing fenpropidin is new on the Danish market (included in the Danish register of approved pesticides in 1999) and fenpropidin therefore have not previously been selected for authority control.

Fluazinam (Figure 2,b) is a dinitroaniline fungicide, which in Denmark is used only on potatoes controlling fungal diseases. Fluazinam is like fenpropidin a new fungicide (included in the Danish register of approved pesticides in 1999) and fluazinam have not previously been selected for authority control.

Kresoxim-methyl (Figure 2,c) is a strobilurin analogue type of fungicide that in Denmark is approved only to use on ornamentals, winter wheat and winter barley. Kresoxim-methyl is a new fungicide (included in the Danish register of approved pesticides in 2000) and formulations containing kresoxim-methyl have not previously been selected for authority control.

2.2.2 Samples

At the time of sampling for the control campaign (February-August 2000) only one product containing fenpropidin and one product containing fluazinam were approved for use in Denmark. Two products containing kresoxim-methyl as active ingredient were approved for use in Denmark. All the products were available on the market during the sampling period. One sample of each pesticide product was collected. A list of the samples is given in Appendix I.

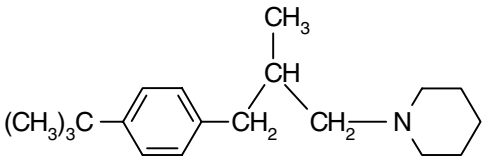
The samples containing kresoxim-methyl were analysed at NERI in the period June - September 2000, the sample containing fluazinam in October 2000, and the sample containing fenpropidin was analysed in November - December 2000.

2.2.3 Results and Discussion

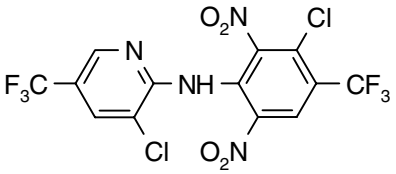
The content of fenpropidin was determined using gas chromatography with flame ionisation detector (GC-FID) *(Krongaard, 2000f)*. As no CIPAC method on fenpropidin exists, the method is developed based on information from the manufacturer.

The content of fluazinam was determined using gas chromatography with flame ionisation detector (GC-FID) *(Krongaard, 2000g)*. As no CIPAC method on fluazinam exists, the method is developed based on information from the manufacturer.

Similarly, the contents of kresoxim-methyl were determined using gas chromatography with flame ionisation detector (GC-FID) *(Krongaard, 2000d)*. As no CIPAC method on kresoxim-methyl exists, we developed a new method in the laboratory, which can be used on products containing quinoclamine and buprofezin too.



(a)



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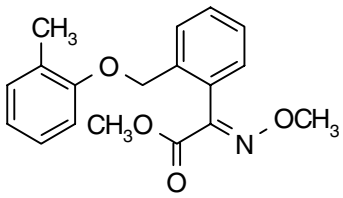


(c)

Figure 2
Chemical structure of the fungicide active ingredients fenpropidin (a), fluazinam (b), kresoxim-methyl (c).

Table 2.3 Content of active ingredient in samples of fungicides.

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
fenpropidin	81,7%	(750 g/l)	82,28 ± 0,44%	79,2 - 84,2%	0-0041
fluazinam	38,5%	(500 g/l)	39,95 ± 0,16%	36,6 - 40,4%	0-0045
kresoxim-methyl	14,4%	(150 g/l)	14,6 ± 0,1%	13,5 - 15,3%	0-0046
kresoxim-methyl	50%		48,9 ± 0,3%	47,5 - 52,5%	0-0966

1) Mean ± 95% confidence limits.
2) Tolerated limits for content of active ingredients according to Danish regulations *(Miljø- og Energiministeriet, 2000)*.

As apparent from the results in Table 2.3 good agreement between declared and determined content was found for all the samples containing fenpropidin, fluazinam, and kresoxim-methyl Hence, all the samples complied with the tolerated limits for content of active ingredient.

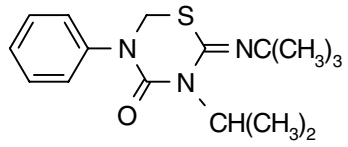
2.3 Insecticides

2.3.1 Introduction

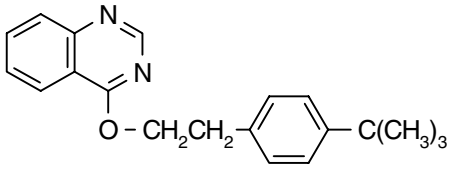
Among the different insecticides available on the Danish market the insecticides containing buprofezin and fenazaquin as active ingredients were selected for control in 2000.

Buprofezin (Figure 3a) is an insecticide that in Denmark is used only for control of greenhouse white flies and cotton white flies on ornamentals in greenhouses. The formulation containing buprofezin is new on the Danish market (included in the Danish register of approved pesticides in 1999) and buprofezin therefore have not previously been selected for authority control.

Fenazaquin (Figure 3b) is an insecticide that in Denmark is used only for control of insects on cucumber, tomatoes, and ornamentals in greenhouses. The formulation containing fenazaquin as active ingredient is like buprofezin new on the Danish market (included in the Danish register of approved pesticides in 1999) and fenazaquin therefore have not previously been selected for authority control.



(a)



(b)

Figure 3
Chemical structure of the insecticide active ingredient buprofezin (a) and fenazaquin (b).

2.3.2 Samples

At the time of sampling for the control campaign (February - August 2000) only one product containing buprofezin and one product containing fenazaquin as active ingredient were approved for use in Denmark. Both products were available on the market during the period of the sample collection (*Miljøstyrelsen, 2000*). One sample of each pesticide product was collected. A list of the samples is given in Appendix I.

The sample containing buprofezin was analysed at NERI during the period May - August and the product containing fenazaquin was analysed in September - October 2000.

2.3.3 Results and Discussion

The content of buprofezin was determined using gas chromatography with flame ionisation detector (GC-FID) *(Krongaard, 2000d)*. We developed a new method in the laboratory as no CIPAC method on buprofezin exists, and as the method provided from the manufacturer was based on packed GC-columns, which we don't have in the laboratory. The method can be used for determination of kresoxim-methyl and quinoclamine too.

The content of fenazaquin was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2000h)*. As no CIPAC method on fenazaquin exists, the method is developed based on information from the manufacturer.

As apparent from the results in Table 2.4 good agreement between declared and determined content was found for the sample containing fenazaquin whereas an exceed in the content of buprofezin was found. According to the importer of the buprofezin-product, the product is imported in drums and decanted to 0,5 L bottles. The product is an inhomogeneous suspension concentrate, so the high content is probably due to insufficiently mixing of the product before decanting.

Table 2.4 Content of active ingredient in samples of insecticides.

Active ingredient	**Content**			**NERI sample no.**
	Label claim	**Analysis[1)]**	**Tolerance[2)]**	
buprofezin	40% (428 g/l)	42,3 ± 0,2%	38,0 - 42,0%	0-0761[*)]
fenazaquin	18,3% (200 g/l)	18,9 ± 0,1%	17,2 - 19,4%	0-0967

1) Mean ± 95% confidence limits.
2) Tolerated limits for content of active ingredients according to Danish regulations *(Miljø- og Energiministeriet, 1998)*.
*) Found content is outside the accepted tolerance.

3 Conclusions

Three different groups of products covered by the pesticide regulation have been included in the 2000 analytical chemical authority control: 1) herbicides containing aclonifen, clopyralid, dicamba, quinoclamine, bromoxynil, ioxynil, simazine, and terbuthylazine. 2) Fungicides containing fenpropidin, fluazinam, and kresoxim-methyl. 3) Insecticides containing buprofezin and fenazaquin. All products were examined for content of active ingredient.

Satisfactory results were found among herbicides containing aclonifen, dicamba, quinoclamine, bromoxynil, and simazine, among fungicides containing fenpropidin, fluazinam, and kresoxim-methyl, and among insecticides containing fenazaquin. Thus, all the eighteen analysed samples of these pesticides complied with the accepted tolerances with respect to content of active ingredients set by the Danish regulation of pesticides.

The only product on the market containing buprofezin did not comply with the accepted limits of content of active ingredient. The content was found to be too high. According to the importer of the buprofezin-product, the product is imported in drums and decanted to 0,5 L bottles. The product is an inhomogeneous suspension concentrate, so the high content is probably due to insufficiently mixing of the product before decanting.

One of the four samples containing terbuthylazine did not comply with the accepted limits of content of active ingredient. The content was found to be too low. Subsequently the manufacturer had documented that the batch complied with the limits when it was produced.

One of eleven samples containing clopyralid and one of four samples containing ioxynil did not comply with the accepted limits of content of active ingredient due to incorrect labels. There were divergences between the contents declared in % and in g/l. Subsequent contact to the manufacturers revealed incorrect labels on the products. The companies will accordingly correct the labels.

4 References

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Appendix I

Samples of pesticides collected from the Danish market in 2000 for authority control

Table 1 Herbicides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Aclonifen	Fenix	SC	Rhône-Poulenc Agro	0-0052
Bromoxynil	Briotril	EC	KVK Agro A/S	0-0047
Bromoxynil	Capture	SC	Rhône-Poulenc Agro	0-0968
Clopyralid	Herbalon	SL	KVK Agro A/S	0-0040
Clopyralid	Matrigon	SL	Dow AgroSciences A/S	0-0048
Clopyralid	Ariane FG	EC	Dow AgroSciences A/S	0-0050
Clopyralid	Kemfiks FG	EC	KemiAgro	0-0051
Clopyralid	Cliophar	SL	Inter-Trade Agro	0-0197
Clopyralid	Herbatox GP	EC	KVK Agro A/S	0-0198
Clopyralid	Bofix Plænerens	EC	Tanaco	0-0762
Clopyralid	Flux Extra	EC	AgroDan A/S	0-0781
Clopyralid	Ariane Super	EC	Dow AgroSciences A/S	0-0782
Clopyralid	LFS Clopyralid	SL	LFS Kemi	0-0969
Clopyralid	Clopyralid 100	SL	KemiAgro	0-0970
Dicamba	Herbatox BV Plænerens	SL	KVK Agro A/S	0-0049
Dicamba	Herbatox GP	EC	KVK Agro A/S	0-0198
Dicamba	Herbatox BV Plænerens	SL	KVK Agro A/S	0-0258
Dicamba	Toxan Plænerens	SL	Bayer A/S	0-0259
Dicamba	Toxan Plænerens	SL	Bayer A/S	0-0260
Dicamba	Herbatox BV Plænerens	SL	KVK Agro A/S	0-0261
Dicamba	Plænerens, klar til brug	SL	Matas	0-0760
Dicamba	Flux Extra	EC	AgroDan A/S	0-0781
Ioxynil	Totril	EC	Rhône-Poulenc Agro	0-0042
Ioxynil	Briotril	EC	KVK Agro A/S	0-0047
Ioxynil	Ariane Super	EC	Dow AgroSciences A/S	0-0782
Ioxynil	Capture	SC	Rhône-Poulenc Agro	0-0968
Quinoclamine	Mogeton WP	WP	KVK Agro A/S	0-0262
Simazine	Simazin 500 SC	SC	KemiAgro	0-0780

Continues

Table 1 Herbicides continued

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Terbuthylazine	Inter-terbutylazin	SC	Inter-Trade A/S	0-0053
Terbuthylazine	Laddok TE	SC	BASF A/S	0-0054
Terbuthylazine	Lido SC	SC	Novartis A/S	0-0055
Terbuthylazine	Kemprim	SC	KeniAgro	0-0056

1) SC: suspension concentrate; EC: emulsifiable concentrate; SL: soluble concentrate; WP: Wettable powder

Table 2 Fungicides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
fenpropidin	Tern	EC	Novartis A/S	0-0041
fluazinam	Shirlan	SC	Zeneca Agro	0-0045
kresoxim-methyl	Mentor	SC	BASF A/S	0-0046
kresoxim-methyl	Candit	WG	BASF A/S	0-0966

1) SC: suspension concentrate; EC: emulsifiable concentrate; WG: Water dispersible granules.

Table 3 Insecticides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
buprofezin	Applaud 40 SC	SC	Cillus A/S	0-0761
fenazaquin	Pride Ultra	SC	Dow AgroSciences A/S	0-0967

1) SC: suspension concentrate

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