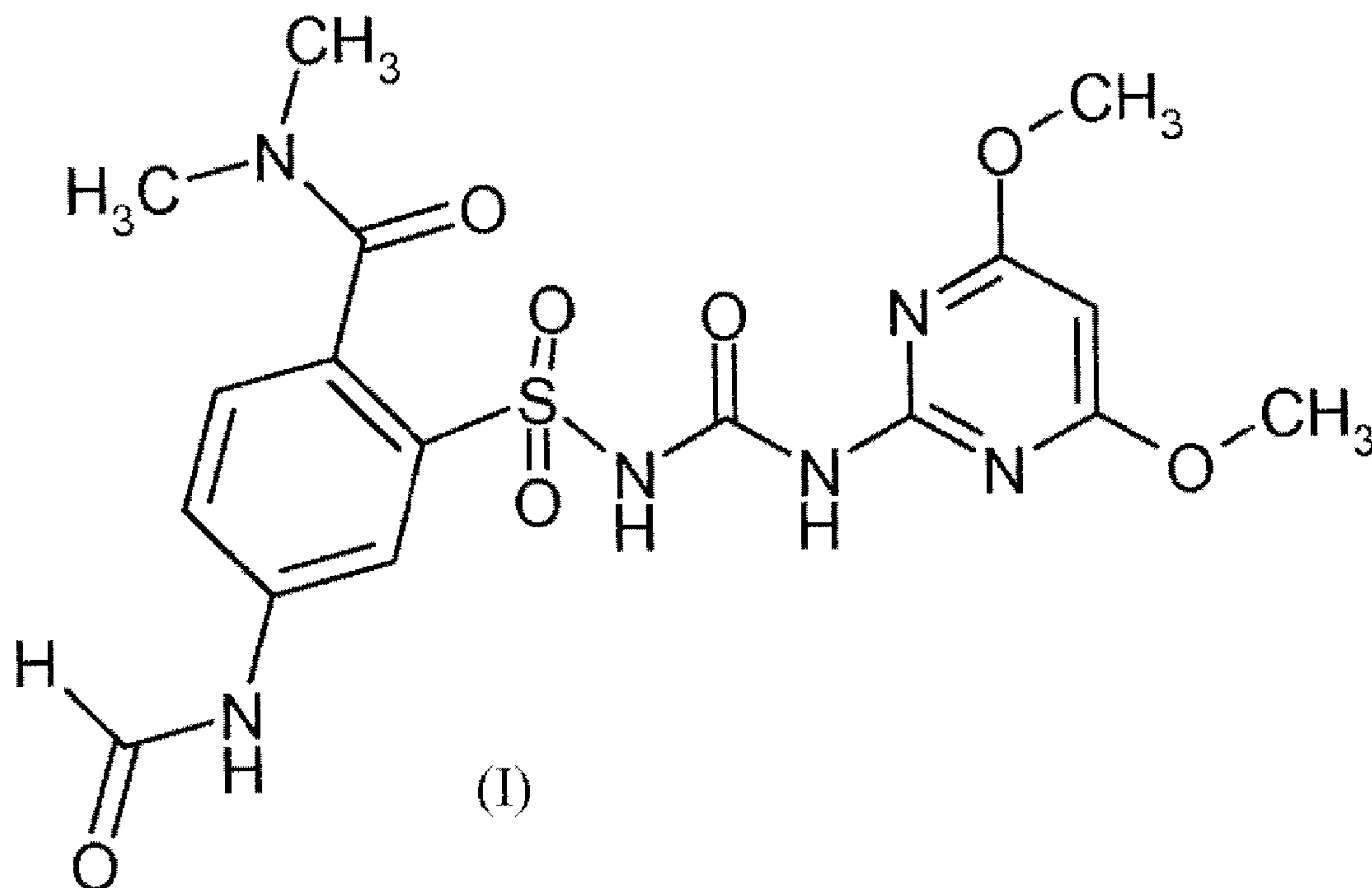




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(54) Titre : NOUVELLES FORMES CRISTALLINES DU SEL MONOSODIQUE DE FORAMSULFURON
(54) Title: NOVEL CRYSTAL FORMS OF THE MONOSODIUM SALT OF FORAMSULFURON



(57) Abrégé/Abstract:

The present invention relates to a novel crystal form of the monosodium salt of foramsulfuron (formula (I)), a method for producing said crystal form, the use thereof in agrochemical preparations as well as certain compositions, mixtures and/or agrochemical preparations containing said crystal form. The invention also relates to a novel monomethanol solvate of the monosodium salt of foramsulfuron.

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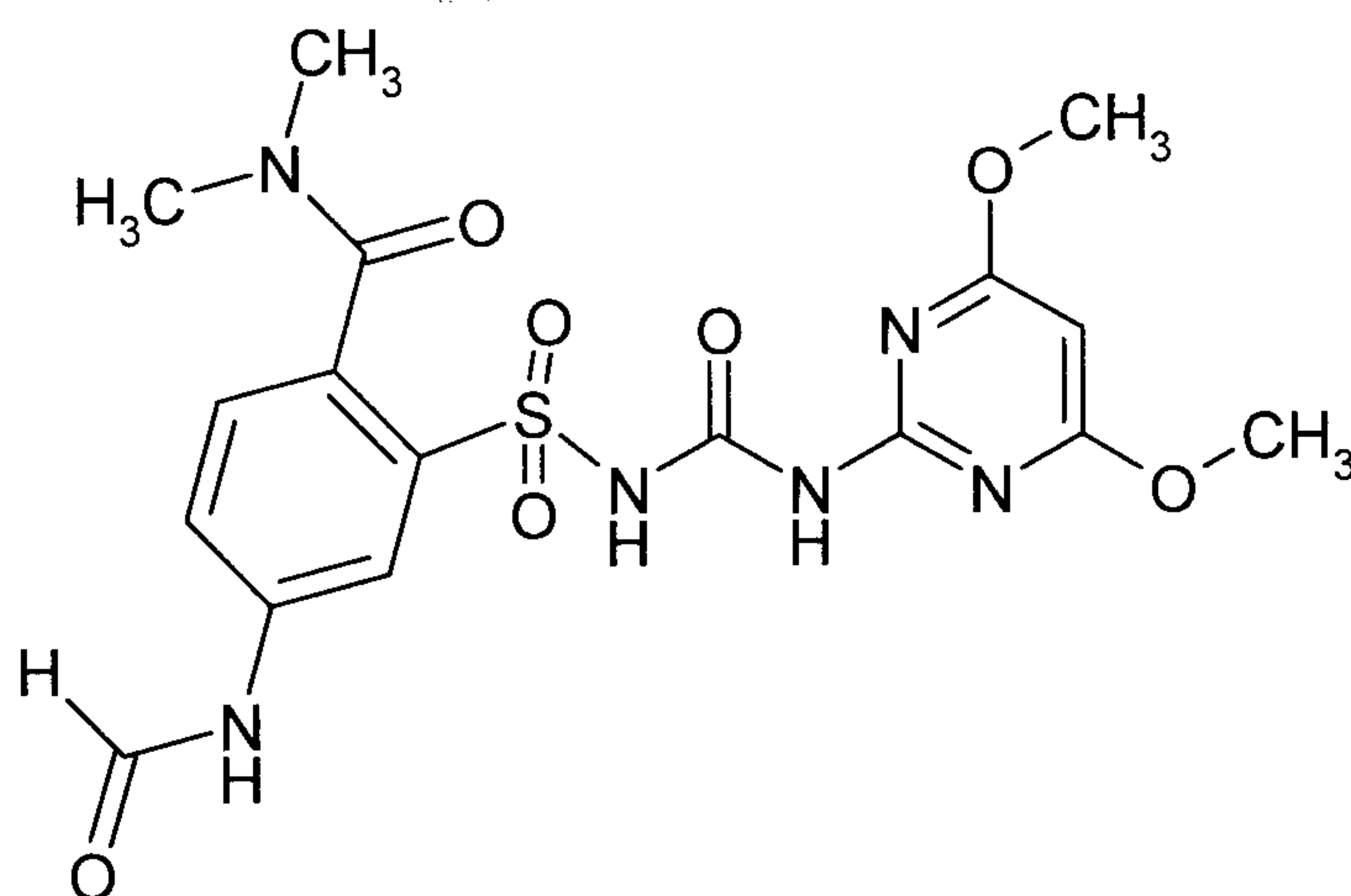
Novel crystal forms of the monosodium salt of foramsulfuron**A b s t r a c t**

The present invention relates to a novel crystal form of the monosodium salt of foramsulfuron, a method for preparing this crystal form, use thereof in agrochemical formulations and also particular compositions, mixtures or agrochemical formulations comprising this crystal form, and also a novel monomethanol solvate of the monosodium salt of foramsulfuron.

Novel crystal forms of the monosodium salt of foramsulfuron

The present invention relates to a novel crystal form of the monosodium salt of foramsulfuron, a method for preparing this crystal form, use thereof in agrochemical formulations and also particular compositions, mixtures or agrochemical formulations comprising this crystal form, and also a novel monomethanol solvate of the monosodium salt of foramsulfuron.

Foramsulfuron of formula (I) below and the monosodium salt thereof are known from EP 0 757 679 A1.



(I)

Foramsulfuron of formula (I) and certain salts of this compound are known herbicidal active ingredients, see "The Pesticide Manual", 16th edition, The British Crop Protection Council and the Royal Society of Chemistry, 2012.

It is also known that foramsulfuron of formula (I) and salts thereof may be used in combination with other herbicidal active ingredients and/or with safeners, described in EP 0 790 771 A1 or EP 1 104 239 A1 for example.

Foramsulfuron has the empirical formula $C_{17}H_{20}N_6O_7S$, CAS number 173159-57-4 and IUPAC name 1-(4,6-dimethoxypyrimidin-2-yl)-3-[2-(dimethylcarbamoyl)-5-formamidophenylsulphonyl]urea, and is also referred to below as N-[(4,6-dimethoxypyridin-2-yl)aminocarbonyl]-2-dimethylaminocarbonyl-5-formylaminobenzenesulphonamide.

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The compound of formula (I) and the monosodium salt thereof can be prepared by the methods described in EP 0 757 679 A1 and US 6,500,952 B1.

EP 1 902 618 A1 describes methods for preparing sulphonamide salts.

Only one crystal form of the monosodium salt of foramsulfuron has been known to date, which is referred to hereinafter as crystal form A. This crystal form A corresponds to a semi-methanol solvate.

The crystal lattice of a solid can be made up of several chemical components. If one of these is a liquid (e.g. a solvent), these are termed solvates.

The occurrence of active ingredients in various crystalline modifications (polymorphs) is of great significance both for the development of production processes and for the development of formulations (agrochemical formulations). For instance, the different crystalline modifications of a chemical compound differ not only in appearance (crystal habit) and hardness, but also in numerous further physicochemical properties. Differences in terms of stability, filterability, solubility, hygroscopicity, melting point, solid density and flowability can exert a strong influence on the quality and the efficacy of plant treatment compositions. It has not been possible to date to predict the occurrence and number of crystalline modifications, including the physicochemical properties thereof. In particular, the thermodynamic stability and also the different behaviour after administration to living organisms cannot be predicted. The above embodiments, referring to polymorphs, are applicable analogously to pseudopolymorphs.

The known crystal form A has some disadvantageous properties which are briefly described below.

Crystal form A may have a disadvantageous effect on the stability or storability of compositions (e.g. agrochemical formulations) comprising crystal form A. This may be the case because, for example, the chemical stability of crystal form A in certain compositions is not sufficient and/or further constituents (e.g. other active ingredients) of these compositions are negatively influenced in terms of their chemical stability by crystal form A, and their content in the composition decreases with time. It may also occur that a composition (e.g. agrochemical formulation) comprising crystal form A is unstable over a long (storage) period, and the physical properties of the composition changes, for example, the viscosity or flowability of the composition changes in an undesirable manner.

It is also known that sulphonylurea herbicides are subjected to chemical degradation reactions in the presence of particular auxiliaries, such as alcoholic diluents, particularly methanol, which leads to a decrease in the active ingredient content of the sulphonylurea herbicide over long storage periods, which is undesir-

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able. This chemical degradation also occurs in compositions (such as mixtures or formulations) comprising foramsulfuron and salts thereof in combination with other sulphonylurea herbicides or salts thereof, for example, in compositions described in EP 1 104 239 A1. This applies in particular to readily chemically degradable / hydrolysable sulphonylurea herbicides such as iodosulfuron, iodosulfuron-methyl and respective salts thereof such as iodosulfuron-sodium or iodosulfuron-methyl-sodium.

In some cases, furthermore, the technical handling of the known crystal form A is difficult. For instance, according to the preparation method described in EP 0 757 679 A1, this crystal form A occurs in the form of flocculent and poorly filterable aggregates.

The object of the invention, therefore, is to remedy one, several or all of the disadvantage(s) mentioned above in connection with the known crystal form A or to improve the disadvantageous properties mentioned above in connection with the known crystal form A.

This object is achieved in accordance with the invention by a novel crystal form of the monosodium salt of the compound of formula (I) having the empirical formula $C_{17}H_{19}N_6O_7SNa$, which is referred to hereinafter as crystal form B.

Therefore, the invention primarily relates to the monosodium salt of foramsulfuron in crystalline form (crystal form B), characterized in that the X-ray powder diffractogram of this salt using Cu $K\alpha$ radiation at 25°C has at least 3 of the following 2Θ (2 theta) values:

2Θ (2 theta) values in °
6.2
6.4
14.4
14.6
14.7
18.4
19.2
20.1
23.2
24.7

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This inventive crystal form B is characterized in that it has an X-ray powder diffractogram having the 2Θ (2 theta) reflections reported in Table 1. The X-ray powder diffractogram of crystal form B is also shown in Figure 2. The most intensive and characteristic 2Θ (2 theta) signals in the X-ray powder diffractogram of crystal form B are at 6.2, 6.4, 14.4, 14.6, 14.7, 18.4, 19.2, 20.1, 23.2, and 24.7° (in each case $\pm 0.2^\circ$).

The inventive crystal form B is characterized in that the X-ray powder diffractogram of this salt using Cu $K\alpha$ radiation at 25°C has at least 4, preferably at least 5, preferably at least 6, more preferably at least 7, particularly preferably at least 8 and especially preferably all of the most intensive 2Θ (2 theta) signals specified above.

The inventive crystal form B is preferably characterized in that the X-ray powder diffractogram of this salt using Cu $K\alpha$ radiation at 25°C additionally has at least two, four, six, eight, ten, twelve or more, preferably at least 15, 20, 23, 25, 27, 30, 33, 35, 38, 40, 42, 44, 46, 48, 50 or more, preferably all of the following 2Θ (2 theta) values:

10.3
10.5
11.1
11.3
11.4
12.0
12.1
12.4
12.6
12.9
13.6
14.0
15.0
15.1
15.4
16.0
16.2
17.0
17.2

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18.2
18.8
20.3
20.6
20.8
21.2
21.6
22.7
23.7
24.6
25.4
25.9
26.2
26.9
27.1
27.7
28.3
29.0
30.2
30.5
30.7
31.0
31.2
31.9
32.5
32.6
33.7
34.8
35.6
35.9
36.2
36.4

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36.9
37.4

The inventive crystal form B, unlike crystal form C described below, is non-hygroscopic and has improved stability in formulations (agrochemical formulations).

The inventive crystal form B is better suited to the preparation of (storage) stable formulations and it is more compatible with other sulphonylurea herbicides and salts thereof, particularly with iodosulfuron and salts thereof, since sulphonylurea herbicides (in particular here iodosulfuron) and salts thereof have unsatisfactory stability, particularly unsatisfactory chemical stability, in mixtures with crystal form A.

All X-ray powder diffractometry data stated in the present text refers to the following measurement parameters:

Scan axis	gonio
Scan Mode	transmission
Start Position [$^{\circ}2\theta$]	2.0066
End Position [$^{\circ}2\theta$]	37.9906
Anode material	Cu
Wavelength K-alpha1 [\AA]	1.54060
Wavelength K-alpha2 [\AA]	1.54443
Wavelength K-beta [\AA]	1.39225
K-A2 / K-A1 ratio	0.50000
Generator	40 mA, 40 kV
Incident Beam Monochromator	focusing X-ray mirror
Spinning	yes

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2 Θ (2 theta) values $\pm 0.2^\circ$

Furthermore, in the context of the present invention, the crystalline form referred to below as crystal form C was found. It takes the form of the monomethanol solvate of the monosodium salt of the compound of formula (I). Crystal form C may be obtained, for example, when crystal form A is stored over a long time period with methanol, which changes crystal form A into crystal form C. Crystal form C is described in further detail below.

Crystal forms A, B and C are characterized by different X-ray powder diffractograms. In Table 1 below, the respective most intensive characteristic 2 Θ (2 theta) reflections are stated, while Table 3 further below shows all 2 Θ (2 theta) reflections.

Table 1: Characteristic reflections – X-ray diffractometry of crystal forms A, B and C (as defined above)

Peak maximum [2 theta], data in °		
Crystal form A	Crystal form B	Crystal form C
7.4	6.2	9.1
8.7	6.4	9.1
9.0	14.4	9.7
9.2	14.6	12.6
9.3	14.7	16.2
15.7	18.4	18.5
23.3	19.2	24.1
23.3	20.1	24.3
23.6	23.2	24.6
26.0	24.7	

If the 2 Θ (2 theta) reflections of the X-ray powder diffractogram specified in the present text for a given crystalline form have the same value twice (for example the 2 Θ peak maximum at 23.3° in the case of crystal form A), this takes the form of two closely spaced peaks. Due to rounding of the measurement value of the respective peak maximum to one decimal place, two peaks with the same value can arise, but which actually take the form of two peaks in the X-ray powder diffractogram.

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The X-ray powder diffractogram of crystal form A is shown in Figure 1.

The X-ray powder diffractogram of crystal form B is shown in Figure 2.

The X-ray powder diffractogram of crystal form C is shown in Figure 3.

The inventive monosodium salt of foramsulfuron in crystalline form is particularly preferably characterized in that the X-ray powder diffractogram using Cu K α radiation at 25°C corresponds essentially to the spectrum shown in Figure 2.

Crystal forms A, B and C are characterized by Raman spectra. In Table 2 below, the most intensive, characteristic bands are given in each case.

All Raman spectroscopy data given in the present text refer to the following measurement parameters, in which the position of the band maxima of the wave number are in each case stated in cm⁻¹:

Instrument	Bruker Raman RFS 100/S
Number of scans	64
Resolution	2 - 4 cm ⁻¹
Laser power	50 mW
Laser wavelength	1064 nm

Inventive crystal form B is preferably characterized in that the Raman spectrum thereof has at least the following bands:

Band maximum [cm ⁻¹]
2959
2915
1686
1587
1526
694
345

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Band maximum [cm^{-1}]
133

The Raman spectrum of crystal form B according to the invention preferably has at least ten of the bands specified in Table 4 below, preferably 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65 or more, preferably all of the bands specified in Table 4 below.

Table 2: Characteristic bands of the Raman spectra of crystal forms A, B and C (as defined above)

Band maximum [cm^{-1}]		
Crystal form A	Crystal form B	Crystal form C
2941	2959	3090
1700	2915	2943
1320	1686	2919
1250	1587	1593
990	1526	1576
697	694	691
362	345	156
103	133	122

The Raman spectrum of crystal form A is shown in Figure 4.

The Raman spectrum of crystal form B is shown in Figure 5.

The Raman spectrum of crystal form C is shown in Figure 6.

The Raman spectrum of inventive crystal form B preferably corresponds essentially to the spectrum shown in Figure 5.

Table 3: X-ray diffractometry of crystal forms A, B and C (as defined above)

Peak maximum [2 theta]

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Crystal form A	Crystal form B	Crystal form C
5.6	6.2	9.1
5.9	6.4	9.1
7.4	10.3	9.7
7.6	10.5	12.0
7.9	11.1	12.6
8.4	11.3	14.8
8.7	11.4	15.7
9.0	12.0	16.2
9.2	12.1	16.3
9.3	12.4	17.8
11.1	12.6	18.0
11.6	12.9	18.2
11.8	13.6	18.5
13.2	14.0	19.0
13.4	14.4	19.5
13.9	14.6	19.9
14.5	14.7	20.1
14.8	15.0	20.9
15.3	15.1	21.1
15.5	15.4	21.7
15.7	16.0	22.1
16.1	16.2	22.6
16.7	17.0	23.5
17.0	17.2	23.8
17.3	18.2	24.1
18.1	18.4	24.3
19.0	18.8	24.5
19.2	19.2	24.6
19.7	20.1	25.1
20.7	20.3	25.6
20.9	20.6	25.8

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Peak maximum [2 theta]		
Crystal form A	Crystal form B	Crystal form C
21.3	20.8	26.5
22.3	21.2	26.8
22.6	21.6	27.1
22.8	22.7	28.8
23.3	23.2	29.2
23.3	23.7	29.7
23.6	24.6	30.0
24.5	24.7	30.5
24.8	25.4	30.8
25.1	25.9	31.3
26.0	26.2	31.7
26.8	26.9	31.9
27.6	27.1	32.0
28.2	27.7	33.1
28.7	28.3	33.2
29.1	29.0	33.5
30.1	30.2	34.2
30.7	30.5	34.4
32.0	30.7	34.9
33.0	31.0	35.4
34.4	31.2	35.8
37.0	31.9	36.2
37.4	32.5	36.6
	32.6	37.2
	33.7	37.7
	34.8	
	35.6	
	35.9	

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Peak maximum [2 theta]		
Crystal form A	Crystal form B	Crystal form C
	36.2	
	36.4	
	36.9	
	37.4	

Table 4: Raman spectroscopy bands of crystal forms A, B and C (as defined above)

Band maximum [cm ⁻¹]		
Crystal form A	Crystal form B	Crystal form C
3114	3338	3302
3.097	3.100	3.090
3.072	3.061	3.030
3.032	3.035	3.016
2.941	3.018	2.999
2.890	2.959	2.943
2.878	2.915	2.919
2.842	2.865	2.870
2.798	2.810	2.839
1.700	1.686	2.812
1.691	1.654	1.693
1.653	1.628	1.628
1.639	1.604	1.617
1.604	1.587	1.607
1.537	1.526	1.593
1.513	1.478	1.576
1.449	1.451	1.533
1.404	1.421	1.517
1.382	1.393	1.480

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Band maximum [cm ⁻¹]		
Crystal form A	Crystal form B	Crystal form C
1.320	1.372	1.449
1.267	1.304	1.415
1.250	1.262	1.404
1.218	1.244	1.384
1.196	1.216	1.372
1.160	1.206	1.303
1.150	1.175	1.261
1.120	1.142	1.243
1.101	1.112	1.215
1.053	1.092	1.207
1.004	1.064	1.168
990	1.048	1.148
936	1.031	1.137
926	1.022	1.111
896	1.002	1.092
760	983	1.074
744	938	1.048
697	925	1.031
684	910	1.015
642	904	1.002
598	882	984
555	864	940
534	823	924
500	812	908
446	786	895
424	763	883
362	735	837
310	713	826
294	694	788
263	688	761

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Band maximum [cm ⁻¹]		
Crystal form A	Crystal form B	Crystal form C
215	649	739
159	623	710
103	614	691
85	594	649
	580	620
	555	593
	512	581
	464	517
	445	469
	421	431
	394	394
	356	370
	345	347
	254	333
	218	283
	186	266
	147	242
	133	156
	98	122
	84	82

In a further aspect, the present invention relates to a composition comprising inventive crystal form B in a total amount of at least 5% by weight, wherein this total amount is preferably at least 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95% by weight or more, based in each case on the total weight of monosodium salt of foramsulfuron present in the composition.

Such a composition according to the invention is preferably characterized in that the composition comprises inventive crystal form B in a total amount of at least 10% by weight, preferably 15% by weight or more, based in each case on the total amount of monosodium salt of foramsulfuron present in the composition.

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A preferred composition according to the invention is thereby characterized in that

it is present in solid form at 25°C and 1013 mbar,

and/or

the content of monosodium salt of foramsulfuron is 80% by weight or more, preferably 85% by weight or more, preferably 90% by weight or more, particularly preferably 95% by weight or more, based in each case on the total weight of the composition.

A preferred composition according to the invention is characterized in that the composition comprises inventive crystal form B in a total amount of at least 25% by weight, preferably 40% by weight or more, based in each case on the total amount of monosodium salt of foramsulfuron present in the composition,

and

the content of monosodium salt of foramsulfuron is 80% by weight or more, preferably 85% by weight or more, based in each case on the total weight of the composition.

A particularly preferred composition according to the invention is characterized in that the composition comprises inventive crystal form B in a total amount of at least 50% by weight, preferably 60% by weight or more, based in each case on the total amount of monosodium salt of foramsulfuron present in the composition,

and

the content of monosodium salt of foramsulfuron is 85% by weight or more, preferably 90% by weight or more, based in each case on the total weight of the composition.

An especially preferred composition according to the invention is characterized in that the composition comprises inventive crystal form B in a total amount of at least 70% by weight, preferably 80% by weight or more, based in each case on the total amount of monosodium salt of foramsulfuron present in the composition,

and

the content of monosodium salt of foramsulfuron is 85% by weight or more, preferably 90% by weight or more, based in each case on the total weight of the composition.

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An especially preferred composition according to the invention is characterized in that the composition comprises inventive crystal form B in a total amount of at least 80% by weight, preferably 85% by weight or more, based in each case on the total amount of monosodium salt of foramsulfuron present in the composition,

and

the content of monosodium salt of foramsulfuron is 90% by weight or more, preferably 95% by weight or more, based in each case on the total weight of the composition.

One of the most particularly preferred configurations is a composition according to the invention characterized in that the composition comprises inventive crystal form B in a total amount of at least 90% by weight, preferably 95% by weight or more, based in each case on the total amount of monosodium salt of foramsulfuron present in the composition,

and

the content of monosodium salt of foramsulfuron is 90% by weight or more, preferably 95% by weight or more, based in each case on the total weight of the composition.

In a further aspect, the present invention relates to the use of crystal form B according to the invention or a composition according to the invention as defined above for preparing agrochemical formulations, preferably for preparing herbicidally active agrochemical formulations.

In a further aspect, the present invention relates to the monomethanol solvate of the monosodium salt of foramsulfuron in crystalline form (crystal form C), characterized in that the X-ray powder diffractogram of this salt using Cu K α radiation at 25°C has at least 3 of the following 2 Θ (2 theta) values:

2 Θ (2 theta) values in °
9.1
9.1
9.7
12.6
16.2

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18.5
24.1
24.3
24.6

The X-ray diffractogram of inventive crystal form C using Cu K α radiation at 25°C preferably has at least 4, preferably at least 6, preferably at least 8, more preferably all of the 2 Θ (2 theta) values mentioned above.

The X-ray powder diffractogram of inventive crystal form C using Cu K α radiation at 25°C more preferably additionally has at least two, four, six, eight, ten, twelve or more, preferably at least 15, 20, 23, 25, 27, 30, 33, 35, 38, 40, 42, 44, 46, 48, 50 or more, preferably all of the following 2 Θ (2 theta) values:

12.0
14.8
15.7
16.3
17.8
18.0
18.2
19.0
19.5
19.9
20.1
20.9
21.1
21.7
22.1
22.6
23.5
23.8

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24.5
25.1
25.6
25.8
26.5
26.8
27.1
28.8
29.2
29.7
30.0
30.5
30.8
31.3
31.7
31.9
32.0
33.1
33.2
33.5
34.2
34.4
34.9
35.4
35.8
36.2
36.6
37.2
37.7

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Inventive crystal form C is preferably characterized in that the Raman spectrum thereof has at least the following bands:

Band maximum [cm ⁻¹]
3090
2943
2919
1593
1576
691
156
122

The Raman spectrum of crystal form C according to the invention preferably has at least ten of the bands specified in Table 4, preferably 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65 or more, preferably all of the bands specified in Table 4.

The Raman spectrum of inventive crystal form C preferably corresponds essentially to the spectrum shown in Figure 6.

The present invention further relates to a composition comprising crystal form C in a total amount of at least 5% by weight, wherein this total amount is preferably at least 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95% by weight or more, based in each case on the total amount of monosodium salt of foramsulfuron present in the composition.

The present invention preferably relates to a composition comprising crystal form C (as defined above), wherein

the composition is present in solid form at 25°C and 1013 mbar,

and/or

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the content of monosodium salt of foramsulfuron is 80% by weight or more, wherein the content of monosodium salt of foramsulfuron is preferably 85% by weight or more, preferably 90% by weight or more, particularly preferably 95% by weight or more, based in each case on the total weight of the composition.

Inventive crystal form B can be prepared by the method described below.

The invention further relates to a method for preparing crystal form B comprising the steps of

(a) suspending a monosodium salt of foramsulfuron (preferably of crystal form A), of crystal form C, or a mixture of these substances in a diluent or diluent mixture,

wherein the diluent or diluent mixture used in step (a) is selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 20% by weight thereof, preferably at least 30% by weight, more preferably at least 40% by weight, even more preferably at least 50% by weight thereof.

Crystal form B according to the invention can be obtained if the diluent or diluent mixture used in the method described above comprises 20% by weight or more of alcohols having 3 to 6 carbon atoms and/or ketones having 3 to 6 carbon atoms.

It is preferable if the diluent or diluent mixture used in the method described above comprises 60% by weight or more of alcohols having 3 to 6 carbon atoms and/or ketones having 3 to 6 carbon atoms, since readily filterable crystals are obtained in this manner, which is of considerable advantage in process engineering terms.

The invention therefore relates particularly to a method for preparing crystal form B comprising the steps of

(a) suspending a monosodium salt of foramsulfuron (preferably of crystal form A), of crystal form C, or a mixture of these substances in a diluent or diluent mixture,

wherein the diluent or diluent mixture used in step (a) is selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 60% by weight thereof.

The invention further relates to a method for preparing crystal form B comprising the steps of

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- (a) suspending foramsulfuron in a diluent or diluent mixture,
- (b) reacting foramsulfuron with a base containing sodium, preferably an organic base, in this case preferably sodium methoxide and/or sodium ethoxide,

wherein the diluent or diluent mixture used in step (a) is selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 20% by weight thereof, preferably at least 30% by weight, more preferably at least 40% by weight, even more preferably at least 50% by weight thereof.

The invention relates particularly to a method for preparing crystal form B comprising the steps of

- (a) suspending foramsulfuron in a diluent or diluent mixture,
- (b) reacting foramsulfuron with an organic base containing sodium, preferably sodium methoxide and/or sodium ethoxide,

wherein the diluent or diluent mixture used in step (a) is selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 60% by weight thereof.

In this case, sodium methoxide in methanol and/or sodium ethoxide in ethanol is preferably used as organic base containing sodium in step (b).

The methods according to the invention for preparing crystal form B are preferably conducted in a manner such that the diluent or diluent mixture used in step (a) is selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 60% by weight thereof, preferably 70% by weight or more, preferably 80% by weight or more, more preferably 90% by weight or more, particularly preferably 95% by weight or more thereof.

The methods according to the invention for preparing crystal form B are preferably conducted in a manner such that the diluent or diluent mixture used in step (a) is selected from the group consisting of 1-butanol, acetone, methyl isobutyl ketone, and mixtures thereof, or comprises 60% by weight or more thereof (preferably 70% by weight or more, preferably 80% by weight or more, more preferably 90% by weight or more, particularly preferably 95% by weight or more thereof).

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The methods according to the invention for preparing crystal form B are carried out preferably at temperatures of at least 0°C. The methods according to the invention for preparing crystal form B are preferably carried out at temperatures in the range of 0 to 150°C, preferably at temperatures in the range of 25 to 130°C.

The methods according to the invention for preparing crystal form B are preferably carried out at temperatures of at least 25°C, preferably of at least 30°C, preferably of at least 40°C. The methods according to the invention for preparing crystal form B are preferably carried out at temperatures in the range of 40 to 150°C, preferably at temperatures in the range of 45 to 130°C, particularly preferably in the range of 50 to 120°C.

In particularly preferred methods according to the invention for preparing crystal form B, acetone is used as a diluent or the diluent in step (a). In this case, the methods according to the invention for the preparation are preferably carried out at temperatures in the range of 0 to 65°C, preferably in the range of 25 to 56°C.

In further particularly preferred methods according to the invention for preparing crystal form B, acetone is used as a diluent or the diluent in step (a). In this case, the methods according to the invention for the preparation are preferably carried out at temperatures in the range of 40 to 65°C, preferably in the range of 45 to 56°C, particularly preferably in the range of 50 to 56°C.

The methods according to the invention for preparing crystal form B are preferably carried out in a manner such that the ratio by weight of the total amount of foramsulfuron, crystal form A and crystal form C, to the total amount of diluent or diluent mixture used in step (a) is less than 2:1. The ratio by weight of the total amount of foramsulfuron, monosodium salts of foramsulfuron (preferably crystal form A) and of crystal form C, to the total amount of diluent or diluent mixture used in step (a) is preferably in the range of 3: 1 to 1: 20, preferably in the range of 2: 1 to 1: 15, more preferably in the range of 1: 1 to 1: 10. In many cases, this ratio by weight is preferably in the range of 2: 3 to 1: 8, and particularly in the range of 1: 2 to 1: 5.

The method according to the invention for preparing inventive crystal form B preferably comprises further steps, preferably a cooling of the resulting mixture containing crystal form B. In this case, the cooling preferably takes place over a period of at least 15 minutes, preferably of at least 30 minutes.

Here, the cooling more preferably takes place over a period of at least 60 minutes, even more preferably of at least 120 minutes, and particularly preferably of at least 180 minutes.

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The method according to the invention for preparing inventive crystal form B preferably comprises further steps, preferably

filtration of the resulting mixture containing crystal form B, and/or

isolation of crystal form B, and/or

drying of crystal form B.

In the context of the method according to the invention for preparing inventive crystal form B, it is preferred if the starting material used, preferably crystal form A and/or crystal form C, is at most sparingly dissolved in the diluent, and in particular – in contrast to recrystallization processes – is not completely dissolved, but rather a solid–solid conversion of the starting material into crystal form B takes place, i.e. a conversion of solid substances.

The invention further relates to a mixture comprising

(i) monosodium salt of foramsulfuron and/or a solvate thereof, preferably comprising crystal form A, crystal form B, crystal form C, or a mixture comprising two or all of these crystal forms, and

(ii) a diluent or diluent mixture selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 20% by weight thereof, preferably at least 30% by weight, more preferably at least 40% by weight, even more preferably at least 50% by weight thereof.

The invention relates particularly to a mixture comprising

(i) monosodium salt of foramsulfuron and/or a solvate thereof, preferably comprising crystal form A, crystal form B, crystal form C, or a mixture comprising two or all of these crystal forms, and

(ii) a diluent or diluent mixture selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 60% by weight thereof, and preferably 70% by weight or more, preferably 80% by weight or more, more preferably 90% by weight or more, particularly preferably 95% by weight or more thereof.

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The diluent or diluent mixture is preferably such a mixture according to the invention selected from the group consisting of 1-butanol, acetone, methyl isobutyl ketone, and mixtures thereof, or it comprises at least 60% by weight thereof (preferably 70% by weight or more, preferably 80% by weight or more, more preferably 90% by weight or more, particularly preferably 95% by weight or more thereof).

The ratio by weight of the total amount of constituent (a), monosodium salt of foramsulfuron, to the total amount of constituent (b), diluent or diluent mixture in a mixture according to the invention, preferably corresponds to the weight ratios specified above (as preferred), based in each case on the total weight of the mixture which are stated in connection with the preparation method of inventive crystal form B.

Inventive crystal form B can be employed as such or in the form of agrochemical formulations (formulations) with other pesticidally active ingredients, such as, for example, insecticides, acaricides, nematocides, herbicides, fungicides, safeners, fertilizers and/or growth regulators, for example as finished formulation or as tank mixes. The combination formulations can be prepared on the basis of the formulations mentioned hereinafter, while taking account of the physical properties and stabilities of the active ingredients to be combined. Inventive crystal form B can be formulated in various ways, in which in general customary formulation auxiliaries in the pesticide field are used and/or other (agrochemical) active ingredients.

The invention therefore relates in a further aspect to an agrochemical formulation comprising

(a) a herbicidally effective amount of crystal form B,

and one or more further constituents selected from the group consisting of the following constituents (b-i), (b-ii) and (b-iii):

(b-i) formulation auxiliaries customary in the pesticide field,

(b-ii) further agrochemical active ingredients,

and

(b-iii) crystal form C.

A formulation according to the invention preferably comprises one or more safeners (here preferably isoxadifen, isoxadifen-ethyl and/or cyprosulfamide) as constituent (b-ii) and/or one or more further herbicidal active ingredients.

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The further herbicidal active ingredients are preferably selected from the herbicidal active ingredients mentioned in "The Pesticide Manual", 16th edition, The British Crop Protection Council and the Royal Society of Chemistry, 2012. In this case, the preferred herbicidal active ingredients are the herbicidal active ingredients mentioned in EP 0 790 771 A1 or EP 1 104 239 A1, particularly other ALS inhibitors (acetolactate synthase inhibitors), in turn preferably thien carbazon-methyl and salts thereof and/or other sulphonylurea herbicides, in turn preferably amidosulfuron, mesosulfuron, mesosulfuron-methyl, iodosulfuron, iodosulfuron-methyl, and respective salts thereof such as iodosulfuron-sodium or iodosulfuron-methyl-sodium (the particular advantages with respect to the (stability) improvement in combination with other sulphonylurea herbicides has already been stated earlier).

In addition, the agrochemical formulations (formulations) mentioned optionally comprise the respective customary stickers, wetters, dispersants, emulsifiers, penetrants, preservatives, antifreeze agents and solvents, fillers, carriers and dyes, defoamers, evaporation inhibitors and agents which influence the pH and the viscosity. Examples of formulation auxiliaries are described, inter alia, in "Chemistry and Technology of Agrochemical Formulations", ed. D. A. Knowles, Kluwer Academic Publishers (1998).

Potential useful formulations for inventive agrochemical formulations comprising crystal form B according to the invention include: wettable powders (WP), water-soluble powders (SP), water-soluble concentrates, emulsifiable concentrates (EC), emulsions (EW) such as oil-in-water and water-in-oil emulsions, sprayable solutions, suspension concentrates (SC), oil- or water-based dispersions, oil-miscible solutions, capsule suspensions (CS), dusting products (DP), seed-dressing products, granules for scattering and soil application, granules (GR) in the form of microgranules, spray granules, coated granules and adsorption granules, water-dispersible granules (WG), water-soluble granules (SG), ULV formulations, microcapsules and waxes.

It has also been found that is advantageous, in particular agrochemical formulations according to the invention such as some oil dispersions (OD), to use a mixture of inventive crystal form B and inventive crystal form C. Such agrochemical formulations according to the invention are in this case based preferably on formulations such as are described in US 2002/0016263 A1 or US 2005/0032647 A1.

Such agrochemical formulations comprising a mixture of inventive crystal form B and inventive crystal form C showed, with respect to otherwise identical formulations which contained only crystal form B, further improved properties, for example, a further improved storage stability, particularly in this case with respect to flowability and viscosity of the formulation.

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In such agrochemical formulations according to the invention, the ratio by weight of the total amount of crystal form B to the total amount of crystal form C is preferably in the range of 20: 1 to 1: 10, preferably in the range of 10: 1 to 1: 5, more preferably in the range of 10: 1 to 1: 3 and particularly preferably in the range from 5: 1 to 1: 1, based in each case on the total weight of the agrochemical formulation according to the invention.

These individual formulation types are known in principle and are described, for example, in: Winnacker-Küchler, "Chemische Technologie" [Chemical Technology],

volume 7, C. Hanser Verlag Munich, 4th ed. 1986; Wade van Valkenburg, "Pesticide Formulations", Marcel Dekker, N.Y., 1973; K. Martens, "Spray Drying" Handbook, 3rd ed. 1979, G. Goodwin Ltd. London.

The formulation auxiliaries required, such as inert materials, surfactants, solvents and further additives, are likewise known and are described, for example, in: Watkins, "Handbook of Insecticide Dust Diluents and Carriers", 2nd ed., Darland Books, Caldwell N.J.; H.v. Olphen, "Introduction to Clay Colloid Chemistry", 2nd ed., J. Wiley & Sons, N.Y.; C. Marsden, "Solvents Guide", 2nd ed., Interscience, N.Y. 1963; McCutcheon's "Detergents and Emulsifiers Annual", MC Publ. Corp., Ridgewood N.J.; Sisley and Wood, "Encyclopedia of Surface Active Agents", Chem. Publ. Co. Inc., N.Y. 1964; Schönfeldt, "Grenzflächenaktive Äthylenoxidaddukte" [Interface-active Ethylene Oxide Adducts], Wiss. Verlagsgesellschaft, Stuttgart 1976; Winnacker-Küchler, "Chemische Technologie" [Chemical Technology], volume 7, C. Hanser Verlag Munich, 4th ed. 1986.

Wettable powders are preparations which can be dispersed uniformly in water and, in addition to the active ingredient, apart from a diluent or inert substance, also comprise surfactants of the ionic and/or nonionic type (wetting agents, dispersants), for example polyoxyethylated alkylphenols, polyoxyethylated fatty alcohols, polyoxyethylated fatty amines, fatty alcohol polyglycol ether sulphates, alkanesulphonates, alkylbenzenesulphonates, sodium lignosulphonate, sodium 2,2'-dinaphthylmethane-6,6'-disulphonate, sodium dibutyl-naphthalenesulphonate or else sodium oleoylmethyltaurate. To produce the wettable powders, the herbicidally active ingredients are finely ground, for example in customary apparatus such as hammer mills, blower mills and air-jet mills, and simultaneously or subsequently mixed with the formulation auxiliaries.

Emulsifiable concentrates are produced by dissolving the active ingredient in an organic solvent, for example butanol, cyclohexanone, dimethylformamide, xylene, or else relatively high-boiling aromatics or

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hydrocarbons or mixtures of the organic solvents, with addition of one or more ionic and/or nonionic surfactants (emulsifiers). Examples of emulsifiers which may be used are: calcium alkylarylsulphonates such as calcium dodecylbenzenesulphonate, or nonionic emulsifiers such as fatty acid polyglycol esters, alkylaryl polyglycol ethers, fatty alcohol polyglycol ethers, propylene oxide-ethylene oxide condensation products, alkyl polyethers, sorbitan esters, for example sorbitan fatty acid esters, or polyoxyethylene sorbitan esters, for example polyoxyethylene sorbitan fatty acid esters.

Dustable powders are obtained by grinding the active ingredient with finely distributed solid substances, for example talc, natural clays such as kaolin, bentonite and pyrophyllite, or diatomaceous earth.

Suspension concentrates may be water- or oil-based. They may be prepared, for example, by wet-grinding by means of commercial bead mills and optional addition of surfactants as have, for example, already been listed above for the other formulation types.

Emulsions, for example oil-in-water emulsions (EW), can be produced, for example, by means of stirrers, colloid mills and/or static mixers using aqueous organic solvents and optionally surfactants as already listed above, for example, for the other formulation types.

Granules can be prepared either by spraying the active ingredient onto adsorptive granular inert material or by applying active ingredient concentrates to the surface of carriers, such as sand, kaolinites or granular inert material, by means of adhesives, for example polyvinyl alcohol, sodium polyacrylate or else mineral oils. Suitable active ingredients can also be granulated in the manner customary for the production of fertilizer granules - if desired as a mixture with fertilizers.

Water-dispersible granules are produced generally by the customary processes such as spray-drying, fluidized bed granulation, pan granulation, mixing with high-speed mixers and extrusion without solid inert material.

For the production of pan granules, fluidized bed granules, extruder granules and spray granules, see, for example, processes in "Spray-Drying Handbook" 3rd ed. 1979, G. Goodwin Ltd., London; J.E. Browning, "Agglomeration", Chemical and Engineering 1967, pages 147 ff.; "Perry's Chemical Engineer's Handbook", 5th ed., McGraw-Hill, New York 1973, pp. 8-57.

Preferred agrochemical formulations according to the invention are those in which the inventive crystal form B is present in solid form. These are, for example, granules, encapsulated granules, tablets, water-dispersible granules, water-dispersible tablets, water-dispersible powders, dust formulations, formulations

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in which the active ingredient is present in dispersed form, such as, for example: suspension concentrates (SC), oil-based suspension concentrates, suspo-emulsions or suspension concentrates.

Particularly preferred agrochemical formulations according to the invention comprising inventive crystal form B are those in which the agrochemical formulation is present in a form selected from the group consisting of wettable powders (WP), water-soluble powders (SP), suspension concentrates (SC), oil dispersions (OD), capsule suspensions (CS), dusting products (DP), granules for scattering and soil application, granules (GR) in the form of microgranules, spray granules, coated granules and adsorption granules, water-dispersible granules (WG), water-soluble granules (SG), ULV formulations, microcapsules and waxes.

For further details regarding the formulation of crop protection compositions, see, for example, G.C. Klingman, "Weed Control as a Science", John Wiley and Sons, Inc., New York, 1961, pages 81-96 and J.D. Freyer, S.A. Evans, "Weed Control Handbook", 5th ed., Blackwell Scientific Publications, Oxford, 1968, pages 101-103.

The agrochemical formulations according to the invention generally comprise 0.1 to 99% by weight, particularly 0.1 to 95% by weight of inventive crystal form B, based on the total weight of the agrochemical formulation, wherein the total amount of inventive crystal form B may be varied depending on the formulations.

In wettable powders, the total amount of inventive crystal form B is typically 10 to 90% by weight, the remainder to 100% by weight consisting of customary formulation constituents.

In emulsifiable concentrates, the total amount of inventive crystal form B may be about 1 to 90% and preferably 5 to 80% by weight. Formulations in the form of dusts generally comprise a total amount of inventive crystal form B of 1 to 30% by weight, preferably 5 to 20% by weight. In water-dispersible granules, the total amount of inventive crystal form B is for example in the range of 1 and 95% by weight, in the range of 10 and 80% by weight, based on the total weight of the agrochemical formulation.

The present invention therefore also provides a method for controlling harmful plants and/or for regulating the growth of plants, characterized in that an effective amount

- of crystal form B,
- a composition comprising crystal form B, as defined above,

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- an agrochemical formulation according to the invention, as defined above,

is applied to the plants, seeds of plants, the soil in which or on which the plants grow or the area under cultivation.

It has also been found that crystal form B according to the invention, mixtures according to the invention, compositions according to the invention and formulations according to the invention, defined in each case in the context of the present invention, are suitable for controlling harmful plants or for regulating the growth of plants. Controlling of harmful plants or regulating the growth of plants is effected advantageously in particular crop plants. In this case, preferred crop plants are in particular oilseed rape, soya bean, cotton, sugar beet and true grasses, in particular here corn, barley, wheat, rye, oats, triticale, millet, rice, wherein corn is particularly preferred. In a preferred configuration, the crop plants, particularly the crop plants specified as preferred, are transgenic plants.

In addition, application to turf areas, for example golf courses, is also possible.

Examples:

The invention is elucidated by the examples which follow. Unless stated otherwise, all data refer to the weight.

The symbol ">" means "greater than" and the symbol "< " means "less than".

Example 1: Preparation of crystal form A

1000 g of N-[(4,6-dimethoxypyridin-2-yl)aminocarbonyl]-2-dimethylaminocarbonyl-5-formylamino-benzenesulphonamide were initially charged in 4750 g of cold 5°C MeOH (6000 mL).

To this were added 32 g of seed crystals of crystal form A (according to EP 0 757 679 A1) and the mixture cooled to 0°C over 20 minutes. After reaching a temperature of 0°C, 418 g (440 mL) of 30% sodium methoxide solution were metered in 2 hours, such that an internal temperature of 5°C was not exceeded.

The resulting very pasty mixture was then divided between two coolable 4 L frits and filtered under suction. After about 2 hours, the filtration was complete and each frit was washed with 500 mL.

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In total, 2220 g of moist product were obtained, which were then dried at 65°C at a pressure < 100 mbar. The drying takes 44 h in total. The drying is terminated at a residual methanol content of 1.5% by weight. 1012 g of a 97% strength product were obtained.

Example 2: Variation of temperature in the preparation of crystal form A in methanol.

In separate containers, 20 g of N-[(4,6-dimethoxypyridin-2-yl)aminocarbonyl]-2-dimethylaminocarbonyl-5-formylaminobenzenesulphonamide were each initially charged in 100 g MeOH.

In each case, 1 g of seed crystals of crystal form A was added and one equivalent of NaOMe as a 30% methanolic solution was added at the temperature stated in each case over a period of 2 hours. The post reaction time was 3 hours in each case.

To isolate the respective product, the respective mixture was heated or cooled to 20°C and then filtered. After drying at 65°C at a pressure < 100 mbar, the residual content of methanol in each product was determined.

Experiment No.	T in °C	Filtration time in s	MeOH content in % by weight
1	0	150	0.53
2	15	50	1.49
3	35	4	2.83
4	50	5	5.19

Example 3: Storage of the methanol-moist crystal form A and conversion thereof into crystal form

C

In separate containers, 5 g each of crystal form A were each stirred with 20 g of MeOH and subsequently filtered off.

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At 20°C, 30°C and 35°C, the moistened products were stored for one week and a sample taken daily. These samples were dried at 65°C and 100 mbar and the respective methanol content subsequently determined.

Already after 2 days (35°C), 3 days (30°C) and 7 days (20°C), crystal form A had converted practically completely into crystal form C (MeOH content about 6.4% by weight).

Example 4: Preparation of crystal form B from crystal form A

1000 g of N-[(4,6-dimethoxypyridin-2-yl)aminocarbonyl]-2-dimethylaminocarbonyl-5-formylamino-benzenesulphonamide Na salt (crystal form A) were suspended in 3000 g of acetone and heated under reflux for 2 hours. After cooling to 20°C, the suspension was filtered. The filtration took 60 minutes.

The moist product thus obtained was then dried overnight at 70°C and a pressure < 100 mbar. 9230 g of a 98.6% strength product were obtained. The MeOH content in this product was < 0.1% by weight, and the acetone content < 0.05% by weight.

Example 5: Preparation of crystal form B from crystal form C

100 g of N-[(4,6-dimethoxypyridin-2-yl)aminocarbonyl]-2-dimethylaminocarbonyl-5-formylamino-benzenesulphonamide Na salt (crystal form C; MeOH content about 6.4%) were suspended in 300 g of acetone and heated under reflux for 2 hours. After cooling to 20°C, the suspension was filtered. The filtration took a few seconds.

The moist product was dried overnight at 70°C and a pressure < 100 mbar.

92 g of a 99.2% strength product were obtained. The methanol content in this product was below the detection limit, and the acetone content was 0.026% by weight.

Example 6: Preparation of crystal form B from foramsulfuron and sodium methoxide

100 g of N-[(4,6-dimethoxypyridin-2-yl)aminocarbonyl]-2-dimethylaminocarbonyl-5-formylaminobenzenesulphonamide were suspended in 300 g of acetone and treated with one equivalent of NaOMe as a 30% methanolic solution (40.21 g) at 40°C over 1 hour. Subsequently, the resulting mixture was heated under reflux for 2 hours. After cooling to 20°C, the suspension was filtered. The filtration took ca. 30 seconds.

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The moist product was dried overnight at 70°C and a pressure < 100 mbar.

104 g of a 98.4% strength product were obtained. The methanol content in the product obtained was 0.006% by weight and the acetone content was 0.048% by weight.

Example 7: Preparation of crystal form B from foramsulfuron and sodium ethoxide

100 g of N-[(4,6-dimethoxypyridin-2-yl)aminocarbonyl]-2-dimethylaminocarbonyl-5-formylamino-benzenesulphonamide were suspended in 400 g of acetone and treated with one equivalent of NaOEt as a 21% ethanolic solution (73.1 g) under reflux over 1 hour. The mixture was subsequently heated further under reflux for 2 hours. After cooling to 20°C, the suspension was filtered. The filtration took ca. 60 seconds.

The moist product was dried overnight at 70°C and a pressure < 100 mbar.

102 g of a 98.6% strength product were obtained. The ethanol content in the product obtained was 0.0105% by weight and the acetone content was 0.024% by weight.

Example 8: Stability test of crystal form B in methanol

10 g of crystal form B (MeOH content < 0.01%) were suspended in 100 g of methanol and stirred for 7 days at 30°C. The product was filtered and then dried overnight at 70°C and a pressure < 100 mbar.

9.1 g of a 99.4% strength product were obtained. The methanol content in the product obtained was 0.004% by weight and the acetone content was 0.0003% by weight.

Example 9: Investigation of the chemical storage stability of crystal forms A and B

Crystal forms A and B were each incorporated separately in an otherwise identical formulation in the form of oil dispersions (OD) and stored under the same conditions.

The oil dispersions were stored under the following storage conditions and were analysed with respect to the chemical degradation of crystal form A or B:

Storage for two weeks at 40°C (specified below as 2W 40°C)

Storage for four weeks at 40°C (specified below as 4W 40°C)

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Storage for two weeks at 54°C (specified below as 2W 54°C)

In this manner, storage over a longer time period at a correspondingly lower temperature is also simulated.

The crystal forms were incorporated in three different formulations in the form of oil dispersions (OD), where these formulations, in addition to the agrochemical active ingredients specified below, comprised customary formulation constituents such as emulsifiers, thickeners and diluents, and also in some cases pH regulators and/or defoamers.

In addition to 3.05% by weight of crystal form A or B, formulation OD1 comprised as further active ingredients 0.1% by weight iodosulfuron-methyl-sodium (a sulphonylurea herbicide) and 2.91% by weight isoxadifen-ethyl (a safener).

In addition to 3.21% by weight of crystal form A or B, formulation OD2 comprised as further active ingredients 1.02% by weight thien carbazole-methyl and 1.53% by weight cyprosulfamide (a safener).

In addition to 3.21% by weight of crystal form A or B, formulation OD3 comprised as further active ingredients 0.11% by weight iodosulfuron-methyl-sodium (a sulphonylurea herbicide), 1.02% by weight thien carbazole-methyl and 1.53% by weight cyprosulfamide (a safener).

Table 9-1: Chemical stability of crystal forms A and B in formulation OD 1

Crystal form	Degradation in %	
	4W 40°C	2W 54°C
Crystal form A	3.4	7.7
Crystal form B	1.5	3.4

Table 9-2: Chemical stability of crystal forms A and B in formulation OD 2

Crystal form	Degradation in %	
	2W 40°C	2W 54°C
Crystal form A	1.8	8.6
Crystal form B	0.6	1.8

Table 9-3: Chemical stability of crystal forms A and B in formulation OD 3

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Crystal form	Degradation in %	
	Hardness (40°C)	2W 54°C
Crystal form A	2.1	4.8
Crystal form B	0.3	1.4

Example 10: Preparation of crystal form B from foramsulfuron and sodium methoxide

100 g of N-[(4,6-dimethoxypyridin-2-yl)aminocarbonyl]-2-dimethylaminocarbonyl-5-formylamino-benzenesulphonamide were suspended in 300 g of an acetone/methanol mixture (80:20 parts by weight) and treated with one equivalent of NaOMe as a 30% methanolic solution at 30°C over 2 hours. Subsequently, the mixture was stirred at 30°C for another 2 hours. After cooling to 20°C, the suspension was filtered. The filtration took 50 seconds.

The moist product was dried overnight at 70°C and a pressure < 100 mbar.

102 g of a 98.6% strength product were obtained. The methanol content in the product obtained was 0.03% by weight and the acetone content was 0.014% by weight.

Example 11: Preparation of crystal form B from foramsulfuron and sodium methoxide

100 g of N-[(4,6-dimethoxypyridin-2-yl)aminocarbonyl]-2-dimethylaminocarbonyl-5-formylamino-benzenesulphonamide were suspended in a mixture of 150 g of acetone and 100 g of methanol and heated to 30°C. To this were added at the same time 38.6 g of NaOMe as a 30% methanolic solution over two hours. Stirring was continued at 30°C for one hour. The temperature was then increased to 40°C, and after 1 hour at this temperature a further hour at 45°C.

After cooling to 20°C, the suspension was filtered and the filter cake was washed with 100 g of acetone.

The moist product was dried overnight at 70°C and a pressure < 100 mbar.

The methanol content in the product obtained was 0.10% by weight and the acetone content was 0.13% by weight.

Example 12: Sorption/desorption curve of crystal form B

Sorption and desorption curves of crystal form B were measured isothermally at 25°C.

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The sorption curve gives the water uptake at increasing relative humidity and the desorption curve gives the drying behaviour on moisture reduction.

Relative humidity	Sorption (% by weight)	Desorption (% by weight)
10.0%	0.100	0.846
20.0%	0.201	1.227
30.0%	0.313	1.495
40.0%	0.444	1.760
50.0%	0.566	2.086
60.0%	0.684	2.269
70.0%	0.864	2.485
80.0%	1.085	3.016
90.0%	2.335	5.151

The result of the investigation shows that crystal form B is not hygroscopic.

Example 13: Investigation of the hygroscopicity of crystal forms A, B and C

100 mg each of crystal forms A, B and C were separately filled into small glass vials with snap-on caps. These three glass vials with snap-on caps were placed unsealed in a glass beaker of which the bottom was covered with a small amount of water. The glass beaker was then sealed with a reversible sealing film and stored for one week at 25°C. After this storage period, the water content of the respective sample was determined by Karl Fischer titration. The water content of the sample of crystal form B was 0.4% by weight, and the water content of the samples of crystal forms A and C was 15.7 and 21.3% by weight.

The samples of crystal forms A and C were hygroscopic and after storage were very ductile and sticky whereas the sample of crystal form B was still crystalline and powdery.

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Claims

1. Monosodium salt of foramsulfuron in crystalline form, characterized in that the X-ray powder diffractogram of this salt using Cu K α radiation at 25°C has at least 3 of the following 2 Θ (2 theta) values:

2 Θ (2 theta) values in °
6.2
6.4
14.4
14.6
14.7
18.4
19.2
20.1
23.2
24.7

2. Monosodium salt of foramsulfuron according to Claim 1, characterized in that the X-ray powder diffractogram of this salt using Cu K α radiation at 25°C has at least 4, preferably at least 6, preferably at least 8, more preferably all of the 2 Θ (2 theta) values specified in Claim 1.
3. Monosodium salt of foramsulfuron according to Claim 1, characterized in that the X-ray powder diffractogram of this salt using Cu K α radiation at 25°C in addition has at least two, four, six, eight, ten, twelve or more of the following 2 Θ (2 theta) values:

10.3
10.5
11.1
11.3
11.4
12.0

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12.1
12.4
12.6
12.9
13.6
14.0
15.0
15.1
15.4
16.0
16.2
17.0
17.2
18.2
18.8
20.3
20.6
20.8
21.2
21.6
22.7
23.7
24.6
25.4
25.9
26.2
26.9
27.1
27.7
28.3
29.0
30.2

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30.5
30.7
31.0
31.2
31.9
32.5
32.6
33.7
34.8
35.6
35.9
36.2
36.4
36.9
37.4

4. Monosodium salt of foramsulfuron according to any of Claims 1 to 3, characterized in that the Raman spectrum thereof has at least the following bands:

Band maximum [cm ⁻¹]
2959
2915
1686
1587
1526
694
345
133

5. Composition comprising the monosodium salt of foramsulfuron according to any of Claims 1 to 4 in a total amount of at least 5% by weight, based on the total amount of monosodium salt of foramsulfuron present in the composition.

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6. Composition according to Claim 5, wherein
the composition is present in solid form at 25°C and 1013 mbar,
and/or
the content of monosodium salt of foramsulfuron is 80% by weight or more, based on the total weight of the composition.
7. Use of the monosodium salt of foramsulfuron according to any of Claims 1 to 4 or of a composition according to Claim 5 or 6 for preparing agrochemical formulations.
8. Monomethanol solvate of the monosodium salt of foramsulfuron in crystalline form, characterized in that the X-ray powder diffractogram of this salt using Cu K α radiation at 25°C has at least 3 of the following 2 Θ (2 theta) values:

2 Θ (2 theta) values in °
9.1
9.1
9.7
12.6
16.2
18.5
24.1
24.3
24.6

9. Method for preparing the monosodium salt of foramsulfuron in crystalline form according to one or more of Claims 1 to 4, comprising the steps of

(a) suspending a monosodium salt of foramsulfuron, the monomethanol solvate of the monosodium salt of foramsulfuron according to Claim 8, or a mixture of these 2 crystal forms, in a diluent or diluent mixture,

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wherein the diluent or diluent mixture used in step (a) is selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 20% by weight thereof.

10. Method for preparing the monosodium salt of foramsulfuron in crystalline form according to any of Claims 1 to 4, comprising the steps of

(a) suspending foramsulfuron in a diluent or diluent mixture,

(b) reacting foramsulfuron with a base containing sodium, preferably an organic base, in this case preferably sodium methoxide and/or sodium ethoxide,

wherein the diluent or diluent mixture used in step (a) is selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 20% by weight thereof.

11. Method according to Claim 9 or 10, characterized in that the method is carried out at a temperature of at least 0°C.

12. Method according to any of Claims 9 to 11, characterized in that the ratio by weight of the total amount of foramsulfuron, monosodium salt of foramsulfuron, and monomethanol solvate of the monosodium salt of foramsulfuron according to Claim 8, to the total amount of diluent or diluent mixture used in step (a) is less than 2:1.

13. Mixture comprising

(i) monosodium salt of foramsulfuron and/or a solvate thereof, and

(ii) a diluent or diluent mixture selected from the group consisting of alcohols having 3 to 6 carbon atoms, in this case preferably primary alcohols having 3 to 6 carbon atoms, and ketones having 3 to 6 carbon atoms, and mixtures thereof, or comprises at least 20% by weight thereof.

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14. Agrochemical formulation comprising
- (a) a herbicidally effective amount of the monosodium salt of foramsulfuron in crystalline form according to any of Claims 1 to 4, and one or more further constituents selected from the group consisting of the following constituents (b-i), (b-ii) and (b-iii):
- (b-i) formulation auxiliaries customary in the pesticide field,
- (b-ii) further agrochemical active ingredients,
- and
- (b-iii) the monomethanol solvate of the monosodium salt of foramsulfuron according to Claim 8.
15. Method for controlling harmful plants or for regulating the growth of plants, characterized in that an effective amount
- of the monosodium salt of foramsulfuron according to any of Claims 1 to 4,
 - a composition according to Claim 5 or 6, or
 - an agrochemical formulation according to Claim 14
- is applied to the plants, seeds of plants, the soil in which or on which the plants grow or the area under cultivation.

Figure 1

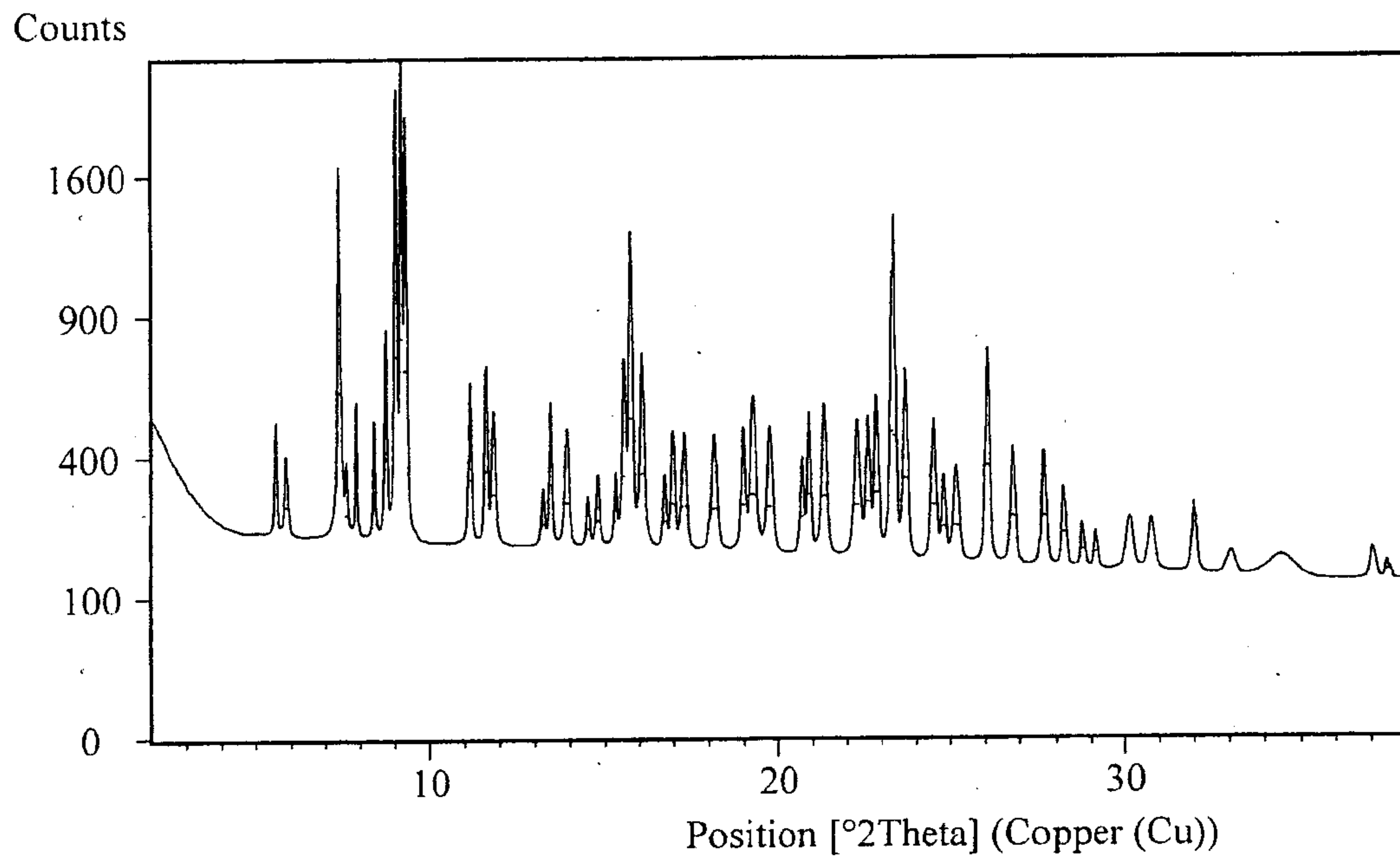


Figure 2

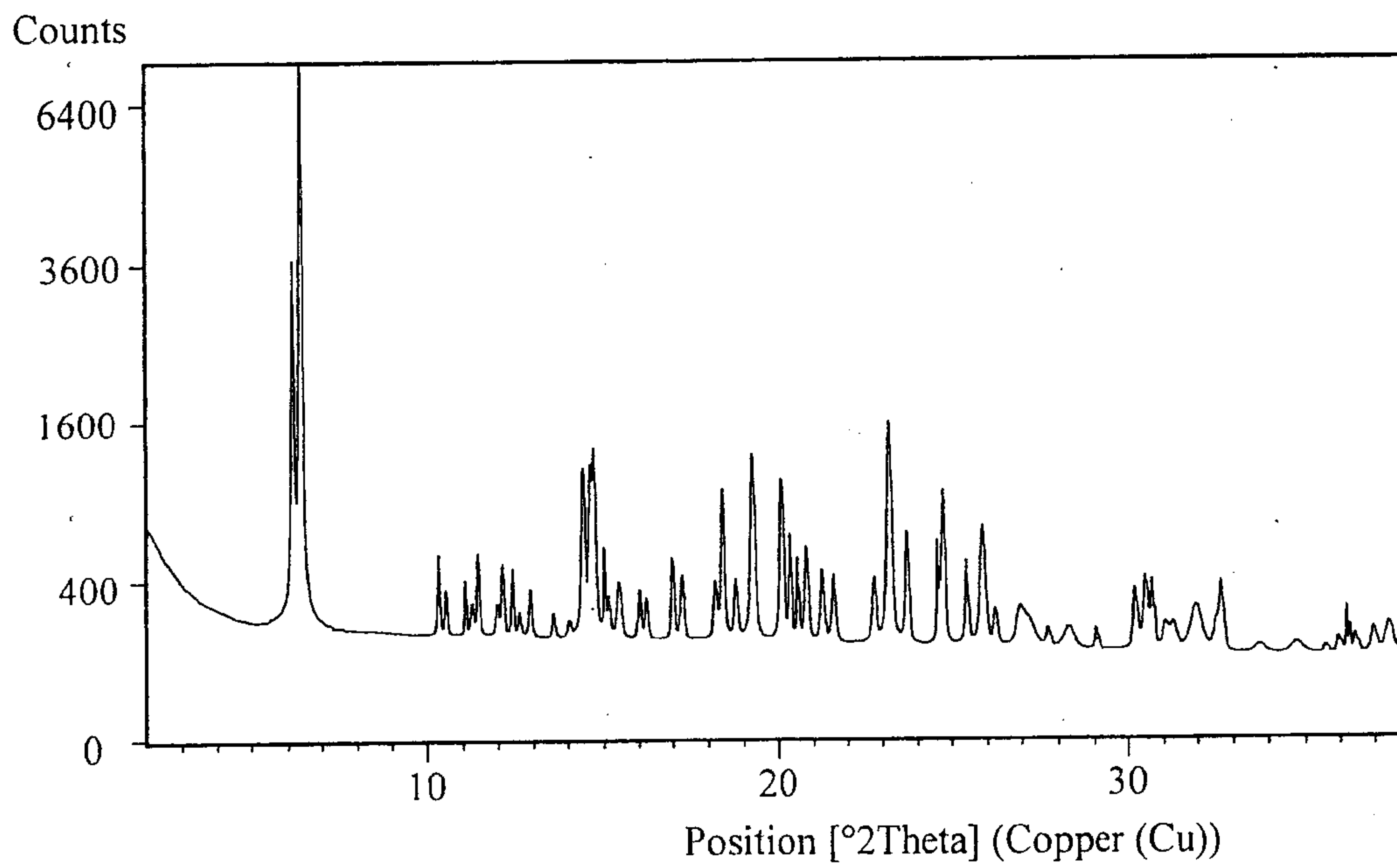


Figure 3

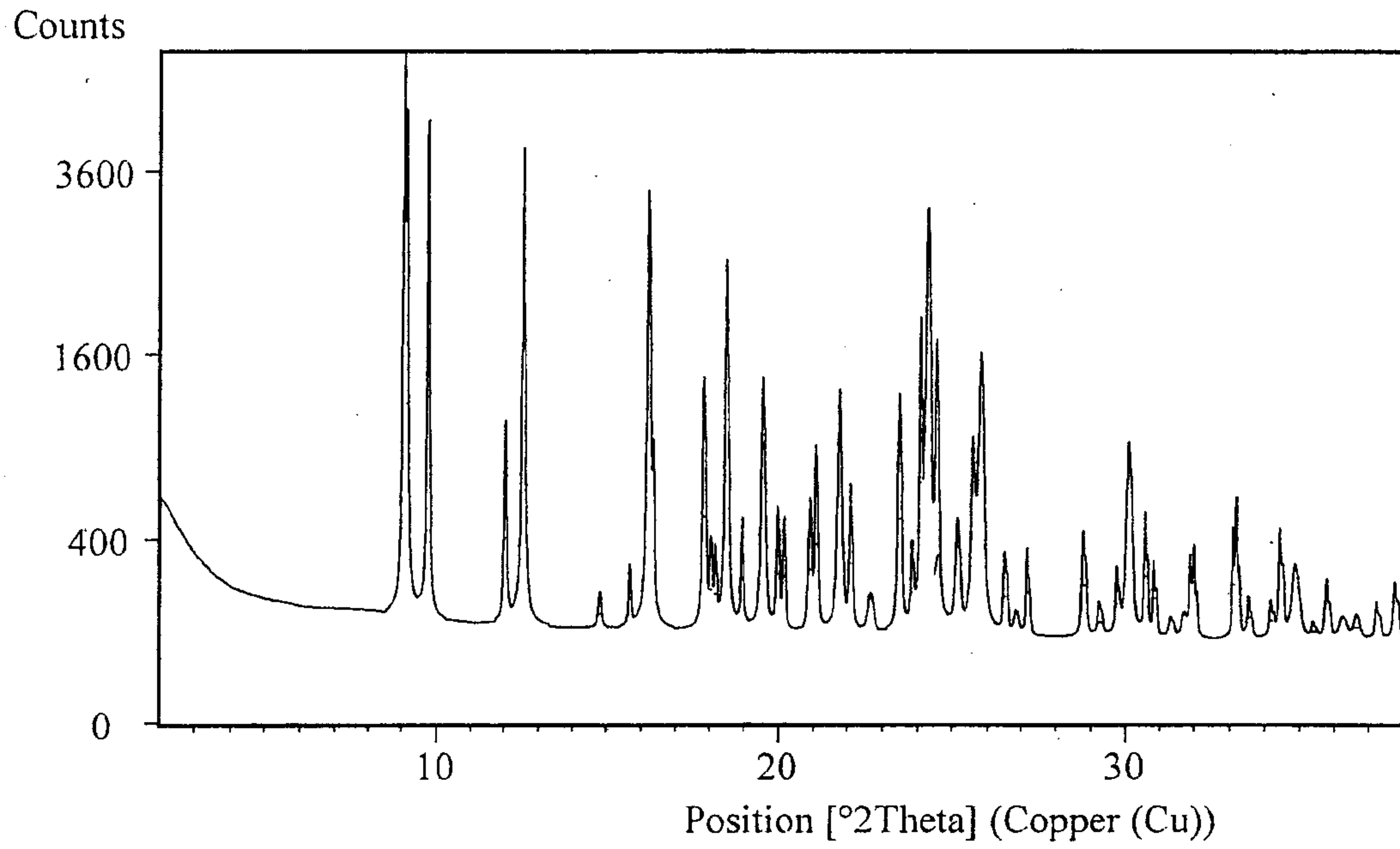


Figure 4

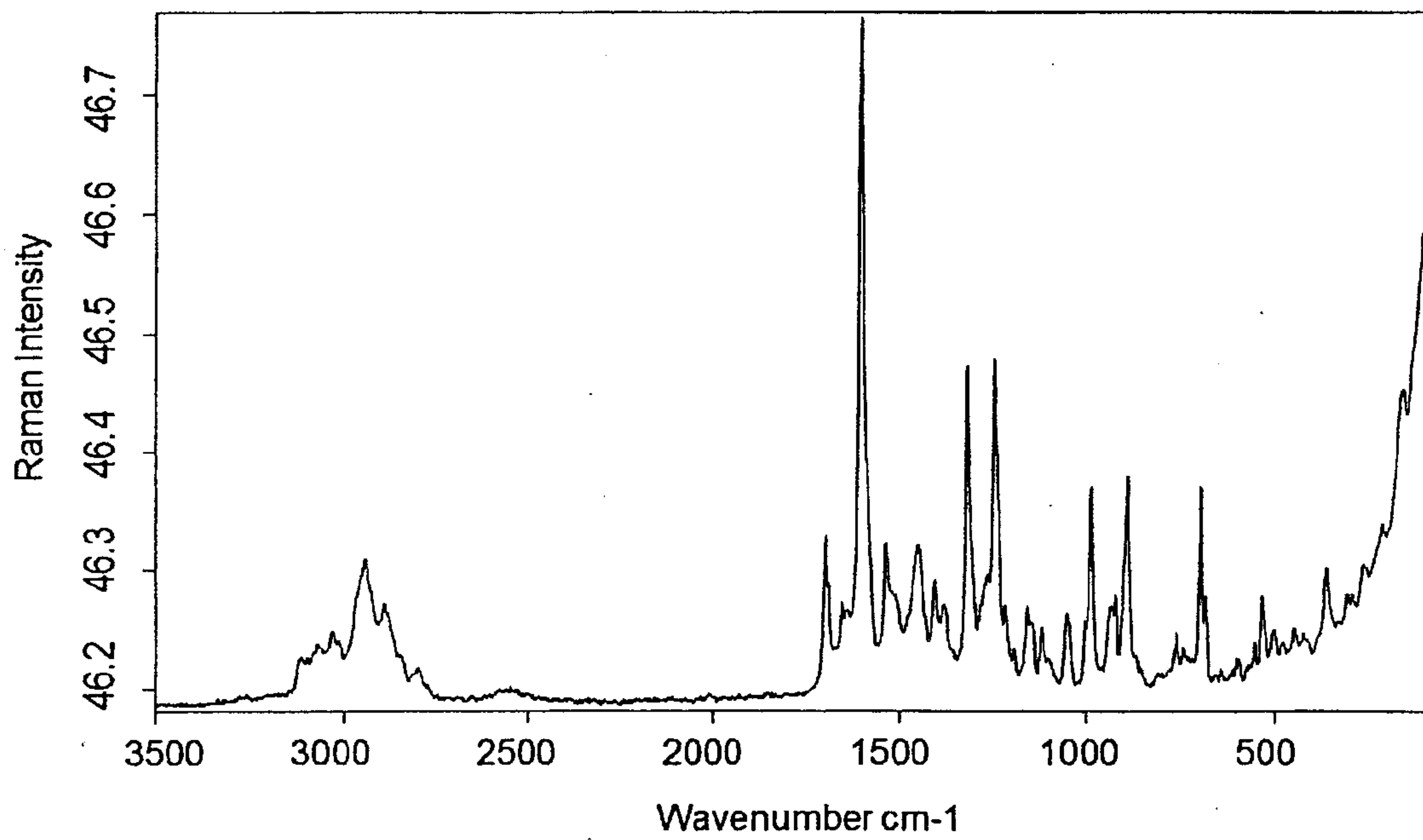


Figure 5

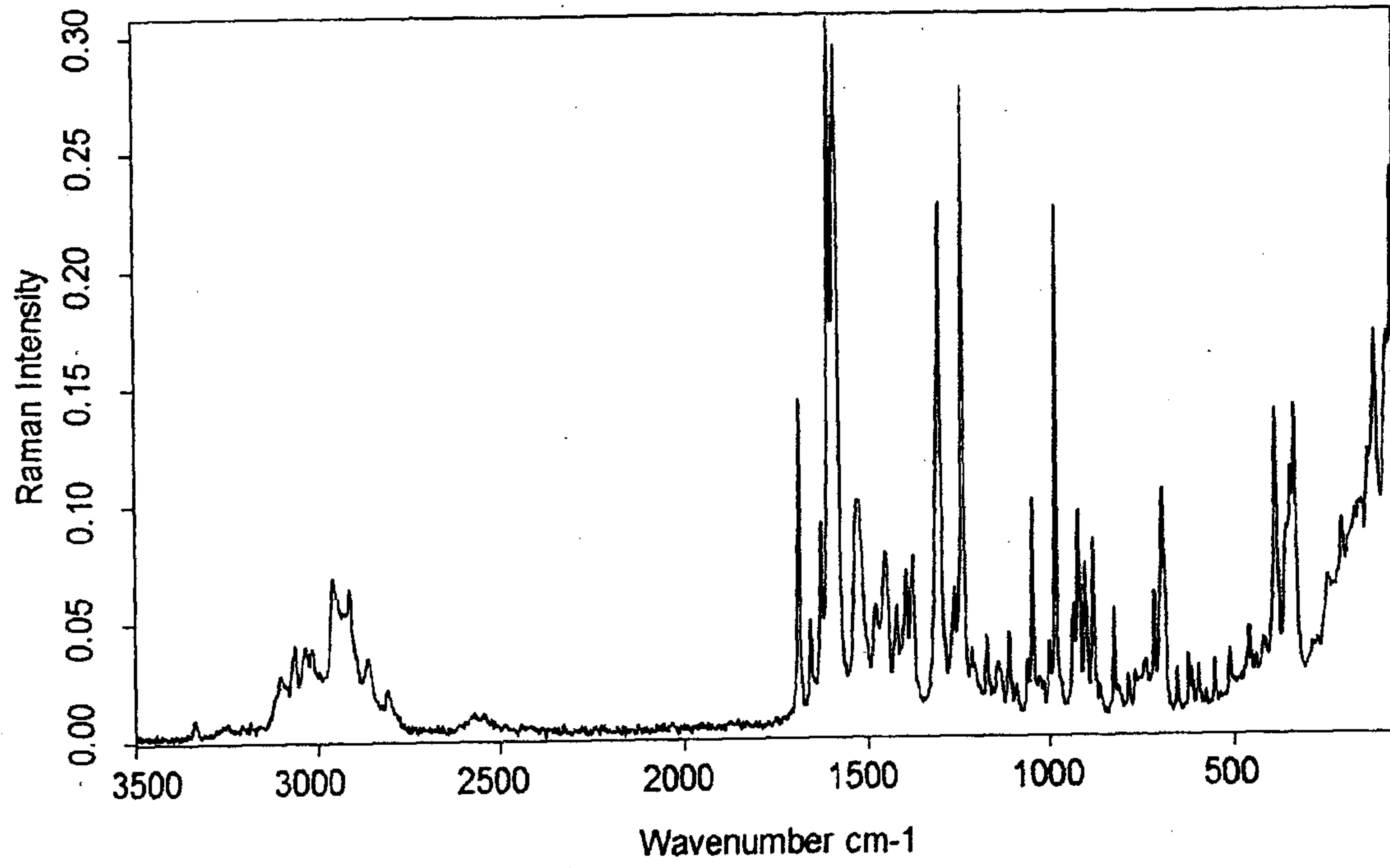


Figure 6

