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## Rapporter og meldinger

Nr. 7/78

RESIDUES OF PIPERONYL BUTOXIDE  
IN DRIED FISH

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SENTRALLABORATORIET

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RESIDUES OF PIPERONYL BUTOXIDE  
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June 1978

(original in Norwegian, March 1978)

## RESIDUES OF PIPERONYL BUTOXIDE IN DRIED FISH

### Introduction

Producers of dried fish, may on permission from the Director General of Fisheries, use pyrethrum treatment to prevent damage by worms. The treatment must not result in residues above the maximum limit of 20 mg/kg recommended by FAO for piperonyl butoxide.

A field experiment was planned by the Central Laboratory to provide data on the connection between the method of treatment and residue levels. The experiment was executed at the State Technical School of Fish Industry in Vardö.

In addition, samples of standard dried fish pyrethrum-treated and untreated were supplied for analysis by the Division of Fish Quality Control, District of Nordland.

### Conclusion

The following treatments result in residues below the limit of 20 mg/kg of piperonyl butoxide:

- i) dipping once in a solution containing 0,12 % pyrethrum and 0,24 % piperonyl butoxide
- ii) mist spraying once (working solution as above)
- iii) up to two times spraying with an ordinary spray (working solution as above).

### Experimental

Materials. Samples of treated and untreated dried fish made from cod, haddock and pollack were received from District Inspector Svein Johansen, Svolvær, Nordland. A total of 18 treated and 2 untreated fish were analysed. The raw fish were treated according to instructions in a solution containing 0,12 % pyrethrum and 0,24 % piperonyl butoxide.

The field experiment in Vardö was carried out during the summer and autumn of 1977. The raw material was cod 40-60 cm long. Fourteen separate treatment groups were prepared, totalling 3800 kg.

The following set of treatments were used: The two official methods, dipping and spraying (0,12 % pyrethrum), dipping plus spraying, repeated spraying, mist spraying at various concentrations, and repeated mist spraying. Further details on the field experiment are available in a report from the State Technical School of Fish Industry in Vardö (in Norwegian).

Analytical method. Principle. Samples taken from whole fish are chopped and homogenised, and then extracted with ethanol/ether. The extract is chromatographed on a Florisil column, the eluate is analysed by GLC after concentration and addition of pyrene as internal standard. A detailed description of the method will be published elsewhere. Some samples were also analysed according to the official American method, FDA, Pesticide Analytical Manual, Vol. II, section 180. 127, method I.

### Results

Table 1 Field experiment Vardö - Residues of piperonyl butoxide in cod (mg/kg)

Treatment group	Treatment	Sample no.					Mean
		1	2	3	4	5	
1A	untreated	0.03-0.3					
1B	untreated	0.3	0.1				
1C	untreated	<0.1	0.1	<0.1	<0.1	0.3	
2	dipped	9.5	19.2	12.1	5.7	8.9	11
3	dipped+sprayed	17.5	12.9	7.2	23.3	9.9	14
4	dipped+2xsprayed	30.4	29.6	17.0	27.1	28.2	26
5	sprayed	5.1	1.8	2.5	4.2	2.3	3.2
6	2xsprayed	7.1	7.9	6.4	5.4	15.1	8.4
7	3xsprayed	22.6	36.4	36.6	39.9	30.7	33
8	mist sprayed 0.12%	4.6	4.8	6.6	4.7	2.2	4.6
9	2xmist sprayed 0.12%	46.2	14.6	19.9	11.5	37.0	26
10	3xmist sprayed 0.12%	10.5	14.8	39.2	18.4	29.9	23
11	mist sprayed 0.24%	53.8	61.1	17.7	38.0	25.2	39
12	mist sprayed 0.48%	19.2	10.7	11.7	7.0	19.7	14
13	mist sprayed 0.06%	4.6	3.5	4.7	3.8	3.2	4.0
14	mist sprayed 0.03%	1.7	1.5	1.9	0.3	1.2	1.3

Table 2 Production samples Svolvær - Residues of piperonyl butoxide (mg/kg)

Type of fish	Treated by dipping (0.12% solution)	Untreated
cod	1.1 0.5 1.9 0.6 1.4 2.2 1.9 3.1 3.8 1.9 0.4	0.2 0.1
haddock	0.5 2.1	
pollack	3.1 3.5 2.0 5.6 0.8	

Mean 2,1, standard dev. 1.45

Discussion

Table 1 indicates a difference between the treatment groups. This may be studied further by means of analysis of variance which gives the following results for treated fish:

	Sum of squares	Degrees of freedom	Mean square	Estimate of
between columns	132	4	32.9	
between rows	9146	12	762.2	$\sigma_i^2 + 13 \cdot \sigma_r^2$
residual	3456	48	72.0	$\sigma_i^2$
total	12733	64	-	

$F$  (columns) = 0.457  $v_1 = 4$   $v_2 = 48$   $F$  (P<0.05) = 2.57

$F$  (rows) = 10.59  $v_1 = 12$   $v_2 = 48$   $F$  (P<0.05) = 1.96

$\sigma_{i2}^2 = 72$  variance within rows, residual variance

$\sigma_r^2 = 53$  variance between rows

The F-values demonstrate that there are significant differences between treatment groups, but no differences between the sample numbers. The concentrations of piperonyl butoxide found in dried fish increase with repeated treatment and with increasing concentration in the working solution. The residual variance is considerable compared to the variance between treatments. This implies that factors not measured, such as the condition of the raw material, climatic factors, and individual differences contribute as much to the total variance as the pyrethrum treatment itself.

Concerning the maximum limit of 20 mg/kg it must be accepted that a sample taken randomly from the universe of dried fish could give values higher than the residue

limit in a small number of cases (for example in 5 % of all cases). The mean value for a particular sample must be lower than 20 mg/kg, based on the t-test it should be lower by an amount of 1.65 times the standard deviation:

$$\bar{x} + 1.65 \cdot s = G$$

$\bar{x}$  = residue mean value  
 $s$  = standard deviation  
 $G$  = residue limit

An average standard deviation  $s$  may be calculated for all treated samples in Table 1, and the result is  $s = 0,37 \cdot \bar{x}$ , where  $\bar{x}$  is the mean value found in a row (treatment group).

$\bar{x}$  may then be calculated from the formula (1):  
 $\bar{x} = 12$  mg/kg.

Treatments resulting in mean residue values below 12 mg/kg are therefore acceptable. From Table 1 this includes: dipping once, spraying once or twice, and mist spraying once, all at 0,12 % pyrethrum.

The results in Table 2 show much lower residue values (2,1 mg/kg) than for similar treatments in Table 1 (11 mg/kg). This demonstrates that for a given (official) treatment quite large differences may be expected in the concentration of piperonyl butoxide found in dried fish, even in samples of reasonable size.

#### Acknowledgement

The technical assistance of K. Heggstad is gratefully acknowledged.