# Evaluation of glassy frits as micronutrient fertilizers.

# 1. Copper and molybdenum frits

CH. H. HENKENS and K. W. SMILDE

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CH. H. HENKENS 1 and K. W. SMILDE 2

- Agricultural Advisory Officer for Matters relating to Soil and Manuring, Wageningen, The Netherlands
- <sup>2</sup> Institute for Soil Fertility, Groningen, The Netherlands

#### Summary

In 1954, 1955, 1956 and 1958 the response to fritted trace elements was studied in pot and field experiments. The copper containing glassy frits FN 501 (8 % Cu) and FN 502 (3.2 % Cu) were found to control copper deficiency in oats and wheat to a certain extent, their effect being inferior to that of copper sulphate, however. In field experiments 400 kg of frit FN 502 (12.8 kg Cu) was as effective as 15-20 kg of copper sulphate (3.8-5.1 kg Cu). There was found to be a distinct difference in response between FN 501 and FN 502, copper from the former material being less available. This was confirmed by the results of various extraction procedures, i.e. Aspergillus niger, EDTA, acetic acid. Considering the large quantities of frit FN 502 needed to control copper deficiency, the costs involved in application of this material may be prohibitory.

Molybdenum frits FN 701, FTE 25 and FTE 27 proved good sources of this nutrient. The immediate effect of sodium molybdate appeared to be somewhat larger, the residual effect somewhat smaller than of the molybdenum frits FTE 25 and FTE 27. No data are available as yet as to the behaviour of the latter products under field conditions. Suitable methods for evaluating and characterizing molybdenum frits in agricultural practice should be developed.

#### 1. Introduction

During the last 10-15 years application of glasses as a source of trace elements in crop production has received attention, especially in the U.S.A. (WYND and STROMME, 1951; RHOADS et al., 1956). Under some conditions slowly soluble glassy frits proved of considerable interest in providing a steady flow of available nutrient over a long period, thus preventing deficiencies due to leaching, or toxic conditions. The latter problems are particularly important in the boron nutrition of perennial crops (e.g. lucerne) when grown on coarse-textured soils of low buffering capacity (HORTENSTINE et al., 1958; HOLDEN and ENGEL, 1958; HOLDEN et al., 1962). Glassy frits were found

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to be no satisfactory carriers for iron (Rhoads et al., 1956). At present, however, the need for efficient iron fertilizers is sufficiently met by iron chelates.

In The Netherlands Middelburg and van Baren (1962a, 1962b, 1965) obtained good results with molybdenum, boron and manganese containing glassy frits in pot experiments with soil, using cauliflower, sugar beets and oats as test crops. At the Institute for Soil Fertility (Groningen, The Netherlands) experiments with frits have been performed in the period 1954–1959, the results on copper and molybdenum containing frits being presented here. In a following paper the results of some experiments on manganese frits will be discussed.

#### 2. Materials and Methods

# 2.1. Pot experiments with copper frits

In pot experiments the effect of copper frits on oat and wheat plants growing on a copper deficient sandy soil <sup>1</sup> low in organic matter was compared with that of copper sulphate and copper slags, i.e. fertilizers commonly in use in The Netherlands to control copper deficiency. Two copper frits, obtained from Ferro Enamels (Holland) Ltd. at Rotterdam, were tested, viz. FN 501 (8.0 % Cu<sup>2</sup>) and FN 502 (3.2 % Cu<sup>2</sup>). The copper contents of copper sulphate and copper slags were 25.6 % en 2.0 % <sup>2</sup>, respectively. The pots were of the ordinary Mitscherlich type (volume 5.2 l), containing 6.5 kg of soil each. Twenty-four plants were grown in each pot and watered with demineralized water, the moisture content of the soil being aimed at 60 % of the water capacity. Each treatment consisted of three pots, the locations of which being altered at regular intervals. A basal dressing of A.R. chemicals at the following levels was supplied to each pot: 1.71 g NH<sub>4</sub>NO<sub>8</sub> (0.6 g N), 1.14 g Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>. 2H<sub>2</sub>O (0.6 g P<sub>2</sub>O<sub>5</sub>), 1.67 g K<sub>2</sub>SO<sub>4</sub> (0.9 g K<sub>2</sub>O) and 1.0 g MgSO<sub>4</sub>. 7H<sub>2</sub>O (0.16 g MgO). The corresponding quantities in kg per hectare can be calculated by multiplying by 100/0.3141.

In the first experiment with oats, carried out in 1954, the following treatments were given: 0, 0.047, 0.126 and 0.314 g CuSO<sub>4</sub>. 5H<sub>2</sub>O; 0.377, 1.005 and 2.513 g copper frit FN 502; 0.151, 0.401 and 1.005 g copper frit FN 501 per pot, each copper compound supplying 0.0119, 0.0320 and 0.0804 g copper per pot, respectively (corresponding with 3.8, 10.2 and 25.6 kg Cu per hectare respectively).

In a second experiment with oats of similar design carried out in 1955 some more treatments were included, viz. copper slags, supplied at levels of 0.2356, 0.6282 and 1.5705 g per pot (corresponding with 1.5, 4.0 and 10.0 kg Cu per hectare, respectively), copper sulphate spray and a soil dressing just before appearance of the ears, and glassy frit carrier of FN 502, without copper, supplied at 2.513 g per pot.

This experiment was repeated in 1956, using wheat as test crop, to determine the residual effect of the various copper bearing products applied in 1955.

A Bartlett test was used to verify the homogeneity of the variances within each group of copper fertilizer. When the variances were found to be homogeneous an analysis of variance was applied. The *n*-ranking test by Friedman was applied to investigate whether the copper compounds differed significantly in their response.

<sup>1 0.5</sup> p.p.m. Cu (Aspergillus niger method).

<sup>&</sup>lt;sup>2</sup> Extraction in 3 N HCl.

### 2.2. Field experiments with copper frits

14

Five experiments with spring wheat (Pr 1961—Pr 1695) were performed in 1956, the following relevant data of which are presented here: pH(KCl) 4.5, 4.8, 4.9, 4.5 and 4.0; organic matter content 4.5, 11.7, 6.7, 6.4 and 5.4 %; copper content (Aspergillus niger method) 1.5, 0.5, 3.0, 0.5 and 0.5 p.p.m., respectively. An adequate dressing of nitrogen, phosphate, potash and magnesium fertilizer was given. The following treatments were compared: 0, 25, 50 and 100 kg copper sulphate; 400 kg copper frit FN 502; 300 and 500 kg copper slags, the quantities being expressed on a hectare basis. The quantity of copper in 400 kg of frit FN 502 (3.2 % Cu) is equal to that in 50 kg of copper sulphate. According to practical experience the fertilizing effect of 300 and 500 kg of copper slags is not much different from that of 50 and 100 kg of copper sulphate respectively. Each trial had a Youden square lay-out with four replications (4  $\times$  7 = 28 plots). The results were analysed statistically according to the usual Cochran and Cox methods, With Duncan's multiple range test the significance of the differences in response between the various copper compounds was tested,

## 2.3. Pot experiments with molybdenum frits

Molybdenum frits were tested in 1.2 litre polythene pots, containing 1.6 kg of a soil on which beets showed distinct symptoms of molybdenum deficiency in practice. After thinning out nine to ten sugar beet plants (variety Klein Wanzleben) were left in each pot and harvested  $2\frac{1}{2}$  months after sowing. Demineralized water was used for watering the plants. A basal dressing of A.R. chemicals at the following levels was supplied to each pot before sowing: 0.86 g NH<sub>4</sub>NO<sub>3</sub> (0.3 g N), 0.98 g K<sub>2</sub>HPO<sub>4</sub> (0.4 g P<sub>2</sub>O<sub>5</sub> and 0.5 g K<sub>2</sub>O) and 0.3 g MgSO<sub>4</sub>. 7H<sub>2</sub>O (0.05 g MgO). The conversion factor for calculating the quantities in kg per hectare is 100/0.0727 for these pots. Each treatment consisted of three replications (= three pots).

In 1955 an experiment with the following treatments was performed: no molybdenum, 8 mg Na<sub>2</sub>MoO<sub>4</sub>. 2H<sub>2</sub>O (39.6 % Mo), 115 and 280 mg molybdenum frit FN 701 (2 % total Mo) per pot, i.e. 0, 3.2, 2.3 and 5.6 mg Mo per pot, respectively.

Two other glassy frits, FTE 25 en FTE 27, were tested in another pot experiment in 1958. FTE 25 is a soft frit containing 3 % total Mo, 93 % of which dissolves in 0.1 N H<sub>2</sub>SO<sub>4</sub> (5 g in 250 ml 0.1 N H<sub>2</sub>SO<sub>4</sub>, shake for 1 hour); FTE 27 is a hard frit with 3 % total Mo, 10 % of which dissolves in 0.1 N H<sub>2</sub>SO<sub>4</sub> (1 g in 250 ml 0.1 N H<sub>2</sub>SO<sub>4</sub>, shake for 1 hour). The following treatments were given: 0, 0.091, 0.182, 0.364, 0.728, 1.092 and 1.456 mg Na<sub>2</sub>MoO<sub>4</sub>. 2H<sub>2</sub>O; 1.2, 2.4, 4.8, 9.6, 14.4 and 19.2 mg of both FTE 25 and FTE 27 per pot, each molybdenum fertilizer supplying 0.036, 0.072, 0.144, 0.288, 0.432 and 0.576 mg Mo per pot, respectively, or 49.5, 99.0, 198.0, 396.0, 594.0 and 792.0 g Mo per hectare, respectively. Moreover, FTE 27, because of its lower content of H<sub>2</sub>SO<sub>4</sub> soluble molybdenum, was supplied at 48, 96 and 144 mg per pot.

#### 3. Results and Discussion

#### 3.1. Pot experiments with copper frits

In the 1954 experiment with oats copper deficiency caused profuse tillering (Table 1), a phenomenon which has been described by various research workers, e.g. Brandenburg (1935), PIPER (1940), HEWITT et al. (1954), SCHARRER and SCHAUMLÖFFEL (1960).

The number of tillers decreased with increasing applications of copper, the effect being largest with copper sulphate and smallest with copper frit FN 501. Straw yields showed a rather similar trend, copper sulphate having the largest negative effect, and frit FN 501 almost none. Grain production increased with increasing quantities of frit FN 502 and was only little affected by frit FN 501, whilst the higher levels of copper sulphate gave no further response. At the highest copper level frit FN 502 gave a 69 % higher grain yield than copper sulphate. Average grain weight increased with increasing applications of both copper sulphate and copper frit FN 502, but glassy frit FN 501 hardly had an effect. This increase in grain weight results from the absence of void grains. A more comprehensive discussion is given in the section below (Table 2).

The high grain yield obtained with FN 502 is rather spectacular. An explanation can be found in the degree of tillering and the development of the grains. On 24th July the number of tillers was not much different for either frit treatment. Thereafter, profuse tillering continued in the FN 501 but not in the FN 502 treated plants. It would appear, therefore, that the copper supply of the latter gradually improved. The number of tillers did not increase and those already formed could develop normally and produce mature ears. Further evidence is given in Table 2 which presents total number of grains, number of fully developed grains and their average weights. The

Table 1. Straw and grain yields, number of tillers and average grain weight (1000 grains) of oat plants supplied with different copper fertilizers in the 1954 pot experiment (each figure represents the mean of three pots)

Quantity of Cu			Yield per	pot (in g)		
(kg/ha)	CuSO <sub>4</sub>	. 5H <sub>2</sub> O		FN 502 6 Cu)	•	FN 501 % Cu)
	grain	straw	grain	straw	grain	straw
0	12.6	39.9				
3.8	16.1	28.1	15.1	42.2	12.3	41.4
10.2	17.0	23.8	23.9	33.5	12.5	42.5
25.6	17,9	21.5	30.2	31.3	14.1	38.2
Significance	*	***	*	*	N.S.	N.S.
	<del> </del>		Number	of tillers		
	24/7	6/8	24/7	6/8	24/7	6/8
0	71.0	99.3				
3.8	44.5	52.5	68.3	88.7	58. <del>6</del>	94.7
10.2	37.0	36.0	49.0	<i>55.</i> <b>7</b>	64.0	93.7
25.6	40.0	38.0	47.0	43.7	51.0	84.3
		Aver	age grain wei	ght × 1000	(in g)	-
0 ,	8	.95				
3.8	19	.08	9.9	92	8.	.35
10.2	24	.38	19.	65	8.	.25
25.6	26	.93	27.5	95	12.	.07

oat plants which received no copper produced many grains most of which were void. With increasing applications of copper sulphate the total number of grains decreased but more grains fully developed. It is clear from Table 2 that the average weight of fully grown grains is almost constant, irrespective of copper treatment. All frit treated plants produced a large number of grains. However, the number of fully developed grains was totally different, being much larger in the case of FN 502. With the higher copper applications FN 502 also produced more fully grown grains than copper sulphate. From these results it would appear that copper deficiency at an early stage which stimulates tillering, may be advantageous, provided enough copper is supplied at a later stage for the production of mature ears with fully grown grains. This was investigated in the 1955 experiment, described below, in which copper sulphate was supplied late, either as a spray or a soil dressing. The high yield obtained with FN 502 might also have been due to some special component of the glassy frit carrier (silica?). Therefore, in the 1955 experiment a treatment with the glassy frit carrier was also included.

For the 1955 experiment a similar soil type from another site was used. The results are presented in Table 3.

Neither treatment influenced the number of tillers significantly, suggesting that the soil was not seriously copper deficient. This also appears from the yield data. The increases in grain yield as a result of application of copper compounds were rather small; only those for copper sulphate and frit FN 501 were significant. The response to copper sulphate was larger than that to either frit FN 501 or FN 502, but the difference between the frits was not significant in this respect. Application of copper sulphate as a soil dressing ("applied late" in Table 3) or as a spray just before appearance of the ears was found to be ineffective in curing copper deficiency. Cop-PENET (1955) is of the opinion that spraying is not an efficient means of controlling copper deficiency in cereals. However, CALDWELL (1955) obtained good results with a Bordeaux mixture spray. For a further discussion, which is not relevant here, see VAN ALPHEN (1957). The glassy frit carrier without copper had no influence on grain yield. Therefore, it seems unlikely that the unexpectedly large effect of frit FN 502 in the 1954 experiment was caused by components other than copper. All copper bearing materials decreased straw yield, only the effect of copper slags and frit FN 501 being significant however. Frit FN 501 increased the average grain weight significantly, the other copper compounds having no significant effect.

# 3.2. Residual effect

The residual effect of the various copper compounds given in 1955 was tested in the following year, using spring wheat as test crop. The results are shown in Table 4. An overall analysis of variance could not be applied as the variances of the copper sulphate and copper slags treatments were not homogeneous. Therefore, only the significance of the differences between the control and the medium level of copper sulphate and copper slags, respectively, was determined. All copper treatments given in 1955 caused a highly significant increase in grain yield in 1956, straw yield being hardly affected however. The response to copper in the second experimental year (test crop wheat) was much larger than that of the first year (test crop oats). Copper slags at 200 kg per hectare (3.8 kg Cu) and copper sulphate at 40 kg per hectare (10.2 kg Cu) had a similar residual effect on grain yield which was larger than that of either

plants, supplied with different copper fertilizers in the 1954 pot experiments (each figure represents the mean of three pots) Total number of grains, number of fully developed grains and average grain weight (1000 grains) in grams of oat Table 2.

Quantity		CuSO	CuSO5H2O			Cu frii	Cu frit FN 502			Cu frii	Cu frit FN 501	ı
oj Cu (kg/ha)	all grains		fully developed grains	oped grains	all g.	all grains	fully develo	oped grains	all g	all grains	fully devel	oped grains
	number	200	number	average weight	number	average weight	number	number average weight	number	average weight	e number average t weight	average weight
0	1410	8.95	2	34.0								
3.8	800	19.08	332	38.0	1623	9.92	182	33.0	1473	8 35	S	34.0
10.2	700	24.38	427	36.5	1216	19.65	537	34.6	1519	8.23	8 &	500
25.6	665	26.93	48	34.8	1080	27.95	830	34.2	1168	12.07	183	35.4

Average weight × 1000

Table 3. Straw and grain yields, number of tillers and average grain weight (1000 grains) of oat plants supplied with different copper fertilizers in the 1955 pot experiment (each figure represents the mean of three pots)

Treatment				Yield per	pot (in	g)		
	CuSO	4 . 5H2O	Cu frit	FN 502	Cu fri	t FN 501	Copp	er slags
	grain	straw	grain	straw	grain	straw	grain	straw
Glassy frit carrier	16.3	23.4						
Copper spray	16.4	23.0						
0 kg Cu/ha	16.4	24.1						
1.5 "							18.3	22.3
3.8 ,,	18.8	22.4	17.4	23.2	17.5	22.5	17.8	22.3
10.2 ,,	18.3	21.2	16.6	23.8	16.4	21.9	17.6	21.3
25.6 ,	19.1	23.6	17.8	22.0	18.2	22.8		
25.6 , applied late	16.7	23.1						
				Number	of tiller:	5		
Glassy frit carrier		<b>4</b> 1						
Copper spray	3	38						
0 kg Cu/ha	3	39						
1.5 "							4	3
3.8 ,	3	38		15	4	13	4	0
10.2 "	3	37	:	38	4	13	4	1
25.6 "	3	38		<b>1</b> 1	4	15		
25.6 ,, applied late	4	13						
		·	Average	grain wei	ight × 10	000 (in g)		
Glassy frit carrier	24	1.97						
Copper spray	. 25	5.15						
0 kg Cu/ha	27	.76						
1.5 ,							28.	.73
3.8 ,,	28	3.50	29	38	28	3.05	28.	32
10.2 ,,		3.34		.24		.16	-28	
25.6 ,		3.36	29	49		,42		
25.6 , applied late		,63						

Table 4. Grain and straw yields of spring wheat in grams per pot, showing the residual effect of various copper compounds applied to the preceding crop (oats, 1955 pot experiment), each figure representing the mean of three pots

Treatn	nent	CuSO	4.5H <sub>2</sub> O	Cu frit	FN 502	Cu frit	FN 501	Coppe	er slags
e -1	,	grain	straw	grain	straw	grain	straw	grain	straw
Glassy	frit carrier	4.3	40.3						
0 kg	Cu/ha	4.4	42.4						
1.5	3)							16.3	39.7
3.8	37	15.4	40.0	13.9	36.7	11.2	39.3	17.5	39.3
10.2	,,	17.4	39.7	15.5	40.2	13.6	38.3	17.4	39.4
25.6	33	16.4	40.4	17.4	41.0	15.5	39.6		

Table 5. Copper content of frits FN 501 and FN 502 as determined by different extraction methods

	3 N HCl	Aspergillus method	EDTA extraction	Acetic acid extraction
FN 501	8.0 %	0.14 %	0.051 %	0.060 %
FN 502	3.2 %	0.20 %	0.069 %	0.103 %

frit at the medium levels. With the ranking test it was found that the response of wheat to the various copper compounds decreased in the following order: copper slags = copper sulphate > frit FN 502 > frit FN 501, the difference between copper slags and frit FN 502 being significant, but not that between the latter and copper sulphate. The glassy frit carrier had no effect.

In order to find an explanation for the superior effect of frit FN 502 (3.2 % Cu) relative to frit FN 501 (8.0 % Cu), the copper content of each frit was estimated microbiologically (Aspergillus niger method) and chemically, using 0.5 N acetic acid or EDTA as extracting agents. From the results (Table 5) it is clear that frit FN 502 has a higher content of available copper than FN 501.

## 3.3. Field experiments with copper frits

Table 6 shows straw and grain yields of spring wheat obtained in five field trials with different copper compounds. The grain yields of the field trials showing a response to copper are arranged in ascending order at the bottom of Table 6. Results underlined by a joint line do not significantly differ from each other (P = 0.05).

In field experiments Pr 1692, 1964 and 1695 a significant response to copper was obtained, but not in Pr 1691 and 1693. Probably this is related to the higher soil copper contents in the latter two experimental fields (cf. p. 167). The response to copper sulphate, in terms of grain production, was very large in Pr 1694 and 1695 (a 119 and 51 % yield increase over the control, respectively at the medium level of copper sulphate), small (8 % yield increase) in Pr 1692, and nihil in Pr 1691 and 1693. In Pr 1694 and 1695 the lower levels of copper sulphate also had a favourable effect, only that in Pr 1695 being significant however. Application of 100 kg of copper sulphate per hectare did not give significantly better results than 50 kg. Frit FN 502 also favoured grain production in field trials Pr 1694 and 1695, but only in the latter one the effect just about reached the level of significance. Although equal amounts of copper are supplied by 50 kg of copper sulphate and 400 kg of frit FN 502, in field trial Pr 1694 a significantly better response was obtained with the former compound, whereas in Pr 1695 the difference between the two products was not significant. It can be postulated by interpolation that 400 kg of FN 502 equals 15 and 20 kg of copper sulphate, in Pr 1694 and 1695, respectively, as regards copper response.

Copper slags gave somewhat disappointing results in experiment Pr 1694 and 1695, showing that the assumption that 500 kg of copper slags are almost as effective as 100 kg of copper sulphate (cf. p. 167) is not always tenable. As a matter of fact, the effect of 500 kg of copper slags does not amount to more than 20 and 35 kg copper sulphate, in Pr 1695 and 1694, respectively. It should be realised, however, that 500 kg of copper slags do not contain more copper than 40 kg of copper sul-

phate. The response to 400 kg of FN 502 frit was not significantly larger than that to 500 kg of copper slags, although 2.8 kg copper more is supplied in the former case. In Pr 1694 the response was even smaller, not significant though.

No definite trend in straw yields was found. The results were somewhat erratic and neither copper fertilizer had a significant effect on straw production. In experiment Pr 1694 copper sulphate at 50 kg per hectare produced an almost significant increase in straw yield. Average grain weight was hardly affected by the various copper treatments and the results are not presented here.

Just before appearance of the ears foliage samples were taken for analysis of copper. After harvesting grain samples were also analysed for copper (Table 7). From the results it appears that the effect of application of copper compounds is not reflected in the copper content of either foliage (sampled just before appearance of the ears) or grain.

Summarizing the results of the pot and field experiments, it is true that the copper frits used may to a certain extent control copper deficiency, their effect being inferior to that of copper sulphate however. According to the field experiments 400 kg of frit FN 502 (12.8 kg Cu) equalled 15–20 kg of copper sulphate (3.8–5.1 kg Cu). A possible explanation for the relatively low efficiency of frit FN 502 is its copper being present in a rather stable form. Quite interesting is the peculiar difference between frit FN 502 and FN 501 in "available" copper, as determined by weak extracting agents (see p. 172), which probably accounts for the differences in response observed. The question arises whether the manufacturing procedure can be sufficiently standardized to guarantee a reproducible product with a constant amount of "available" copper.

# 3.4. Pot experiments with molybdenum frits

In a preliminary experiment in 1955 it was found that application of molybdenum frit FN 701 increased dry matter production of sugar beet plants considerably (Table 8). More comprehensive experiments were performed in 1958 using molybdenum frit FTE 25 and FTE 27 (see p. 167). In the first experiment there was a negative relationship between dry matter production and degree of molybdenum deficiency (Table 9). The highest yield was obtained with sodium molybdate at 594 and 792 g of molybdenum per hectare. The plants receiving these applications did not show symptoms of molybdenum deficiency. Frit FTE 25 at 792 g of molybdenum per hectare was slightly less effective, whereas frit FTE 27 proved inadequate in curing the deficiency at this level. It further appears that the amount of 0.1 N sulphuric acid soluble molybdenum of frits is of no great value in characterising and evaluating these products in agricultural practice. Application of 1980 g of molybdenum as FTE 27 was more effective than 396 g of molybdenum as FTE 25. However, the quantity of molybdenum soluble in 0.1 N H<sub>2</sub>SO<sub>4</sub> is only 198 g for FTE 27 as compared with 368 g for FTE 25 (Table 9).

#### 3.5. Residual effect

The first experiment was repeated to study the residual effect of the various molybdenum products. For that purpose the soil used in the first experiment was mixed per treatment and supplied with another dose of nitrogenous fertilizer prior to filling the pots. Some pots, i.e. those having been supplied with a quantity of molybdenum equivalent to 49.5, 59.4 and 99.0 g per hectare, received a fresh application in the

2.6 2.1 2.4 2.0 2.2 2.1

10.4 9.8 9.1 10.0 9.3 9.3

Cu per CuSO, CuSO, CuSO, frit FN 502 copper slags

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grain yields of spring wheat in 100 kg/ha in five field experiments (each	
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Table	
177	

0 kg.Cu per ha 20.0 25 kg CuSO, 19.4 50 kg CuSO, 20.4 400 kg frif FN 502 , 20.4 500 kg copper slags , 20.1 500 kg copper slags , 19.2 Significance , N.S. Pr 1692	in strow	7 7 7	Fr 1692	Å	Pr 1693	Pr	Pr 1694	Pr	Pr 1695
ad " " " " ; ; ; ; ; ; ; ; ; ; ; ; ; ; ;		grain	straw	grain	straw	grain	straw	grain	straw
4/ 5		41.9	66.7	27.7	61.8	12.7	59.6	18.7	66.7
		41.2	65.8	27.8	62.2	18.6	61.0	27.0	64.2
4/ 5		45.2	67.5	28.8	62.0	27.8	9.99	28.3	6.09
41,		44.0	68.5	28.4	57.9	26.0	63.6	30.0	64.3
4.	0 30.6	42.4	67.4	26.6	59.7	16.7	62.1	26.1	64.1
* : : : 4/ <i>t</i>		43.4	0'69	25.3	61.0	21.1	64.0	23.8	54.3
÷ ; ;		43.3	623	29.0	61.8	23.6	61.3	25.8	62.0
		*	Z.	Z.S.	Z.	*	Z.S.	# #	Z.
	41.9		42.4	43.3	44.0		45.2		
L1 1304 12.1	16.7		21.1	23.6	27.8				
Pr 1695 18.7	23.8		26.1	30.0					
Table 7. Copper content	content of spring wheat foliage and orain expressed in n m on dry matter	foliave an	grain	expressed i	E	dr mat	rej Te		
	Pr 1691	Pr 1692	92	Pr	Pr 1693	Pr	Pr 1694	Pr	Pr 1695
toliane	acon once	toligae	airea.	toliana	and the same	toliane	1	Lalland	

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month

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Relation between dry matter production (means of three pots) of tops of sugar beet plants after

9.

Table

Dry matter production of tops of sugar beet plants (in grams per pot) after a 2½ month

Table 8.

growing period as affected by different mo-

Quantity		Na:MOO. 2H2C	04.2H2O			Mo frit FTE 25	FTE 25			Mo frit	Mo frit FTE 27	
of Mo (e/ha)	rel. yield	vield	def. sympt.	ympt.	rel. yield	yield	def. s	def. sympt.	rel. yield	yield	def.	def. sympt.
	Ist expt.	2nd expt.	Ist expt.	2nd expt.	Ist expt.	2nd expt.	Ist expt.	2nd expt.	1st expt.	2nd expt.	1st expt.	2nd expt.
0	1001	100	+ + +	+++++++++++++++++++++++++++++++++++++++			:					
49.5	114		+		121		+		92		+ · + ·	
99.0	136	70,0	+ - +	-	136	140	<del> </del>	-	121	110	<b>+ -</b> +	-
198.0	<u>\$</u>	971	+	<b>+</b> ·	200	148	+-	<del> </del>	143	178	<del> -</del> -	+ -
396.0	279	189	<del>+</del> I	+	236	167	+	+	186	193	+	+
594.0	343		l		236		ŧI		236		ti	
792.0	321	196	l	]	293	207	1	]	143	226	+	1
1980.0									271	226	I	ĺ
3960.0									286	181	l	[
5940.0									250	200	1	[
$49.5^2 + 742.5^3$		267		Ì		263		ļ		281		1
594.02 + 594.03		222		1		278		ι		259		1
$99.0^{2} + 1485.0^{3}$		389		1		307		l		197		1

+++= very severe, ++= severe, += moderate,  $\pm=$  slight, -= no symptoms.

Applied at beginning of 1st experiment. Applied at beginning of 2nd experiment.

Mean of six replications.

same form as it was given originally, amounting to 742.5, 594.0 and 1485.0 g of molybdenum per hectare, respectively. The results are also presented in Table 9. The results of the second experiment show that there was a residual effect of the various molybdenum fertilizers. However, the response to molybdenum was smaller than in the first experiment, especially as regards sodium molybdate. FTE 27 was somewhat exceptional in this respect as the response at the lower levels of supply was larger than in the first experiment. Whatever the residual effect may be, a fresh supply of molybdenum proved still advantageous as is shown by the results at the bottom of Table 9. As a matter of fact, with a total quantity of 792 g of molybdenum per hectare better results were obtained with a fresh molybdenum application (742.5 g of Mo per hectare) at the beginning of the second experiment than without. With a fresh supply of 594.0 g of Mo per hectare, given at the beginning of the second experiment, in addition to the original dose of 594.0 g of Mo per hectare (first experiment), the yields of the frit treatments were highest. As in the first experiment the reverse was found at the 594.0 g of Mo per hectare level, it would seem reasonable to ascribe this difference in yield between the sodium molybdate and the frit treatments to the residual effect of the latter.

Summarizing the results, the conclusion seems justified that molybdenum frits are good sources of molybdenum. The immediate effect of sodium molybdate seemed to be somewhat larger and the residual effect somewhat smaller than that of the molybdenum frits. It is difficult, however, to give an agricultural evaluation of these glassy materials; the solubility in 0.1 N sulphuric acid did not prove a good measure, and other methods should be developed. No advise can be given as yet as to application of molybdenum frits under field conditions.

The results presented here are in good agreement with those obtained by MIDDEL-BURG and VAN BAREN (1962a, b), but their conclusion that sodium molybdate is less effective than FTE 25 at the lower levels of molybdenum supply could not be confirmed.

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Neth. J. Agric. Sci., Vol. 14 (1966) No. 3 (August)

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MILES. P.

#### GLASSY FRITS AS MICRONUTRIENT FERTILIZERS. I. COPPER AND MOLYBDENUM FRITS

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