Section A3	Physical and Chemical Properties of Active Substance							
.	Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
3.1 Melting point, boiling point, relative density (IIA3.1)								
3.1.1 Melting point	OECD 102	[redacted]	**result:** 103.2°C (at the beginning of melting)	Temperature at final stage of melting was 104°C	Y	1	Schneider, J., 2001 Bayer AG, Study No. 1400541054	X
3.1.2 Boiling point				Not measurable, substance decomposes and its not distillable				X
3.1.3 Bulk density/ relative density								
Relative density	EC method A.3	[redacted]	**result:** 1.575 at 20°C		Y	1	Jungheim, 2001, Bayer AG Study No. N01/0054/00 LEV	X
Bulk density			**result:** 470 kg/m^3		N	2	Bayer Chemicals, 2003, SDS No. 014730/28	X
3.2 Vapour pressure (IIA3.2)	EC method A.4	[redacted]	**result:** 2.15 x 10^{-7} hPa at 20 °C 5.37 x 10^{-7} hPa at 25 °C 3.03 x 10^{-5} hPa at 50 °C		Y	2	Treckmann, D.I., 1994, Bayer AG, Reg No. 93/237,	X

Section A3	Physical and Chemical Properties of Active Substance							
	Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
							PC 184	
3.2.1 Henry's Law Constant (Pt. I-A3.2)	Calculation (quotient of vapour pressure and water solubility)		**calculated:** **result:** 4.5 Pa m^3 $mole^{-1}$		N	2		
3.3 Appearance (IIA3.3)								
3.3.1 Physical state		[redacted]	Solid		Y	1	Bayer Chemicals, 2003, SDS No. 014730/28	X
3.3.2 Colour		[redacted]	Straw coloured (yellow/brown).		Y	1	Bayer Chemicals, 2003, SDS No. 014730/28	
3.3.3 Odour		[redacted]	Slight amine odour.		Y	1	Bayer Chemicals, 2003, SDS No. 014730/28	
3.4 Absorption spectra (IIA3.4)								
UV/VIS		[redacted]	UV: Solvent: Methanol Maxima:final absorption only, Absorptivity: none		N	2	Krohn, 1986, Bayer AG	X
IR		[redacted]	IR (KBr tablet)		N	2	Krohn, 1986, Bayer AG	X

Section A3		Physical and Chemical Properties of Active Substance						
	Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
NMR		[redacted]	^{1}H-NMR (250 MHz, $CDCl_3$) ^{1}C-NMR (50.32 MHz, $CDCl_3$)		N	2	Krohn, 1986, Bayer AG	X
MS		[redacted]	MS (electron impulse ionization)		N	2	Krohn, 1986, Bayer AG	X
3.5 Solubility in water (IIA3.5)	EC method A.6/OECD 105	[redacted]	**result:** 0.92 g/l **temperature:** 10 °C **pH:** 4 **result:** 1.58 g/l **temperature:** 20 °C **pH:** 4 **result:** 2.69 g/l **temperature:** 30 °C **pH:** 4	The solubility in water is independent on pH in the range of pH 4 to pH 9 The test was conducted at one pH only, because dichlofluanid shows no acidic or basic properties in water in the range pH4 to pH9 (see log P_{ow}).	Y	1	Schneider, J., 2002 Bayer AG, Study No. 1400321074	X
3.6 Dissociation constant (-)				Dichlofluanid has no acidic or basic properties in water in the range pH4 to pH9 (see log P_{ow})	Y	1	Schneider, J., 2002 Bayer AG, Study No. 1400321074	
3.7 Solubility in organic solvents, including the effect of temperature on solubility (IIIA3.1)	OECD Guideline 105 (shake flask method)	[redacted]	**result:** Xylene: 81.2 g/l Shellsol D60: 2.54 g/l Di(propylene glycol)methyl ether:86.4 g/l 2-methyl-2,4-pentanediol: 20.7 g/l Due to the decomposition of dichlofluanid in 1-methyl-2-pyrrolidone the solubility in this solvent cannot be		Y	2	Jungheim, 2004, Bayer Industry Services Study No. A02/0108/03 LEV	

Section A3		Physical and Chemical Properties of Active Substance						
		Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
				determined. **temperature: 20 °C**					
3.8	**Stability in organic solvents used in b.p. and identity of relevant breakdown products (IIIA3.2)**				Active substance as manufactured does not include an organic solvent.				
3.9	**Partition coefficient n-octanol/water (IIA3.6)**	OECD 117	[redacted]	**result:** log P_{ow} = 3.5 **temperature:** 10 °C/20 °C/ 30 °C **pH:** 4/7/9	The partition was determined to be independent on temperature in the range of 10 °C to 30 °Cand to be independent on the pH in the range pH4 to pH9.	Y	1	Schneider, J., 2002 Bayer AG, Study No. 1400321074	X
3.10	**Thermal stability, identity of relevant breakdown products (IIA3.7)**	OECD Guideline 113	[redacted]	DTA: endothermic effect (melting) <150 °C, no exothermic effect (decomposition); TGA: weight loss due to evaporation, sublimation and transition to decomposition, commencing at 120 °C	Substance may be considered stable at room temperature	N	2	Klusacek,H. Krasemann, R., 1986, Bayer AG Study No. 86/10046TA	X
3.11	**Flammability, including auto-flammability and identity of combustion products (IIA3.8)**	EC method A.12 (Flammability in contact with water) EC method A.16 (Auto-flammability)	[redacted] [redacted]	**result:** the test substance does not evolve gas when in contact with water. **result:** auto-ignition temperature = 370°C		Y Y	1 1	Heinz, U, 2003, Bayer AG, ID No. 03/00256	

Section A3	Physical and Chemical Properties of Active Substance							
	Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
	EC method A.10 (Flammability)	[redacted]	**result:** the test substance is not highly flammable		Y	1		
	EC method A.13 (Pyrophoric properties)	[redacted]	**result:** the test was not carried out due to no indications of pyrophoric properties during EC A10 or EC A12		Y	1		
3.12 Flash-point (IIA3.9)	EC method A.9	[redacted]		Test not required as test substance is a solid	Y	1	Heinz, U, 2003, Bayer AG, ID No. 03/00256	X
3.13 Surface tension (IIA3.10)	EC method A.5	[redacted]	**result:** 72.75 mN/m **temperature:** 20°C	The test substance is not surface active	Y	1	Olf, G, 2001, Bayer AG, Study No. 01/008/03	X
3.14 Viscosity (-)				Not required as the test substance is a solid				
3.15 Explosive properties (IIA3.11)	EC method A.14	[redacted]	From the structural formula of dichlofluanid it can be concluded that the test substance is not explosive		Y	1	Heinz, U, 2003, Bayer AG, ID No. 03/00256	X
3.16 Oxidizing properties (IIA3.12)	EC method A.17	[redacted]	From a close inspection of the chemical structure it is obvious that the test substance will not react exothermically with flammable materials. Therefore, the test substance dichlofluanid does not exhibit any oxidizing properties.		Y	1	Heinz, U, 2003, Bayer AG, ID No. 03/00256	X

Section A3	Physical and Chemical Properties of Active Substance							
.	Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
3.17 Reactivity towards container material (IIA3.13)			Recommended container materials for the direct contact with the active substance: Polypropylene plastic material (PP), High and Low density Polyethylene plastic materials (HDPE, LDPE) – Sales pack Epoxy-phenolic resin lined steel drums		N	2	Wittmann 2004	X

[1] OECD = Organisation for Economic Co-operation and Development

Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	*July 2006*
Evaluation of data submitted under section A3	The applicant's version is acceptable with the following amendments:- 3.1.1 Melting point Method Method used was OECD guideline 102, which is equivalent to EC method A.1. This method uses a Melt microscope. Result Active substance had a melting point of 103.2-104.0ºC. 3.1.2 Boiling point Method Method used was OECD guideline 113. Purity Active substance purity was not determined to be [redacted] Result The boiling point of the active substance could not be determined because at 120 °C it began to decompose. Reference Study reference added, (Klusacek, H, and Krasemann, R., 1986). 3.1.3 Relative density Method Method used was EC method A3, which is equivalent to OECD guideline 109. This uses Pycnometer method 3.1.3 Bulk Density Method Calculation used was EC method A.4, which is equivalent to OECD 104. This uses the EFFusion method – Vapour Pressure balance Remarks/Justification 30 measurements were made over a temperature range 55.9-108.6 °C. The results were then extrapolated to get the vapour pressures at 20, 25 and 50 °C 3.3.1 Physical State Results The results should indicate that this is a solid powder 3.4 Absorption spectra Purity Active substance purity was determined to be [redacted]. Result Spectra confirmed the chemical structure.

3.5 Solubility in water

Method

Method used was OECD guideline 105, which is equivalent to EC method A.6. This uses the Column elution method.

Purity

Active substance purity was determined to be [redacted]

3.8 Stability in organic solvents

Remarks/Justification

This annex point was addressed in the product storage stability (see Doc III-B, B3)

3.9 Partition coefficient n-octanol/water

Method

Method used was OECD guideline 117, which is equivalent to EC method A.8. This is the Partition Coefficient (n-octanol/water) high performance liquid chromatography (HPLC) method

Purity

Active substance purity was determined to be [redacted]

3.10 Thermal stability, identity of relevant breakdown products

Results

The results should be expanded to indicate that dichlofluanid did not decompose until 120 ºC, a temperature that dichlofluanid is unlikely to be exposed to, when used in a biocidal product. In addition the TNG only requires thermal breakdown products to be evaluated, if possible.

3.11 Flammability, including auto-flammability and identity of combustion products

Purity

Tests were carried out on Preventol A4-S, which had stabilisers added and the active substance content was determined to be [redacted] (and not [redacted] as stated). These tests were conducted on Preventol A 4-S, and not the technical material dichlofluanid, as the latter is never placed on the market.

Remarks/Justification

'No self-ignition at temperatures up to the melting point (103.2 ºC)' should be included in the remarks/justification box for Auto-flammability

3.12 Flash point

Method

The test method should be removed, and replaced with 'No test conducted, as a waiving argument was used'.

Purity

Preventol A4-S had a stabilisers added and the active substance content was determined to be [redacted] (and not [redacted] as stated).

Remarks

This test is not applicable as the active substance is not a liquid.

3.13 Surface tension

Method

Method used was OECD guideline 115, which is equivalent to EC method A.5.

This use the Ring method. The concentration of the test solution was 1.17 mg/l.

3.15 Explosive properties

Method

The test method should be removed, and replaced with 'No test conducted, as a waiving argument was used'.

Purity

Preventol A4-S had stabilisers added and the active substance content was determined to be [redacted] (and not [redacted] as stated).

3.16 Oxidising properties

Method

The test method should be removed, and replaced with 'No test conducted, as a waiving argument was used'.

Purity

Preventol A4-S had stabilisers added and the active substance content was determined to be [redacted] (and not [redacted] as stated).

3.17 Reactivity towards container material

Method

No test conducted – information obtained from experience in use and chemical structure, as allowed by TNG (Chapter 2 part A 3.17).

It should be noted that the data above were considered and accepted for the approval of the active in PT 8.

Section A3		Physical and Chemical Properties of DIMETHYLAMINOSULFANILID (DMSA)							
		Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
3.2	**Vapour pressure (IIA3.2)**	OECD 104	[redacted]	**result:** 2.5 x 10^{-4} Pa at 20 °C 4.9 x 10^{-4} Pa at 25 °C		N	2	Krohn,J. 1999, Bayer AG, Laboratory Project ID 146600961	
3.2.1	**Henry's Law Constant (Pt. I-A3.2)**	Calculation (quotient of vapour pressure and water solubility)		**calculated:** **result:** 3.8 x 10^{-5} Pa m^3 $mole^{-1}$		N	2		
3.5	**Solubility in water (IIA3.5)**	OECD 105	[redacted]	**result:** 1.3 g/l **temperature:** 20 °C **pH: -**		N	2	Krohn,J. 1985, Bayer AG, Report No. 5/0050 (PC 836)	
3.6	**Dissociation constant (-)**	OECD 112	[redacted]	**result:** Diss.const.:2.0x10^{-9}, pK(a)-value:8.7 **temperature:** 20 °C		N	2	Rosenfeldt, 1989 Bayer AG, Report No. Q5110418 (PC839)	

Section A3		Physical and Chemical Properties of DIMETHYLAMINOSULFANILID (DMSA)							
		Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
3.9	**Partition coefficient n-octanol/water (IIA3.6)**	OECD 107	[redacted]	**result:** log P_{ow} = 1.59 **temperature:** 20 °C **pH: -**		N	2	Krohn,J. 1989, Bayer AG, Report No. Q5050408 (PC 835)	

Section A3		Physical and Chemical Properties of N,N-DIMETHYLSULFAMIDE (DMS)							
		Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
3.2	**Vapour pressure (IIA3.2)**	OECD 104	[redacted]	**result:** 1.8 x 10E-6 hPa at 20°C 7.2 x 10E-6 hPa at 25°C 3.8 x 10E-3 hPa at 50°C		Y	1	Smeyka (2007)	
3.2.1	**Henry's Law Constant (Pt. I-A3.2)**	Calculation (ratio between vapour pressure and water solubility)		**calculated:** **result:** 1.34 x 10E-7 Pa m³/mol (pH 5) 1.60 x 10E-7 Pa m³/mol (pH 7) 1.35 x 10E-7 Pa m³/mol (pH 9)		N	1	Bogdoll (2007)	
3.5	**Solubility in water (IIA3.5)**	OECD 105	[redacted]	**result:** 167 g/L (pH 5) at 20°C 140 g/L (pH 7) at 20°C 165 g/L (pH 9) at 20°C		Y	1	Eyrich (2007)	
3.6	**Dissociation constant (-)**	OECD 112	[redacted]	**result:** pK_a = 10		N	2	Bogdoll (2007a)	

Section A3	Physical and Chemical Properties of N,N-DIMETHYLSULFAMIDE (DMS)							
	Method	Purity/ Specifi-cation	Results Give also data on test pressure, temperature, pH and concentration range if necessary	Remarks/ Justification	GLP (Y/N)	Relia bility	Reference	Offici al use only
3.9 Partition coefficient n-octanol/water (IIA3.6)	OECD 107	[redacted]	**result:** Log Pow = - 0.8 (pH 5) at 20°C Log Pow = - 0.8 (pH 7) at 20°C Log Pow = - 0.9 (pH 9) at 20°C		Y	1	Eyrich (2007a)	

	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	
Date	02/02/11	
Materials and methods	The applicant's version of the relevant metabolite is acceptable.	
Conclusion	Applicant's version is acceptable. It should be noted that the data above were considered and accepted for the approval of the active in PT 8.	
Reliability	1	
Acceptability	Acceptable	
Remarks	Document and data submitted was of an acceptable quality.	
	COMMENTS FROM...	
Date	*Give date of comments submitted*	
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub) heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*	
Conclusion	*Discuss if deviating from view of rapporteur member state*	
Reliability	*Discuss if deviating from view of rapporteur member state*	
Acceptability	*Discuss if deviating from view of rapporteur member state*	
Remarks		

Section A4 (4.1) **Annex Point IIA, IV.4.1**	**Analytical Methods for Detection and Identification of Active Substance**	
	1 REFERENCE (REF. A4.1/01, A4.1/02, A4.1/03 AND A4.1/04) Analytical method for the determination of pure Dichlofluanid and impurities in the active substance as manufactured	**Official use only**

Section A4 (4.1) Annex Point IIA, IV.4.1	Analytical Methods for Detection and Identification of Active Substance	
1.1 Reference	**REF. A4.1/01** [redacted], 2005, Validation of analytical methods of Dichlofluanid and impurities in technical Dichlofluanid, Bayer Industry Services GmbH & Co. [redacted] (unpublished), 2005-02-16.	
1.2 Data protection	Yes	
1.2.1 Data owner	LANXESS Deutschland GmbH	
1.2.2 Company with Letter of Access	-	
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s. for the purpose of its entry into Annex I/IA.	
	2 GUIDELINE AND QUALITY ASSURANCE	
2.1 Guideline study	The validation was performed according to SANCO/3030/99, rev.4 11/07/00, guidance document of the European Commission for generating and reporting methods of analysis in support of pre- and post-registration data requirements for Annex II and Annex III of Directive 91/414.	
2.2 GLP	Yes (certified laboratory)	
2.3 Deviations	No	
	3 MATERIALS AND METHODS	
3.1 Preliminary treatment		
3.1.1 Enrichment	[redacted]	
3.1.2 Cleanup	[redacted]	
3.2 Detection		
3.2.1 Separation method	[redacted]	

Section A4 (4.1) Annex Point IIA, IV.4.1	Analytical Methods for Detection and Identification of Active Substance	
	[redacted]	
3.2.2 Detector	HPLC method: UV-DAD-detector, 220 nm Potentiometric titration: potentiometric end point detection	
3.2.3 Standard(s)	[redacted]	
3.2.4 Interfering substance(s)	[redacted]	
3.3 Linearity		
3.3.1 Calibration range	[redacted]	
3.3.2 Number of measurements	[redacted]	
3.3.3 Linearity	[redacted]	

Section A4 (4.1) Annex Point IIA, IV.4.1	Analytical Methods for Detection and Identification of Active Substance	
3.4 Specifity: interfering substances	[redacted]	
3.5 Recovery rates at different levels	[redacted]	
3.5.1 Relative standard deviation	The relative standard deviations obtained are compiled in Table A4_1-2.	
3.6 Limit of determination	[redacted]	
3.7 Precision		
3.7.1 Repeatability	[redacted]	
3.7.2 Independent laboratory validation	No independent laboratory validation available.	

Section A4 (4.1) Annex Point IIA, IV.4.1	Analytical Methods for Detection and Identification of Active Substance	
	4 APPLICANT'S SUMMARY AND CONCLUSION	
4.1 Materials and methods	[redacted]	
4.2 Conclusion	[redacted]	
4.2.1 Reliability	1	
4.2.2 Deficiencies	No	
	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	
Date	03/03/2005	
Materials and methods	Study was carried out to the Guidance document SANCO/3030/99 rev.4 11/07/00 of the Directorate General Health and Consumer Protection of the European Commission	
Conclusion	This method has fulfilled the requirements set out in Guidance document SANCO/3030/99 rev.4 11/07/00 of the Directorate General Health and Consumer Protection of the European Commission	
Reliability	1	
Acceptability	Acceptable	
Remarks	UK CA agrees with the applicant's summary and conclusions. It should be noted that the data above were considered and accepted for the approval of the active in PT 8.	
	COMMENTS FROM...	
Date	Give date of comments submitted	
Results and discussion	Discuss additional relevant discrepancies referring to the (sub) heading numbers and to applicant's summary and conclusion. Discuss if deviating from view of rapporteur member state	
Conclusion	Discuss if deviating from view of rapporteur member state	
Reliability	Discuss if deviating from view of rapporteur member state	

Section A4 (4.1) Annex Point IIA, IV.4.1	Analytical Methods for Detection and Identification of Active Substance	
Acceptability	Discuss if deviating from view of rapporteur member state	
Remarks		

Table A4 1-1: Linearity

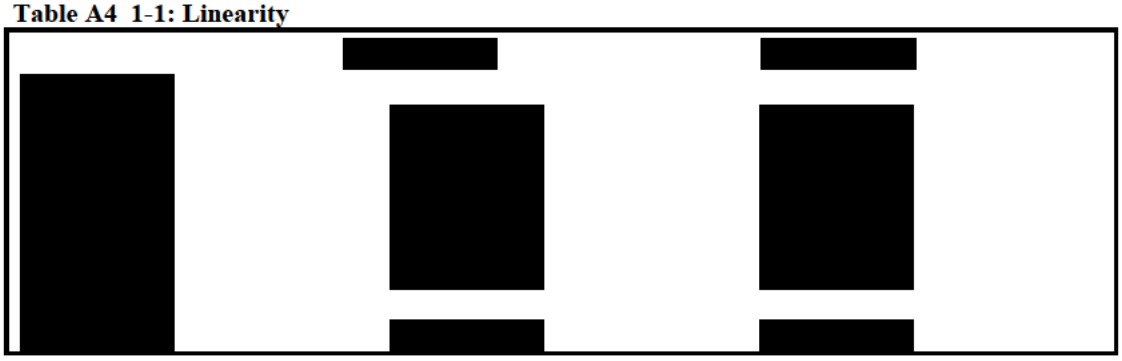


Table A4_1-2: Recoveries

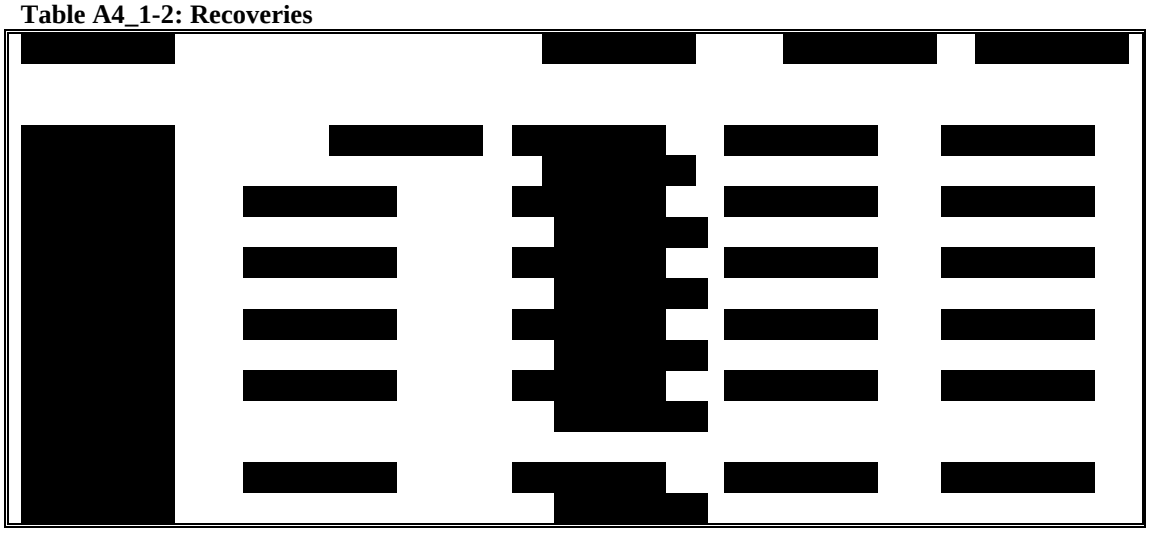


Table A4_1-3: Precision

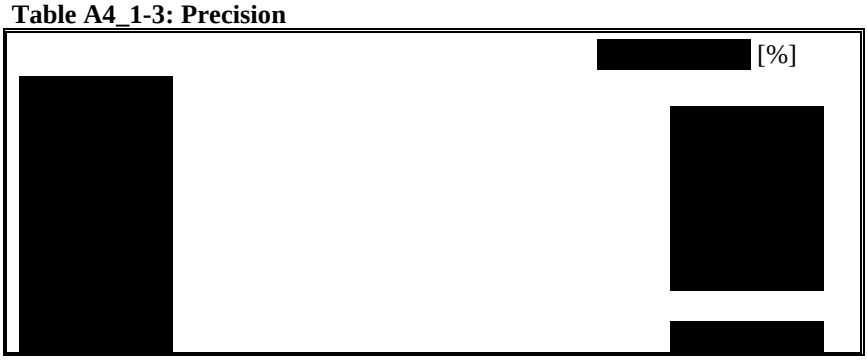


Table A4_1-4: Intermediate precision

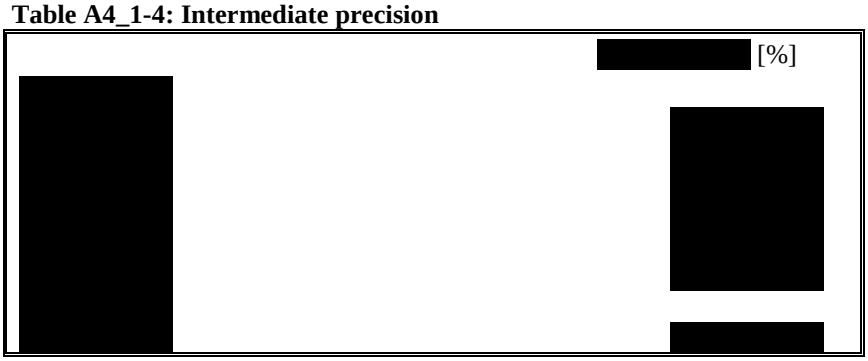


Table A4 1-5: Repeatability

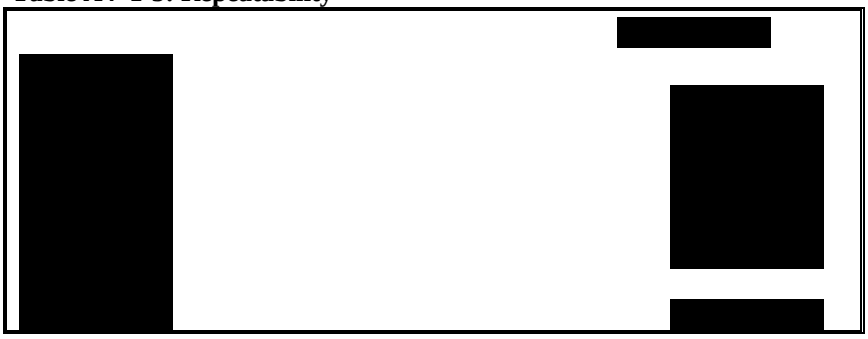
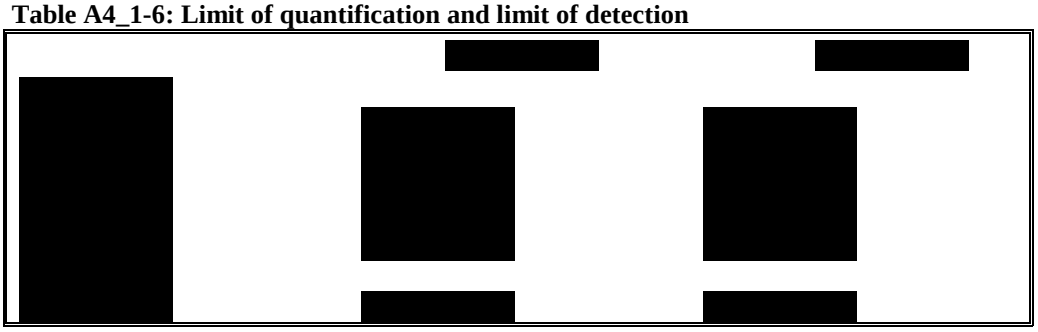


Table A4_1-6: Limit of quantification and limit of detection



Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on: (a) soil**; (b) air; (c) water; (d) animal and human body fluids and tissues	
	1 REFERENCE (REF. A4.2/02)	**Official use only**
1.1 Reference	S. Lakaschus and S. Rzepka, 2003, Method for the determination of residues of Dichlofluanid and DMSA in soil-Validation of the DFG Method S19 (Extended and revised version), Dr. Specht & Partner, Chemische Laboratorien GmbH, Hamburg, Germany, Specht & Partner Report No.: BAY-0315V, Az. G03-0105 (unpublished), 2003-10-29 DFG Method S 19: Specht, W.; in: Organochlorine, organophosphorus, nitrogen-containing and other pesticides, edited by Thier, H. P., Verlag Chemie, Weinheim, 1991	
1.2 Data protection	Yes	
1.2.1 Data owner	Bayer Chemicals AG	
1.2.2 Companies with letter of access	-	
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s. for the purpose of its entry into Annex I/IA	
	2 GUIDELINES AND QUALITY ASSURANCE	
2.1 Guideline study	The applicability of the DFG Method S 19 (extended version) was validated. The following documents were used: Guidance Document SANCO/825/00 rev.6 of 20/06/00 of the European Commission; BBA Guideline: Residue Analytical Methods for Post-Registration Control Purposes of July 21, 1998 and Council Directive 91/414/EEC as amended by Commission Directive 96/46/EC 4.2.3.	
2.2 GLP	Yes	
2.3 Deviations	No	
	3 MATERIALS AND METHODS	
3.1 Preliminary treatment	Before analysis, the soil (LUFA Speyer standard soil 2.2) was mixed thoroughly without further preparation. The soil samples (20 g per analysis) were extracted with ethylacetate / cyclohexane (1/1, v/v) using accelerated solvent extraction (ASE) under specific extraction conditions.	
3.1.1 Enrichment	None	
3.1.2 Cleanup	The obtained extracts were evaporated to dryness, redissolved and the remaining solutions were cleaned-up by gel permeation chromatography on Bio Beads S-X3 polystyrene gel using a mixture of ethylacetate / cyclohexane (1/1, v/v) as eluant. Further, the GPC fractions containing the target compounds were purified using silica gel columns with toluene / acetone (95/5, v/v) as eluant. The concentrated and cleaned extracts were analysed using gas chromatography. *Concentrations in specimen extracts were determined by comparing the detector response peak area of the specimen with the pertinent*	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on: (a) soil**; (b) air; (c) water; (d) animal and human body fluids and tissues	
	detector responses obtained from the neighbouring external standard.	
3.2 Detection		
3.2.1 Separation method	Determination of dichlofluanid and DMSA using mass selective detector: Column: 30 m fused silica capillary column DB-5 MS (J&W), internal diameter: 0.25 mm, film thickness: 0.25 µm; Gas flow rate: Carrier: helium, 2.1 ml/min; Temperatures: Oven: initial 60 °C, hold for 1 min, heat rate 40 °C/min to 100 °C, heat rate 10 °C/min to 250 °C, hold for 5 min, heat rate 40 °C/min to 280 °C, hold for 7 min, Injector: 250 °C, Interface: 280 °C; Injection volume: 1 µl, splitless; Ionization method: electron ionization (EI); Ionization energy: 70 eV; Retention time: dichlofluanid approx. 14.6 min and DMSA approx. 11.1 min. Determination of DMSA using nitrogen/phosphorus detector: Column: 15 m fused silica capillary column DB-1 (J&W), internal diameter: 0.53 mm, film thickness: 0.15 µm; Gas flow rates: Carrier: helium, 5.0 ml/min, Make-up: helium, 30 ml/min, Detector: synth. air, 60 ml/min, hydrogen, 3.0 ml/min; Temperatures: Oven: initial 60 °C, hold for 1 min, heat rate 7 °C/min to 250 °C, hold for 10 min, Injector: 250 °C, Interface: 280 °C; Injection volume: 5 µl, splitless; Retention time: DMSA approx. 9.3 min.	
3.2.2 Detector	All dichlofluanid specimens were analysed with mass selective detection (MSD) using m/z 224 for routine analysis and m/z 123, 167 for verification. The DMSA specimens were analysed with mass selective detection during routine analysis using m/z 200 and during confirmatory analysis nitrogen/phosphorus detection (NPD) was used.	
3.2.3 Standard(s)	Dichlofluanid and DMSA (analytical grade) were used for preparing the external standard solutions.	
3.2.3 Interfering substance(s)	Substances of sample matrix	
3.3 Linearity		
3.3.1 Calibration range	The linearity of the GC-MSD was confirmed by injecting 7 standard solutions ranging from 0.0138 to 0.990 µg/ml dichlofluanid covering the analytical working range. For DMSA 8 standard solutions between 0.0313 and 4.00 µg/ml were injected on the GC-MSD and GC-NPD covering the corresponding working ranges. Concentrations used for linearity: Dichlofluanid: 0.0138, 0.0275, 0.0495, 0.0990, 0.198, 0.495 and 0.990 µg/ml; DMSA: 0.0313, 0.0625, 0.1250, 0.250, 0.500, 1.000, 2.00 and 4.00 µg/ml	
3.3.2 Number of measurements	Single measurements of the standard solutions.	
3.3.3 Linearity	Correlation coefficients: Dichlofluanid (m/z 224): 0.9997, Dichlofluanid (m/z 167): 0.9998,	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on: (a) soil**; (b) air; (c) water; (d) animal and human body fluids and tissues	
	Dichlofluanid (m/z 123): 0.9997; DMSA (m/z 200): 0.9997, DMSA (NPD): 0.9995	
3.4 Specifity: interfering substances	The GC-MSD spectra of untreated soil specimens yielded no residues of dichlofluanid. Interfering compounds were present, but could be separted sufficiently from the ion signals used for dichlofluanid on the selected column. For DMSA no signals were detected in the control specimens using the ion m/z 200, indicating that no background levels of DMSA were present before the beginning of the study. Due to the fragmentation pattern of DMSA no other intensive ion signals were observed. Therefore, the confirmatory analysis was performed on a GC-NPD system. The NPD chromatogram of the control specimen did not exhibit a detectable DMSA level.	
3.4 Recovery rates & Standard deviations at different levels	The accuracy (analytical recovery) of the method was determined by comparing measured and theoretically expected concentrations from the recovery experiments. A series of recovery experiments was performed by fortifying control (untreated) specimen of LUFA Speyer standard soil 2.2. Fortification experiments were performed at the limit of quantification (LOQ) and ten times that level (0.01 mg/kg and 0.1 mg/kg). Fortified specimen were analysed in quintuple and control specimen were analysed in duplicate for each fortification level in routine analysis. For the results of recovery experiments during routine analysis and during confirmatory analysis see tables A4_2-1 to A4_2-3.	
3.4.1 Relative standard deviation	Relative standard deviations are given in tables A4_2-1 to A4_2-3	
3.5 Limit of determination	For dichlofluanid and DMSA in soil the limit of quantification (LOQ) was 0.01 mg/kg with a limit of detection of 0.002 mg/kg. The chromatographic peaks were greater than the signal equivalent to three times the background noise.	
3.6 Precision		
3.6.1 Repeatability	The repeatability of the method was assessed on the basis of the obtained relative standard deviations for each commodity and each fortification level (see recovery rates (point 3.5).	
3.6.2 Independent laboratory validation	The validation was performed by an external laboratory (see point 1.1: "Reference")	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on: (a) soil**; (b) air; (c) water; (d) animal and human body fluids and tissues	
	4 APPLICANT'S SUMMARY AND CONCLUSION	
4.1 Materials and methods	The purpose of this study was to examine the applicability of the DFG Method S 19 (extended revision) with accelerated solvent extraction (extraction module E 9) for the determination of dichlofluanid and DMSA in soil by means of gas chromatography using mass selective detection (D 4) for routine analysis and nitrogen/phosphorus detection (D 3) for confirmatory analysis.	
4.2 Conclusion	The analysis of control specimen yielded no residues of dichlofluanid and DMSA above the limit of detection, indicating that no background levels of both compounds were present in the system before the beginning of the study. Mean recovery values obtained for dichlofluanid and DMSA in soil for both fortification levels (LOQ and ten times LOQ) comply with the standard acceptance criteria of SANCO guideline 825/00, which demand that the recovery at each fortification level should be in the range of 70-110%. It is therefore concluded, that the enforcement method DFG Method S 19 has proven its applicability for the determination of dichlofluanid and DMSA in soil. Moreover all corresponding relative standard deviations indicate that the method features good precision and repeatability for all matrices at the validated levels. Furthermore, the obtained recovery values of the fortification experiments proved the stability of dichlofluanid under the ASE extraction conditions. The results of the recoveries obtained during confirmatory analysis prove unequivocally the peak identity and thus demonstrate the principle applicability of DFG Method S 19 (extended revision) for the determination of dichlofluanid and DMSA in soil. The data presented demonstrate that DFG Method S 19 (extended revision) is applicable for the determination of dichlofluanid and DMSA in soil with satisfactory accuracy, precision and repeatability.	
4.2.1 Reliability	1	
4.2.2 Deficiencies	No	
	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	
Date	20/07/2006	
Materials and methods	Study complied with EU-Guideline: 91/414 (as amended by guideline 96/46EC 4.2.3), Guidance document SANCO/825/00 rev. 6 of 20/06/2000 of the European Commission and BBA Guideline: Residue Analytical Methods for Post-Registration Control Purposes (21/07/1998).	
Conclusion	The study was carried out to assess if the specific study (DFG Method S 19), was applicable to measure dichlofluanid and DMSA residues in soil. The study has matched the criteria set out, i.e. applicability of this method to measure residues of dichlofluanid and DMSA because it demonstrated correct analysis and full	

Section A4 (4.2) Annex Point IIA, IV.4.2	Analytical Methods for Detection and Identification Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on: (a) soil**; (b) air; (c) water; (d) animal and human body fluids and tissues	
	results for methods of analysis, carried out to GLP. The Applicant has also indicated that soil and sediment are comparable matrices, and that the method of analysis, for any specific analyte (eg dichlofluanid or DMSA), can be used for both matrices. The UK CA and TMI06 both agreed.	
Reliability	1	
Acceptability	Acceptable	
Remarks	The UK CA agrees with the applicant's summary and conclusions. It should be noted that the data above were considered and accepted for the approval of the active in PT 8.	
	COMMENTS FROM...	
Date	*Give date of comments submitted*	
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub) heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*	
Conclusion	*Discuss if deviating from view of rapporteur member state*	
Reliability	*Discuss if deviating from view of rapporteur member state*	
Acceptability	*Discuss if deviating from view of rapporteur member state*	
Remarks		

Table A4_2-1: Recoveries obtained during routine analysis using GC-MSD

Compound/ion	Fortification level [mg/kg]	Recoveries[%]	Mean recovery (n=5) [%]	Relative standard deviation RSD [%]	Overall mean (n=10) [%]	Overall RSD [%]
Dichlofluanid (m/z 224)	0.01	112, 104, 108, 106, 93	105	6.8	107	8.4
	0.1	118, 120, 106, 93, 111	110	9.8		
DMSA	0.01	109, 101, 115, 100, 101	105	6.3	97	10.5
	0.1	89, 89, 94, 85, 85	88	4.2		

Table A4_2-2: Recoveries obtained during confirmatory analysis using GC-MSD

Compound/ion	Fortification level [mg/kg]	Recoveries[%]	Mean recovery (n=5) [%]	Relative standard	Overall mean	Overall RSD

				deviation RSD [%]	(n=10) [%]	[%]
Dichlofluanid (m/z 123)	0.01	112, 107, 105, 109, 103	107	3.3	109	6.3
	0.1	122, 111, 114, 96, 110	111	8.5		
Dichlofluanid (m/z 167)	0.01	113, 111, 109, 103, 95	106	6.9	108	6.9
	0.1	116, 117, 104, 98, 112	109	7.5		

Table A4_2-3: Recoveries obtained during confirmatory analysis using GC-NPD

Compound/ion	Fortification level [mg/kg]	Recoveries[%]	Mean recovery (n=5) [%]	Relative standard deviation RSD [%]	Overall mean (n=10) [%]	Overall RSD [%]
DMSA	0.01	79, 75, 84	79	5.7	82	5.1
	0.1	81, 83, 87	84	3.7		

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	1 REFERENCE (REF. A4.2/03)	**Official use only**
1.1 Reference	R.D. Weeren and S. Pelz, 1999, Validation of an analytical method (analogous to DFG method W 5) for the determination of residues of Dichlofluanid in drinking and surface water, Dr. Specht & Partner, Chemische Laboratorien GmbH, Hamburg, Germany, Specht & Partner Report No.: BAY-9904V, Az. M5893/99 (unpublished), 1999-06-25 DFG Method W 5: R. Brennecke, K. Vogeler in: Manual of Pesticides Residue Analysis, edited by Thier HP and Zeuner H, Weinheim, New York, 1992, Vol.2, p. 377-386	
1.2 Data protection	Yes	
1.2.1 Data owner	Bayer Chemicals AG	
1.2.2 Companies with letter of access	-	
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s. for the purpose of its entry into Annex I/IA	
	2 GUIDELINES AND QUALITY ASSURANCE	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
2.1 Guideline study	The analytical method P-14.112 of Dr. Specht & Partner (analogous to DFG Method W 5) was validated. The following documents were used: BBA Guideline: Residue Analytical Methods for Post-Registration Control Purposes of July 21, 1998, Draft working document 8064/VI/ 97 rev. 4 from 15.12.98 of the European Commission and NL-guideline: Surface water (G.2.5, Handbook CTB).	
2.2 GLP	Yes	
2.3 Deviations	No	
	3 MATERIALS AND METHODS	
3.1 Preliminary treatment	Samples are thawed, if frozen, and allowed to equilibrate to room temperature. Samples are centrifuged at 3,000 rpm for ~ 10 minutes. A 5 mL aliquot of the supernatant is taken for analysis. Fortification samples were prepared by adding appropriate volumes of a stock solution of 4-(2-nitrobutyl) Morpholine in acetonitrile.	
3.1.1 Enrichment	Method P-14.112 (analogous to DFG Method W 5): The water sample is extracted three times with dichloromethane. The organic phases are filtered through sodium sulfate. The combined filtrates are evaporated. The residue is dissolved in ethyl acetate and cyclohexane.	
3.1.2 Cleanup	An aliquot of this solution is cleaned up by gel permeation chromatography on Bio Beads S-X3 polystyrene gel using a mixture of ethyl acetate/cyclohexane (1+1) as eluant and an automated gel permeation chromatograph. After supplemental cleanup on a small silica gel column the concentrated solution is analysed for dichlofluanid by gas chromatography according to the indicated conditions. Concentrations of dichlofluanid in sample extracts were determined by comparing the detector response (peak height in counts) of the sample with the pertinent detector response obtained from the neighbouring external standard.	
3.2 Detection		
3.2.1 Separation method	Analysis for dichlofluanid was done by gas chromatography using a fused silica capillary column (DB-608, length: 30 m, internal diameter: 0.32 mm, film thickness: 0.5 µm). Gas flow rates: Carrier: argon/methane, 1.2 ml/min, Make-up: argon/methane, 39 ml/min; Temperatures: Oven: initial 100 °C, hold for 1 min, with a rate of 40 °C/min to 120 °C, hold for 0 min, with a rate of 10 °C/min to 280 °C, hold for 12 min; Injection volume: 2 µl, splitless; Injector temperature: 250 °C. For confirmation technique, gas chromatography using a fused silica capillary column (XTI-5, length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 µm) was used. Gases: helium, 1 ml/min; Temperatures: Oven: initial 100 °C, hold for 1 min, heat rate 20	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	°C/min to 250 °C, hold for 12 min, Interface: 280 °C; Injection volume: 1 µl, splitless; Injector temperature: 250 °C.	
3.2.2 Detector	Electron capture detector (ECD) and confirming mass selective detector (MSD). Selected ions: m/z 123 (quantification) m/z 224, 167, 332 (verification)	
3.2.3 Standard(s)	External standard (dichlofluanid)	
3.2.3 Interfering substance(s)	Substances of sample matrix: Surface water from the German river Alster, Hamburg (pH 8.5, DOC: 4.0 mg C/l, total hardness 10.6 °dH, TOC: 15 mg C/l)	
3.3 Linearity		
3.3.1 Calibration range	The linearity of the electron capture detector response was confirmed by injecting standard solutions ranging from 0.002 to 0.286 µg/ml dichlofluanid covering the working range (see table A4_2-1).	
3.3.2 Number of measurements	Single measurement of 10 concentrations (see table A4_2-1)	
3.3.3 Linearity	Correlation coefficient r = 0.9993	
3.4 Specifity: interfering substances	Analysis of control samples yielded no residues of dichlofluanid above the limit of detection, indicating that no background levels of dichlofluanid were present in the systems before the beginning of the study. No significant interferences from the sample matrix were detected at the retention	
3.4 Recovery rates & Standard deviations at different levels	The accuracy (analytical recovery) of the method was determined by comparing observed and theoretical concentrations from the recovery data. Fortification experiments were performed over the range from 0.1 µg/l to 1 µg/l. Fortified samples were analysed in quintuplet for each fortification level. The overall mean recovery over the whole validation range from 0.1 µg/l to 1 µg/l was 88% (range: 81% - 95%, (n = 10)) for drinking water and 88% (range: 72% - 101%, (n = 10)) for surface water. For confirmation, one fortified sample of each fortification level was analysed in addition with GC/MSD. The overall mean recovery over the whole validation range from 0.1 µg/l to 1 µg/l was 91.5% (range: 90-93%, (n = 2)) for drinking water and 93.5% (range: 96-91%, (n = 2)) for surface water.	
3.4.1 Relative standard deviation	Drinking water: Standard deviation: 4.5%, coefficient of variation: 5.1%, Surface water: Standard deviation: 12%, coefficient of variation: 13%	
3.5 Limit of determination	Limit of quantification (LOQ): 0.1 µg/l, Limit of detection (LOD): 0.02 µg/l; The chromatographic peaks were greater than the signal equivalent to three times the background noise.	
3.6 Precision		

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
3.6.1 Repeatability	see recovery rates (point 3.4)	
3.6.2 Independent laboratory validation	The validation was performed by an external laboratory (see point 1.1: "Reference")	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	4 APPLICANT'S SUMMARY AND CONCLUSION	
4.1 Materials and methods	The purpose of this study was to examine the applicability of an analytical method (analogous to DFG W 5) for the determination of dichlofluanid residues in drinking water and surface water by means of gas chromatography using electron capture detection and confirming mass selective detection. Prior to the gas chromatographic analysis an extraction with dichloromethane is performed.	
4.2 Conclusion	The accuracy was considered acceptable since the results were in the range 70-110%. All the results obtained using this method were within this range. The precision results should be better than 20% over the range covered. The precision data obtained fall within these limits. The analytical method P-14.112 (analogous to DFG W 5) permits the reliable determination of residues of dichlofluanid in drinking and surface water over the range 0.1 µg/l to 1 µg/l with satisfactory recoveries using GC/ECD. As a confirmatory technique, GC/MDS was investigated. All the accuracy data obtained using this technique were within 70 – 110%. The recovery data demonstrates the applicability of GC/MS as an alternative technique for the determination of dichlofluanid residues in drinking and surface water. The method was considered valid for the determination of dichlofluanid residues in drinking and surface water. It should be noted that the data above were considered and accepted for the approval of the active in PT 8.	
4.2.1 Reliability	1	
4.2.2 Deficiencies	No	
	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	
Date	06/01/2005	
Materials and methods	The Method used to perform the study complied with: NL_Guideline: Surface water (G.2.5, Handbook CTB), Draft working document 8064/VI/97 rev. 4 of 15.12.98 of the European Commission and BBA Guideline: Residue Analytical Methods for Post-Registration Control Purposes (21/07/1998).	
Conclusion	The study complied with GLP. The study demonstrated satisfactory results for full methods of analysis including an LOQ = 0.1 µg/l for drinking and surface water.	
Reliability	1	
Acceptability	Acceptable	
Remarks	The UK CA agrees with the applicant's summary and conclusions.	

Section A4 (4.2) Annex Point IIA, IV.4.2	Analytical Methods for Detection and Identification Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of the active ingredient 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	COMMENTS FROM...	
Date	*Give date of comments submitted*	
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub) heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*	
Conclusion	*Discuss if deviating from view of rapporteur member state*	
Reliability	*Discuss if deviating from view of rapporteur member state*	
Acceptability	*Discuss if deviating from view of rapporteur member state*	
Remarks		

Table A4 2-1: Linearity of electron capture detector response of dichlofluanid

External standard concentration (µg/ml)	Peak high (count)
0.00200	905
0.00400	1843
0.00800	4276
0.0160	8712
0.0280	18796
0.0400	28348
0.0667	54085
0.100	86321
0.200	187737
0.286	271506

Section A4 (4.2) Annex Point IIA, IV.4.2	Analytical Methods for Detection and Identification Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	1 REFERENCE (REF. A4.2/04)	**Official use only**

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
1.1 Reference	S. Steinhauer, 2003, Validation of an analytical method (analogous to DFG Method W 5) for the determination of residues of N-N-Dimethyl-N`-Phenylsulphamide (DMSA) in drinking and surface water, Dr. Specht & Partner, Chemische Laboratorien GmbH, Hamburg, Germany, Specht & Partner Report No.: BAY-0208V, Az. G02-0060 , Bayer report No.: BCH-MPP-2002-14 (unpublished), 2003-03-13. DFG Method W 5: R. Brennecke, K. Vogeler in: Manual of Pesticides Residue Analysis, edited by Thier HP and Zeuner H, Weinheim, New York, 1992, Vol.2, p. 377-386	
1.2 Data protection	Yes	
1.2.1 Data owner	Bayer Chemicals AG	
1.2.2 Companies with letter of access	-	
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s. for the purpose of its entry into Annex I/IA	
	2 GUIDELINES AND QUALITY ASSURANCE	
2.1 Guideline study	The analytical method P-14.112 of Dr. Specht & Partner (analogous to DFG MethodW 5) was validated. The following documents were used: Guidance Document SANCO/825/00 rev.6 of 20/06/00 of the European Commission; BBA Guideline: Residue Analytical Methods for Post-Registration Control Purposes of July 21, 1998, Council Directive 91/414/EEC as amended by Commission Directive 96/46/EC 4.2.3.	
2.2 GLP	Yes	
2.3 Deviations	Yes, No GPC separation was used in deviation to the original method. This had no effect on the performance of the quality of the used method.	
	3 MATERIALS AND METHODS	
3.1 Preliminary treatment		
3.1.1 Enrichment	**Method P-14.112 (analogous to DFG Method W 5):** The water sample is extracted three times with dichloromethane. The combined organic phases are filtered through sodium sulfate. The combined filtrates are evaporated to dryness and the residue is dissolved by adding 1 ml ethyl acetate with a volumetric pipette. The solution is analysed for dimethylaminosulfanilid (DMSA) by gas chromatography according to the indicated conditions. Concentrations of dimethylaminosulfanilid (DMSA) in specimen extracts were determined by comparing the detector response (peak	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	area of the specimen) with the pertinent detector response obtained from the neighbouring external standard.	
3.1.2 Cleanup	None	
3.2 Detection		
3.2.1 Separation method	Analysis for dimethylaminosulfanilid (DMSA) was done by gas chromatography using a fused silica capillary column (DB-5 MS (J&W), length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 µm). Gas flow rate: Carrier: helium, 1.3 ml/min, Temperatures: Oven: initial 60 °C, hold for 1 min, heat rate 40 °C/min to 100 °C, heat rate 10 °C/min to 250 °C, hold for 5 min, heat rate 40 °C/min to 280 °C, hold for 7 min; Injector: 250 °C, Interface: 280 °C; Injection volume: 1 µl, splitless; Ionisation method: Electron ionisation (EI); Ionisation energy: 70 eV;	
3.2.2 Detector	Mass selective detector (MSD). Selected ions: m/z 200 (quantification); m/z 201, 108 for (verification)	
3.2.3 Standard(s)	External standard (dimethylaminosulfanilid (DMSA))	
3.2.3 Interfering substance(s)	Substances of sample matrix: Surface water from the german river Alster , Hamburg (pH 7.88, DOC: 7.8 mg C/l, total hardness 11.8 °dH, Mud content: 45 mg/l)	
3.3 Linearity		
3.3.1 Calibration range	The linearity of the detector response was confirmed by injecting standard solutions covering the working range of 0.020 – 2.0 µg/ml DMSA (used concentrations see table A4_2-1).	
3.3.2 Number of measurements	Single measurement of 8 concentrations (see table A4_2-1)	
3.3.3 Linearity	Correlation coefficient r = 0.9997	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
3.4 Specifity: interfering substances	Specificity was established by analyzing blank sample preparations and comparing peak area responses of the blanks with the peak area response found in the LOQ standard. Acceptable background should not exceed 30% relative to the LOQ standard. Morpholine was found in surface water matrix. Mass Spectrometric detection with Single Ion Monitoring and confirmatory peaks is recognized in the SANCO Guidelines as a highly specific technique.	
3.4 Recovery rates & Standard deviations at different levels	The accuracy (analytical recovery) of the method was determined by comparing found and theoretical concentrations from the recovery experiments. Fortification experiments were performed over the range from 0.1 µg/l to 1 µg/l. Fortified samples were analysed in quintuplet for each fortification level. The overall mean recovery over the whole validation range from 0.1 µg/l to 1 µg/l was 103% (range: 94% - 126%, (n = 10)) for drinking water and 99% (range: 87% - 109%, (n = 10)) for surface water.	
3.4.1 Relative standard deviation	Overall relative standard deviation (n = 10): drinking water: 9.1%, surface water: 8.0%	
3.5 Limit of determination	Limit of quantification (LOQ): 0.1 µg/l Limit of detection (LOD): 0.03 µg/l The chromatographic peaks were greater than the signal equivalent to three times the background noise.	
3.6 Precision		
3.6.1 Repeatability	The repeatability of the method was assessed on the basis of the obtained relative standard deviations for each commodity and each fortification level (see recovery rates (point 3.5))	
3.6.2 Independent laboratory validation	The validation was performed by an external laboratory (see point 1.1: "Reference")	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	4 APPLICANT'S SUMMARY AND CONCLUSION	
4.1 Materials and methods	The purpose of this study was to examine the applicability of an analytical method (analogous to DFG MethodW 5) for the determination of dimethylaminosulfanilid (DMSA) residues in drinking water and surface water by means of gas chromatography using mass selective detection. Prior to the gas chromatographic analysis an extraction with dichloromethane is performed.	
4.2 Conclusion	Analysis of control specimen of drinking water and surface water yielding no residues of DMSA above the limit of detection, indicating that no background levels of DMSA were present in the test systems before the beginning of the study. The results prove unequivocally the peak identity and thus demonstrate the principle applicability of the analytical method (analogous to DFG MethodW 5) with mass selective detection for the determination of DMSA residues in drinking water and surface water. Mean recovery values obtained for drinking water and surface water for both fortification levels (LOQ and ten times LOQ) comply with the standard acceptance criteria of SANCO Guideline 825/00, which demand that the mean recovery at each fortification level should be in the range of 70 – 110%. It is therefore concluded, that the enforcement method DFG Method W 5 has proven its applicability for the determination of DMSA in drinking water and surface water. Moreover all corresponding relative standard deviations indicate that the method features good precision and repeatability for all matrices at the validated levels. Furthermore, the obtained recovery values of the fortification experiments proved the stability of DMSA in extracts from specimen extraction to GC/MSD analysis. The data presented demonstrate that using suitable liquid-liquid-extraction the enforcement method DFG Method W5 permits the determination of residues of dimethylaminosulfanilid DMSA in drinking water and surface water with satisfactory accuracy, precision and repeatability. The method was therefore considered valid for the determination of residues of dimethylaminosulfanilid (DMSA) in drinking water and surface water.	
4.2.1 Reliability	1	
4.2.2 Deficiencies	No	
	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	

Section A4 (4.2) Annex Point IIA, IV.4.2	Analytical Methods for Detection and Identification Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
Date	08/02/2005	
Materials and methods	The Method used to perform the study complied with: 91/414 (as amended by guideline 96/46/EG 4.2.3). SANCO/825/00 rev.6 (20/06/2000), of the European Commission. BBA Guideline: Residue Analytical Methods for Post-Registration Control Purposes of July 21, 1998.	
Conclusion	The study complied with GLP. The study demonstrated satisfactory results for full methods of analysis including an LOQ = 0.1 µg/l for drinking and surface water.	
Reliability	1	
Acceptability	Acceptable	
Remarks	The UK CA agrees with the applicant's summary and conclusions. It should be noted that the data above were considered and accepted for the approval of the active in PT 8.	
	COMMENTS FROM...	
Date	*Give date of comments submitted*	
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub) heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*	
Conclusion	*Discuss if deviating from view of rapporteur member state*	
Reliability	*Discuss if deviating from view of rapporteur member state*	
Acceptability	*Discuss if deviating from view of rapporteur member state*	
Remarks		

Table A4 2-1: Linearity of mass selective detector response of dimethylaminosulfanilid (DMSA)

External standard concentration (µg/ml)	Peak areas (counts)
0.0200	3531
0.0400	6013
0.100	15045
0.200	28441
0.250	38471
0.500	83586
1.00	174662
2.00	358898

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	1 REFERENCE (REF. A4.2/05)	**Official use only**
1.1 Reference	R. Krebber, M. Braune, 2007, Method 01041 (MR-07/242) for the determination of N,N-dimethylsulfamide in water by HPLC-MS/MS. Bayer Crop Science AG , Monheim am Rhein, Germany, Bayer Method No.: 01041, Report No.: MR-07/242 / M-289492-01-1 (unpublished), 2007-06-27	
1.2 Data protection	Yes	
1.2.1 Data owner	Bayer Crop Chemicals AG	
1.2.2 Companies with letter of access	LANXESS Deutschland GmbH	
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s. for the purpose of its entry into Annex I/IA	
	2 GUIDELINES AND QUALITY ASSURANCE	
2.1 Guideline study	No guideline available.	
2.2 GLP	No	
2.3 Deviations	No	
	3 MATERIALS AND METHODS	
3.1 Preliminary treatment		
3.1.1 Enrichment	Water samples are filtrated and analysed after addition of internal standard solution by direct injection into a HPLC-MS/MS.	
3.1.2 Cleanup	No extraction and clean-up steps are necessary.	
3.2 Detection		
3.2.1 Separation method	Liquid chromatographic conditions: Column: Eclipse® XDB-C8, 5 µm; Length 150 mm,. i.d. 4.6 mm Particle size: 5 µm Injection volume: 100 µL (possibility of adoption to the measurement concentrations) Oven temperature: 60 °C Mobile phases: A: Milli-Q-water B: methanol / acetic acid (1000/0.1; v/v) Gradient Run time: 10 min	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	Flow rate: 1 mL / min Retention time: approximately 2.9 min	
3.2.2 Detector	Mass spectrometric detection (MS/MS) is used by using two Multiple Reaction Monitoring (MRM) transitions with following operation parameters (only a short overview is presented here, more parameters are mentioned in the report): Interface: Electrospray, Turbo ion spray, Temperature: 500 °C - N,N-Dimethylsulfamide 1st MRM for Quantification Precursor ion: 125 amu; Mass of product ion: 108 amu 2nd MRM for Confirmation: Mass of parent ion: 125 amu; Mass of product ion: 44 amu - Internal Standard: N,N-dimethylsulfamide-d_6 1st MRM for Quantification Mass of parent ion: 131 amu; Mass of product ion: 114 amu 2nd MRM for Confirmation: Mass of parent ion: 131 amu; Mass of product ion: 51 amu Ionisation mode: ESP + (positive mode) Collision energy m/z 125->108 and m/z 131/114: 17 eV 125->44: 37 eV 131->51: 25 eV Dwell: 150 msec	
3.2.3 Standard(s)	Internal standard (N,N-dimethylsulfamide-d_6)	
3.2.3 Interfering substance(s)	Substances of specimen matrix may interfere.	
3.3 Linearity		
3.3.1 Calibration range	The linearity of HPLC-MS/MS detection was investigated with standard solutions of N,N-dimethylsulfamide in deionised and surface water between 0.025 µg/L and 10 µg/L for the quantification ion and in the concentration range of 0.05 µg/L to 10 µg/L for the confirmatory ion.	
3.3.2 Number of measurements	-	
3.3.3 Linearity	For both MRM transitions and matrices the correlation coefficients were ≥ 0.9995 (1/x weighted) both MRM transitions. Linear regression product ion m/z 108 of N ;N-dimethylsulfamide in	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	deionised water Y = 0.92989 * X + 0.00145129 m/z 44 ; Y = 1.13741 * X + 0.0313262 Linear regression product ion m/z 108 of N ;N-dimethylsulfamide in surface water Y = 0.911538 * X + 0.00129607 m/z 44 ; Y = 1.11727 * X + 1.14491E-005	
3.4 Specifity: interfering substances	In the blank samples of deionised and surface water N,N-dimethylsulfamide were not detected.	
3.4 Recovery rates & Standard deviations at different levels	Because of the direct measurement of fortified samples without separate extraction and clean-up steps it is not possible to determine recovery rates and an estimate of accuracy of the analytical technique was made by an assessment of the linearity of matrix calibration and by determination of the reproducibility of sample analysis.	
3.4.1 Relative standard deviation	See 3.6.1	
3.5 Limit of determination	The limit of quantification for N,N-dimethylsulfamide is 0.025 µg/L for the quantification ion. For the confirmatory ion 0.05 µg/L.	
3.6 Precision		
3.6.1 Repeatability	Repeatability was tested in deionised and surface water with using of two Multiple Reaction Monitoring (MRM) transitions. Standard solutions of N,N-dimethylsulfamide in deionised water were prepared at concentrations of 0.025 µg/L and 0.5 µg/L. These were injected 10 times each into the HPLC-MS/MS instrument and a relative standard deviations of 7.0 % (0.025 µg/L) and 1.0 %(0.5 µg/L) were obtained, respectively. The relative standard deviation for the confirmatory ion of N;N-dimethylsulfamide (m/z 44) at 0.5 µg/L was 5.2 %. For both fortification levels and MRM transitions the relative standard deviation for the retention time was ≤ 0.4 %. The standard solutions of N,N-dimethylsulfamide in surface water at concentrations of 0.025 µg/L, 0.05 µg/L and 0.5 µg/L were injected 10 times each into HLPC-MS/MS instrument as well. The relative standard deviation of 2.5 % (0.025 µg/L) and 1.1% (0.5 µg/L) were obtained, respectively. The relative standard deviation for the confirmatory ion was 2.5 % (0.05 µg/L) and 1.8 % (0.5 µg/L) were obtained, respectively. For these performed fortification levels the relative standard deviation for the retention time and both MRM transitions were ≤ 0.7%. From single peak areas percent values were calculated relative to the	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	mean area, which was set at 100%. Peak area ratios, retention times as well as percent values are given in Table A4_2-1 – A4_2_4.	
3.6.2 Independent laboratory validation	No independent laboratory validation available.	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
	4 APPLICANT'S SUMMARY AND CONCLUSION	
4.1 Materials and methods	Deionised and surface water samples are analysed for N,N-dimethylsulfamide by direct injection into an HPLC-MS/MS instrument.	
4.2 Conclusion	A method for the determination of N,N-dimethylsulfamide in deionised and surface water was developed and validated successfully. Because of the high selectivity of the HPLC-MS/MS method an additional confirmatory method is not necessary.	
4.2.1 Reliability	2	
4.2.2 Deficiencies	No	
	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	
Date	10 November 2007 13 February 2008	
Materials and methods	Concerning the methodology, a refinement or further validation may be necessary, although the BPD process is not regulated be the SANCO/3029/99 rev 4 which is in use for the parallel evaluation of this method under the PPPD. Based on this it was noted that from a single one stock solution, different standard solutions were prepared by dilution, whereas the SANCO Guideline emphasises preparation of several solutions from independent weighings. Also the multiplicity of injections is under discussion. The company has made progress in the validation of the method. The RMS is not aware of exact status of the validation work. In the ppp area the method is in a consultation procedure.	
Conclusion	The method is considered sufficient for the immediate needs of risk assessment, but may need refinement.	
Reliability	To be confirmed later	
Acceptability	Acceptable for immediate needs, see also the conclusion.	
Remarks	It should be noted that the data above were considered and accepted for the approval of the active in PT 8.	
	COMMENTS FROM...	
Date	*Give date of comments submitted*	
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub) heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*	
Conclusion	*Discuss if deviating from view of rapporteur member state*	
Reliability	*Discuss if deviating from view of rapporteur member state*	

Section A4 (4.2) Annex Point IIA, IV.4.2	Analytical Methods for Detection and Identification Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of degradates of a.s. 4.2 **Analytical methods on:** (a) soil; (b) air; **(c) water**; (d) animal and human body fluids and tissues	
Acceptability	*Discuss if deviating from view of rapporteur member state*	
Remarks		

Table A4_2-1: Validation of N,N-dimethylsulfamide in deionised water (Quantification Ion, m/z 108)

Sample concentration	Peak area Ratio			Retention time	
[µg/L]	Range of single values	Mean	Relative standard deviation [%]	Mean [min]	Relative standard deviation [%]
0.025	0.01785-0.02264	0.02124	7.0	2.91	0.4
0.5	0.4716 – 0.4871	0.4784	1.0	2.93	0.2

Sample concentration	Percentage found		
[µg/L]	Range of single values [%]	Mean value [%]	Relative standard deviation [%]
0.025	86 – 106	100	6.3
0.5	102 - 105	103	1.0

Table A4_2-2: Validation of N,N-dimethylsulfamide in deionised water (Confirmatory Ion, m/z 44)

Sample concentration	Peak area Ratio			Retention time	
[µg/L]	Range of single values	Mean	Relative standard deviation [%]	Mean [min]	Relative standard deviation [%]
0.5	0.4442 – 0.5347	0.4941	5.2	2.92	0.2

Sample concentration	Percentage found		
[µg/L]	Range of single values [%]	Mean value [%]	Relative standard deviation [%]
0.5	84 - 100	93	4.9

Table A4_2-3: Validation of N,N-dimethylsulfamide in surface water (Quantification Ion, m/z 108)

Sample concentration	Peak area Ratio			Retention time	
[µg/L]	Range of single values	Mean	Relative standard deviation [%]	Mean [min]	Relative standard deviation [%]
0.025	0.02067-0.02256	0.02124	2.5	2.80	0.7
0.5	0.4665 – 0.4484	0.4556	1.1	2.78	0.3

Sample concentration	Percentage found		
[µg/L]	Range of single values [%]	Mean value [%]	Relative standard deviation [%]
0.025	96 – 105	100	2.6
0.5	99 - 103	100	1.2

Table A4_2-4: Validation of N,N-dimethylsulfamide in surface water (Confirmatory Ion, m/z 44)

Sample concentration	Peak area Ratio			Retention time	
[µg/L]	Range of single values	Mean	Relative standard deviation [%]	Mean [min]	Relative standard deviation [%]
0.05	0.05252-0.05678	0.05495	2.5	2.77	0.4
0.5	0.5372 – 0.5668	0.5513	1.8	2.77	0.2

Sample concentration	Percentage found		
[µg/L]	Range of single values [%]	Mean value [%]	Relative standard deviation [%]
0.05	94 – 101	98	2.3
0.5	96 - 101	99	1.8

NEEDS RAW DATA TO BE SUBMITTED FOR ALL FOUR METHODS

Section A4 (4.2) Analytical Methods for Detection and Identification (01)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater:

I. Method for the determination of Dichlofluanid in seawater

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1 REFERENCE

Official use only

Section A4 (4.2) Analytical Methods for Detection and Identification (01)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater:

I. Method for the determination of Dichlofluanid in seawater

1.1 Reference	Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments of Greek marinas in the early spring of 2003. TNO report V5119/ **02**. Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments at suspected hotspots of Greek marinas in the early spring of 2003. TNO report V5119/ **03** Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments of Greek marinas in the summer of 2003. TNO report V5119/ **06**. Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments at suspected hotspots of Greek marinas in the summer of 2003. TNO report V5119/ **07**. Schouten, A, JC Ravensberg. 2004. Validation of analytical methods for the determination of dichlofluanid and its metabolite DMSA in seawater and marine sediment. TNO report V5119/ **04**.
1.2 Data protection	Yes
1.2.1 Data owner	LANXESS Deutschland GmbH
1.2.2 Companies with letter of access	Not specified at this stage
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s for the purpose of its entry into Annex I authorisation]
	2 GUIDELINES AND QUALITY ASSURANCE
2.1 Guideline study	No
2.2 GLP	Yes
2.3 Deviations	No
	3 MATERIALS AND METHODS
3.1 Preliminary treatment	
3.1.1 Enrichment	500 ml seawater samples were acidified with 0.5 ml of a 1:1 sulphuric acid in tap water solution to adjust the pH to 3. Extraction of 500 ml seawater on SPE speedisk cartridge (DVB, 50 mm) which first is conditioned with subsequently two times 10 ml of ethyl acetate, two times 10 ml of methanol and two times 10 ml of MilliQ water. Dichlofluanid was eluted with 10 ml ethyl acetate. The ethyl acetate is further concentrated under nitrogen gas flow.
3.1.2 Cleanup	Extraction procedure is also clean-up

Section A4 (4.2) Analytical Methods for Detection and Identification (01)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater:

I. Method for the determination of Dichlofluanid in seawater

3.2	**Detection**	
3.2.1	Separation method	Gas Chromatography GC with a HP-5MS column (cross linked 5% Ph-Me siloxane) of 30 m x 2.5 mm ID, 0.25 µm df and a pre-column of 2.5 m of the same type.
3.2.2	Detector	Mass Spectrometric detection with Selection Ion Monitoring MS-SIM. m/z 123, 167 (both used for confirmation), 224 m/z (used for quantification.
3.2.3	Standard(s)	Internal standards 2,4-dichlorobenzoic acid methyl ester for qualitative check of retention time, hexachlorobenzene to compensate for volume effects during injection and atrazine-d5 to check for the SPE speedisk procedure.
3.2.3	Interfering substance(s)	none
3.3	**Linearity**	
3.3.1	Calibration range	Report 4: The calibration curve used was equivalent to 0 – 125.2 ng/l seawater. Report 2 and 3: The calibration curve used was equivalent to 0 – 125.2 ng/l seawater. Report 6 and 7: The calibration curve used was equivalent to 0 – 266 ng/l seawater.
3.3.2	Number of measurements	5 calibration points
3.3.3	Linearity	The equation for the calibration graph in report 4 was: **m/z 224 $y = 0.01339 + 0.00517x$; $r^2 = 0.9988$ (quantification ion)** The equations for the calibration graphs in report 2 and 3 were: m/z 123 $y = 0.02564 + 0.01802x$; $r^2 = 0.9993$ m/z 167 $y = 0.02082 + 0.01304x$; $r^2 = 0.9990$ **m/z 224 $y = 0.00514 + 0.00577x$; $r^2 = 0.9995$ (quantification ion)** The equations for the calibration graphs in report 6 and 7 were: m/z 123 $y = 0.02557 + 0.01792x$; $r^2 = 0.9995$ m/z 167 $y = 0.00928 + 0.00744x$; $r^2 = 0.9993$ **m/z 224 $y = 0.00544 + 0.00456x$; $r^2 = 0.9993$ (quantification ion)**

Section A4 (4.2) Analytical Methods for Detection and Identification (01)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater:

I. Method for the determination of Dichlofluanid in seawater

3.4	**Specifity: interfering substances**	Not relevant
3.4	**Recovery rates & Standard deviations at different levels**	The accuracy of the extraction and clean-up was determined with the internal standard atrazine-d5. The recovery of dichlofluanid was determined with blank seawater fortified with 10, 50 and 100 ng/l dichlofluanid respectively, resulting in an average recovery of 72, 94% and 85% respectively (see table A1 for details).
3.4.1	Relative standard deviation	1.6 - 9% (see table A1 for details)
3.5	**Limit of determination**	Limit of detection (LOD) = 3 ng/l, limit of quantification (LOQ) = 10 ng/l
3.6	**Precision**	
3.6.1	Repeatability	The repeatability of the method was determined by the analysis of five seawater samples spiked with dichlofluanid (10 and 100 ng/l) and resulted in a RSD of respectively 1.6 and 5.3% (see table A1 for details).
3.6.2	Independent laboratory validation	Not available

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1	**Materials and methods**	Dichlofluanid in seawater was determined by solid phase extraction and subsequent determination by GC-MS-SIM.
4.2	**Conclusion**	The validity criteria of this analytical method for the determination of dichlofluanid in seawater are fulfilled.
4.2.1	Reliability	1. The method was validated according to SANCO/825/00.
4.2.2	Deficiencies	No

Section A4 (4.2) Analytical Methods for Detection and Identification (01)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater:

I. Method for the determination of Dichlofluanid in seawater

Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	03/03/11
Materials and methods	The applicant's version is acceptable, although recoveries (3.4) for the confirmatory ions should have been reported (mean recoveries for the confirmatory ions were acceptable [>70%]).
Conclusion	The applicant's version is acceptable.
Reliability	1
Acceptability	Acceptable
Remarks	Recoveries (3.4) for the confirmatory ions should have been reported.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant´s summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Table A1: Recovery rates of dichlofluanid (added to blank seawater samples) and of the extraction and clean-up internal standard atrazine-d5

Study/report no	Concentration of dichlofluanid added to blank seawater sample	Recovery rates dichlofluanid	Recovery rates of atrazine-d5
4 (validation study)	10 ng/l 100 ng/l	average 72% (n=5, RSD 1.6%) average 87% (n=5, RSD 5.3%)	87.9 – 105.6% (n=5)
2	50 ng/l	94% (n= 1)	95-128% (n = 11)
3			85 – 115% (n = 5)
6	96 ng/l	86.9%	79 – 115% (n = 13)
7		92.1% 76.4% average 85% (n= 3, RSD is 9%)	86 – 115% (n = 7)

Section A4 (4.2)

Analytical Methods for Detection and Identification (02)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT

Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment :

I. Method for the determination of Dichlofluanid in marine sediment

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Official use only

1 REFERENCE

Section A4 (4.2) Analytical Methods for Detection and Identification (02)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT

Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment :

I. Method for the determination of Dichlofluanid in marine sediment

---

1.1 Reference	Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments of Greek marinas in the early spring of 2003. TNO report V5119/ **02**. Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments at suspected hotspots of Greek marinas in the early spring of 2003. TNO report V5119/ **03** Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments of Greek marinas in the summer of 2003. TNO report V5119/ **06**. Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments at suspected hotspots of Greek marinas in the summer of 2003. TNO report V5119/ **07**. Schouten, A, JC Ravensberg. 2004. Validation of analytical methods for the determination of dichlofluanid and its metabolite DMSA in seawater and marine sediment. TNO report V5119/ **04**
1.2 Data protection	Yes
1.2.1 Data owner	LANXESS Deutschland GmbH
1.2.2 Companies with letter of access	Not specified at this stage
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s. for the purpose of its entry into Annex I authorisation]

2 GUIDELINES AND QUALITY ASSURANCE

2.1 Guideline study	No
2.2 GLP	Yes
2.3 Deviations	No

3 MATERIALS AND METHODS

3.1 Preliminary treatment	
3.1.1 Enrichment	Sediments were sieved over 2 mm mesh. 100 ml sediment samples were acidified with 4 to 6 ml of a 1:1 acetic acid in tap water solution to adjust the pH to <6. Extraction of 20 g sediment with 60 ml acetone in a mechanical shaker. 5 ml of the supernatant was diluted with 45 ml diluted sulphuric acid (1:1 sulphuric acid in tap water solution).
3.1.2 Cleanup	The extract was concentrated on SPE speedisk cartridge (DVB, 50 mm) which first is conditioned with subsequently two times 10 ml of ethyl acetate, two times 10 ml of methanol and two times 10 ml of MilliQ water. Dichlofluanid was eluted with 10 ml ethyl acetate. The ethyl acetate is further concentrated under nitrogen gas flow.

Section A4 (4.2) Analytical Methods for Detection and Identification (02)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT

Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment :

I. Method for the determination of Dichlofluanid in marine sediment

3.2	**Detection**	
3.2.1	Separation method	Gas Chromatography GC with a HP-5MS column (cross linked 5% Ph-Me siloxane) of 30 m x 2.5 mm ID, 0.25 µm df and a pre-column of 2.5 m of the same type.
3.2.2	Detector	Mass Spectrometric detection with Selection Ion Monitoring MS-SIM. m/z 123, 167 (both used for confirmation), 224 m/z (used for quantification.
3.2.3	Standard(s)	Internal standards 2,4-dichlorobenzoic acid methyl ester for qualitative check of retention time, hexachlorobenzene to compensate for volume effects during injection and atrazine-d5 to check for the SPE speedisk procedure.
3.2.3	Interfering substance(s)	none
3.3	**Linearity**	
3.3.1	Calibration range	Report 4: The calibration curve used was equivalent to 0 – 250.5 ng/5 ml acetone extract. Report 2 and 3: The calibration curve used was equivalent to 0 – 125.2 ng/5 ml acetone extract. Report 6 and 7: The calibration curve used was equivalent to 0 – 266 ng/ 5 ml acetone extract. The 5 ml acetone extract is the aliquot taken for further analysis.
3.3.2	Number of measurements	5 calibration points
3.3.3	Linearity	Not applicable, dichlofluanid was not stable in fortified sediment but almost completely converted to DMSA (>90%).
3.4	**Specifity: interfering substances**	Not relevant
3.4	**Recovery rates & Standard deviations at different levels**	Not relevant, dichlofluanid was not stable in fortified sediment nor when added to blank sediment extracts but was almost completely converted to DMSA (>90%). The accuracy of the extraction and clean-up was determined with the internal standard atrazine-d5. See table A1 for details.
3.4.1	Relative standard deviation	Not relevant
3.5	**Limit of determination**	Limit of detection(LOD) for dichlofluanid = 3 ng/g dw, limit of quantification (LOQ) for dichlofluanid = 10 ng/g dw
3.6	**Precision**	

Section A4 (4.2)	**Analytical Methods for Detection and Identification (02)**
Annex Point IIA4.1/4.2 & IIIA-IV.1	ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment : I. Method for the determination of Dichlofluanid in marine sediment

3.6.1	Repeatability	Not relevant
3.6.2	Independent laboratory validation	Not available

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1	**Materials and methods**	The analytical procedure for Dichlofluanid in sediment is extraction and subsequent determination by GC-MS-SIM. However, dichlofluanid is not stable in marine sediment and is almost completely converted to DMSA (>90%).
4.2	**Conclusion**	The validity criteria of this analytical method for the determination of dichlofluanid in marine sediment are fulfilled. However, marine sediment is not a relevant matrix for this substance as it is almost completely converted to DMSA.
4.2.1	Reliability	1. The method was validated according to SANCO/825/00.
4.2.2	Deficiencies	No

Section A4 (4.2) Analytical Methods for Detection and Identification (02)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT

Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment :

I. Method for the determination of Dichlofluanid in marine sediment

Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	03/03/11
Materials and methods	Due to dichlofluanid converting to DMSA in sediment and DMSA being determined, the method of analysis must be amended to the method used for the determination of DMSA. In addition the validation data are based on DMSA (see below) not dichlofluanid and the linearity range must start from the lowest calibration standard used plus the LOD and LOQ must be changed from dichlofluanid to DMSA.
Conclusion	The method of analysis for dichlofluanid must be replaced with DMSA method of analysis.
Reliability	3
Acceptability	Not acceptable (DMSA method must replace dichlofluanid method)
Remarks	Method of analysis for dichlofluanid must be replaced with DMSA method of analysis.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant´s summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Table A1: Recovery rates of dichlofluanid measured as DMSA* in blank sediment extracts and of the extraction and clean-up internal standard atrazine-d5

Study/report no	Added concentration of dichlofluanid to blank sediment extract	Recovery* in % of m/z 200 (= DMSA)	Recovery rates (%) of atrazine-d5
4 (validation study)	10 ng/g 100 ng/g	average 101% (n=5, RSD 10.7%) average 109% (n=5, RSD 3.6%)	74.4-127.9% (n=5)
2	Equiv. to 50 ng/g sediment	104% (n= 1)	99 – 124 (n = 11)
3			107 – 124 (n = 5)
6	Equiv. to 96.2 ng/g sediment	102.5%	81 – 130 (n = 13)
7		93.3% 89.8% average 95% (n= 3, RSD is 7%)	81 – 113 (n = 7)

*Dichlofluanid was converted to DMSA, dichlofluanid recoveries were calculated as its DMSA equivalent assuming stochiometric conversion

Section A4 (4.2) Analytical Methods for Detection and Identification (03)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater :

II. Method for the determination of DMSA in seawater

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1 REFERENCE

Official use only

Section A4 (4.2) Analytical Methods for Detection and Identification (03)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater :

II. Method for the determination of DMSA in seawater

1.1 Reference	Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments of Greek marinas in the early spring of 2003. TNO report V5119/ **02**. Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments at suspected hotspots of Greek marinas in the early spring of 2003. TNO report V5119/ **03** Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments of Greek marinas in the summer of 2003. TNO report V5119/ **06**. Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments at suspected hotspots of Greek marinas in the summer of 2003. TNO report V5119/ **07**. Schouten, A, JC Ravensberg. 2004. Validation of analytical methods for the determination of dichlofluanid and its metabolite DMSA in seawater and marine sediment. TNO report V5119/ **04**
1.2 Data protection	Yes
1.2.1 Data owner	LANXESS Deutschland GmbH
1.2.2 Companies with letter of access	Not specified at this stage
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s for the purpose of its [entry into Annex I authorisation]
	2 GUIDELINES AND QUALITY ASSURANCE
2.1 Guideline study	No
2.2 GLP	Yes
2.3 Deviations	No
	3 MATERIALS AND METHODS
3.1 Preliminary treatment	
3.1.1 Enrichment	500 ml seawater samples were acidified with 0.5 ml of a 1:1 sulphuric acid in tap water solution to adjust the pH to 3. Extraction of 500 ml seawater on SPE speedisk cartridge (DVB, 50 mm) which first is conditioned with subsequently two times 10 ml of ethyl acetate, two times 10 ml of methanol and two times 10 ml of MilliQ water. DMSA was eluted with 10 ml ethyl acetate. The ethyl acetate is further concentrated under nitrogen gas flow.
3.1.2 Cleanup	Extraction procedure is also clean-up
3.2 Detection	

Section A4 (4.2) Analytical Methods for Detection and Identification (03)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater :

II. Method for the determination of DMSA in seawater

3.2.1	Separation method	Gas Chromatography GC with a HP-5MS column (cross linked 5% Ph-Me siloxane) of 30 m x 2.5 mm ID, 0.25 µm df and a pre-column of 2.5 m of the same type.
3.2.2	Detector	Mass Spectrometric detection with Selection Ion Monitoring MS-SIM. m/z 92, 108 (both used for confirmation), 200 m/z (used for quantification.
3.2.3	Standard(s)	Internal standards 2,4-dichlorobenzoic acid methyl ester for qualitative check of retention time, hexachlorobenzene to compensate for volume effects during injection and atrazine-d5 to check for the SPE speedisk procedure.
3.2.3	Interfering substance(s)	none
3.3	**Linearity**	
3.3.1	Calibration range	Report 4: The calibration curve used was equivalent to 0 – 129.7 ng/l seawater. Report 2 and 3: The calibration curve used was equivalent to 0 – 129.7 ng/l seawater. Report 6 and 7: The calibration curve used was equivalent to 0 – 248 ng/l seawater.
3.3.2	Number of measurements	5 calibration points
3.3.3	Linearity	The equation for the calibration graph in report 4 was: **m/z 200 $y = 0.00250 + 0.00379x$; $r^2 = 0.9994$ (quantification ion)** The equations for the calibration graphs in report 2 and 3 were: m/z 92 $y = 0.01251 + 0.00502x$; $r^2 = 0.9957$ m/z 108 $y = 0.00613 + 0.00082x$; $r^2 = 0.9931$ **m/z 200 $y = 0.01627 + 0.00582x$; $r^2 = 0.9964$ (quantification ion)** The equations for the calibration graphs in report 6 and 7 were: m/z 92 $y = 0.00071 + 0.00344x$; $r^2 = 0.9998$ m/z 108 $y = 0.00404 + 0.00071x$; $r^2 = 0.9992$ **m/z 200 $y = 0.00458 + 0.00237x$; $r^2 = 1.000$ (quantification ion)**

Section A4 (4.2) Analytical Methods for Detection and Identification (03)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater :

II. Method for the determination of DMSA in seawater

3.4	**Specifity: interfering substances**	Not relevant
3.4	**Recovery rates & Standard deviations at different levels**	The accuracy of the extraction and clean-up was determined with the internal standard atrazine-d5. The recovery of DMSA was determined with blank seawater fortified with 10, 52 and 103.8 ng/l DMSA respectively, resulting in average recoveries between 83%- 108% (see table A1 for details).
3.4.1	Relative standard deviation	4.3-11% (see table A1 for details).
3.5	**Limit of determination**	Limit of detection (LOD) = 3 ng/l, limit of quantification (LOQ)= 10 ng/l
3.6	**Precision**	
3.6.1	Repeatability	The repeatability of the method was determined by the analysis of five seawater samples spiked with DMSA (10 and 103.8 ng/l) and resulted in a RSD of respectively 6.4 and 4.3% (see table A1 for details).
3.6.2	Independent laboratory validation	Not available
	4 APPLICANT'S SUMMARY AND CONCLUSION	
4.1	**Materials and methods**	DMSA in seawater was determined by solid phase extraction and subsequent determination by GC-MS-SIM.
4.2	**Conclusion**	The validity criteria of this analytical method for the determination of DMSA in seawater are fulfilled.
4.2.1	Reliability	1. The method was validated according to SANCO/825/00.
4.2.2	Deficiencies	No

Section A4 (4.2) Analytical Methods for Detection and Identification (03)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN SEAWATER

Method for the determination of Dichlofluanid and its degradation product DMSA in seawater :

II. Method for the determination of DMSA in seawater

Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	03/03/11
Materials and methods	The applicant's version is acceptable, although recoveries (3.4) for the confirmatory ions should have been reported (mean recoveries for the confirmatory ions were acceptable [>70%]).
Conclusion	The applicant's version is acceptable.
Reliability	1
Acceptability	Acceptable
Remarks	Recoveries (3.4) for the confirmatory ions should have been reported.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant´s summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Table A1: Recovery rates of DMSA (added to blank seawater samples) and of the extraction and clean-up internal standard atrazine-d5

Study/report no	Concentration of DMSA added to blank seawater sample	Recovery rates DMSA	Recovery rates of atrazine-d5
4 (validation study)	10.4 ng/l 103.8 ng/l	average 83% (n=5, RSD 6.4%) average 92% (n=5, RSD 4.3%)	87.9 – 105.6% (n=5)
2	52 ng/l	108% (n= 1)	95-128% (n = 11)
3			85 – 115% (n = 5)
6	103.8	111.1%	79 – 115% (n = 13)
7		95.1% 91.2% average 99% (n= 3, RSD is 11%)	86 – 115% (n = 7)

Section A4 (4.2)

Analytical Methods for Detection and Identification (04)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT

Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment :

II. Method for the determination of DMSA in marine sediment

Official use only

1 REFERENCE

Section A4 (4.2) Analytical Methods for Detection and Identification (04)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT

Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment :

II. Method for the determination of DMSA in marine sediment

1.1 Reference	Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments of Greek marinas in the early spring of 2003. TNO report V5119/ **02**. Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments at suspected hotspots of Greek marinas in the early spring of 2003. TNO report V5119/ **03** Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments of Greek marinas in the summer of 2003. TNO report V5119/ **06**. Hamwijk, C, EM Foekema, A. Schouten. 2004. Determination of dichlofluanid and its metabolite DMSA in water and marine sediments at suspected hotspots of Greek marinas in the summer of 2003. TNO report V5119/ **07**. Schouten, A, JC Ravensberg. 2004. Validation of analytical methods for the determination of dichlofluanid and its metabolite DMSA in seawater and marine sediment. TNO report V5119/ **04**
1.2 Data protection	Yes
1.2.1 Data owner	LANXESS Deutschland GmbH
1.2.2 Companies with letter of access	Not specified at this stage
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s.. for the purpose of its entry into Annex I authorisation]

2 GUIDELINES AND QUALITY ASSURANCE

2.1 Guideline study	No, no guideline available
2.2 GLP	Yes
2.3 Deviations	No

3 MATERIALS AND METHODS

3.1 Preliminary treatment	
3.1.1 Enrichment	Sediments were sieved over 2 mm mesh. 100 ml sediment samples were acidified with 4 to 6 ml of a 1:1 acetic acid in tap water solution to adjust the pH to <6. Extraction of 20 g sediment with 60 ml acetone in a mechanical shaker. 5 ml of the supernatant was diluted with 45 ml diluted sulphuric acid (1:1 sulphuric acid in tap water solution).
3.1.2 Cleanup	The extract was concentrated on SPE speedisk cartridge (DVB, 50 mm) which first is conditioned with subsequently two times 10 ml of ethyl acetate, two times 10 ml of methanol and two times 10 ml of MilliQ water. Dichlofluanid was eluted with 10 ml ethyl acetate. The ethyl acetate is further concentrated under nitrogen gas flow

Section A4 (4.2) Analytical Methods for Detection and Identification (04)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT

Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment :

II. Method for the determination of DMSA in marine sediment

3.2	**Detection**	
3.2.1	Separation method	Gas Chromatography GC with a HP-5MS column (cross linked 5% Ph-Me siloxane) of 30 m x 2.5 mm ID, 0.25 µm df and a pre-column of 2.5 m of the same type.
3.2.2	Detector	Mass Spectrometric detection with Selection Ion Monitoring MS-SIM. m/z 92, 108 (both used for confirmation), 200 m/z (used for quantification.
3.2.3	Standard(s)	Internal standards 2,4-dichlorobenzoic acid methyl ester for qualitative check of retention time, hexachlorobenzene to compensate for volume effects during injection and atrazine-d5 to check for the SPE speedisk procedure.
3.2.3	Interfering substance(s)	none
3.3	**Linearity**	
3.3.1	Calibration range	Report 4: The calibration curve used was equivalent to 0 – 259.4 ng/5 ml acetone extract. Report 2 and 3: The calibration curve used was equivalent to 0 – 129.7 ng/5 ml acetone extract. Report 6 and 7: The calibration curve used was equivalent to 0 – 248 ng/5 ml acetone extract. The 5 ml acetone extract is the aliquot taken for further analysis.
3.3.2	Number of measurements	5 calibration points
3.3.3	Linearity	The equation for the calibration graph in report 4 was: **m/z 200 $y = -0.00448 + 0.00450x$; $r^2 = 0.9978$ (quantification ion)** The equations for the calibration graphs in report 2 and 3 were: m/z 92 $y = -0.06516 + 0.00800x$; $r^2 = 0.9930$ m/z 108 $y = -0.00798 + 0.00142x$; $r^2 = 0.9927$ **m/z 200 $y = -0.06343 + 0.00927x$; $r^2 = 0.9944$ (quantification ion)** The equations for the calibration graphs in report 6 and 7 were: m/z 92 $y = 0.08070 + 0.00717x$; $r^2 = 0.9970$ m/z 108 $y = 0.01644 + 0.00135x$; $r^2 = 0.9982$ **m/z 200 $y = 0.02962 + 0.00727x$; $r^2 = 0.9985$ (quantification ion)**

Section A4 (4.2) Analytical Methods for Detection and Identification (04)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT

Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment :

II. Method for the determination of DMSA in marine sediment

3.4	**Specifity: interfering substances**	Not relevant
3.4	**Recovery rates & Standard deviations at different levels**	The accuracy of the extraction and clean-up was determined with the internal standard atrazine-d5. The recovery was based on DMSA added to blank sediment extracts at concentrations of 10.4, 52 and 103.8 ng/g respectively, resulting in recoveries ranging between 80% and 108% (see table A1 for details).
3.4.1	Relative standard deviation	6.7 - 9% (see table A1 for details).
3.5	**Limit of determination**	Limit of detection (LOD) = 3 ng/g dw, limit of quantification (LOQ) = 10 ng/g dw
3.6	**Precision**	
3.6.1	Repeatability	The repeatability of the method was determined by the analysis of five marine sediment samples spiked with DMSA (10 and 103.8 ng/g) and resulted in a RSD of respectively 6.7 and 7.6% (see table A1 for details).
3.6.2	Independent laboratory validation	Not available

4 APPLICANT'S SUMMARY AND CONCLUSION

4.1	**Materials and methods**	DMSA in marine sediment was determined by liquid extraction, solid phase clean-up and subsequent determination by GC-MS-SIM.
4.2	**Conclusion**	The validity criteria of this analytical method for the determination of DMSA in marine sediment are fulfilled.
4.2.1	Reliability	1. The method was validated according to SANCO/825/00.
4.2.2	Deficiencies	No

Section A4 (4.2) Analytical Methods for Detection and Identification (04)

Annex Point IIA4.1/4.2 & IIIA-IV.1

ANALYTICAL METHOD FOR THE DETERMINATION OF ACTIVE SUBSTANCE RESIDUES IN MARINE SEDIMENT

Method for the determination of Dichlofluanid and its degradation product DMSA in marine sediment :

II. Method for the determination of DMSA in marine sediment

Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	03/03/11
Materials and methods	The applicant's version is acceptable, although recoveries (3.4) for the confirmatory ions should have been reported (mean recoveries for the confirmatory ions were acceptable for the high level spike [0.1 mg/kg] however for the low level spike [0.005 mg/kg] were 68 and 46% respectively for the confirmatory ions 92 and 108). In addition the linearity range must start from the lowest calibration standard used.
Conclusion	The applicant's version is acceptable.
Reliability	1
Acceptability	Acceptable
Remarks	Recoveries (3.4) for the confirmatory ions should have been reported.
	COMMENTS FROM ...
Date	*Give date of comments submitted*
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant´s summary and conclusion.* *Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Reliability	*Discuss if deviating from view of rapporteur member state*
Acceptability	*Discuss if deviating from view of rapporteur member state*
Remarks	

Table A1: Recovery rates of DMSA in blank sediment extracts and of the extraction and clean-up internal standard atrazine-d5

Study/report no	Added concentration of DMSA to blank sediment extract	Recovery of DMSA	Recovery rates of atrazine-d5
4 (validation study)	10 ng/g 103.8 ng/g	average 101% (n=5, RSD 6.7%) average 80% (n=5, RSD 7.6%)	74.4-127.9% (n=5)
2	52 ng/g	99% (n= 1)	99 – 124 (n = 11)
3			107 – 124 (n = 5)
6	103.8 ng/g	117.7%	81 – 130 (n = 13)
7		99.3% 107.0% average 108% (n= 3, RSD is 9%)	81 – 113 (n = 7)

Section 4.3 **Annex Point IIA4.2(e)**	**Analytical Methods for Seawater and Sediment** **- N,N-dimethylsulfamide -**	
	JUSTIFICATION FOR NON-SUBMISSION OF DATA	Official use only
Other existing data [...] **Limited exposure [...]**	**Technically not feasible [ ]** **Scientifically unjustified [x]** **Other justification [ ]**	
Detailed justification:	Seawater and sediment According to the TGD, Data Requirements for Active Substances and Biocidal Products, ECB, February 2008 p. 31ff information on analytical methods is required concerning degradation products which are of toxicological or ecotoxicological concern (i.e. which are relevant for risk assessment). Attached Table 1 shows test results of N,N-dimethylsulfamide for aquatic species. According to the results there is no need to classify the substance for acute or chronic environmental hazards (67/548/EEC and CLP). Thus analytical methods for the marine compartment, comprising seawater and the sediment, are not submitted. Sediment Regarding sediment further reference can be made to the soil adsorption/desorption behaviour of the substance (Reference: Stupp, H. P. (2007 b). Adsorption characteristics of [N-methyl-14C]N,N-dimethylsulfamide was investigated in five different soils. N,N-dimethylsulfamide showed no adsorption to soil in the batch equilibrium experiment. Koc can be therefore set to zero. No other behaviour of the substance is expected in sediment. Thus, an analytical method for determination of N,N-dimethylsulfamide in sediment is deemed not necessary.	
Undertaking of intended data submission [ ]	–	

Section 4.3 Annex Point IIA4.2(e)	Analytical Methods for Seawater and Sediment - N,N-dimethylsulfamide -
	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	03/05/11
Evaluation of applicant's justification	The applicant's case is acceptable.
Conclusion	Applicant's case is acceptable.
Remarks	Applicant's case is acceptable.
	COMMENTS FROM OTHER MEMBER STATE *(specify)*
Date	*Give date of comments submitted*
Evaluation of applicant's justification	*Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Remarks	

Table 1: Toxicity of N,N-dimethylsulfamide to aquatic organisms.

Guideline/ Test method *	Species	Endpoint/ Type of test	Exposure Design	Exposure Dura-tion	Results [mg compound/L] NOEC	Results [mg compound/L] LOEC	Results [mg compound/L] LC / EC_{50}	Remark	Reference
Acute toxicity									
OECD 203	*Oncorhynchus mykiss*	mortality	static	96 h	> 100	> 100	>100	nominal conc.	Dorgerloh, 2007
OECD 202	*Daphnia magna*	immobility	static	48 h	> 100	> 100	> 100	nominal conc.	Bruns, 2007a
OECD 201	*Pseudokirch-nerella subcapitata*	growth rate	static	72 h	> 100	>100	>100	nominal conc.	Grade, 2007
Chronic toxicity									
OECD 215	*Oncorhynchus mykiss*	reproduction	static	28 days	> 100	> 100	n.a.	nominal conc.	Bomke, 2007
OECD 211	*Daphnia magna*	reproduction	static	21 days	> 100	> 100	n.a.	nominal conc.	Bruns, 2007b

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of pure active substance 4.2 **Analytical methods on:** (a) soil; **(b) air;** (c) water; (d) animal and human body fluids and tissues	
	1 REFERENCS (REF. A4.6)	**Official use only**
1.1 Reference	K. Riegner, 1992, Method for the validation of Dichlofluanid in air, Bayer AG, Institute for Product information and residue analysis, Leverkusen, Germany, Report No. RA-620/92, method No. 00293 (unpublished), 1992-12-16	
1.2 Data protection	Yes	
1.2.1 Data owner	Bayer Crop Science AG	
1.2.2 Companies with letter of access	Bayer Chemicals AG	
1.2.3 Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s. for the purpose of its entry into Annex I/IA	
	2 GUIDELINES AND QUALITY ASSURANCE	
2.1 Guideline study	No No guideline available	
2.2 GLP	No	
2.3 Deviations	No	
	3 MATERIALS AND METHODS	
3.1 Preliminary		

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of pure active substance 4.2 **Analytical methods on:** (a) soil; **(b) air;** (c) water; (d) animal and human body fluids and tissues	
treatment		
3.1.1 Enrichment	The adsorption tube contains two adsorption layers, which are separated from each other by cotton wool, with the larger layer facing the inlet of the tube during air sampling. The second, smaller adsorption layer is used for detection of a possible breakthrough of active ingredient during sampling. For sampling air is sucked through Tenax or XAD-2 adsorption tubes with a rate of 2 l/min during a period of 6 hours. Both adsorption layers are extracted separately for extraction of the active ingredient from the adsorption material, with the cotton wool separating both layers and the upper cotton wool facing the inlet of the tube being analysed together with the first, larger layer. The individual layers are removed from the glass tube and the adsorbed active ingredient is extracted from the adsorption material with n-butylacetate in an ultrasonic bath for 10 minutes. The determination of the active ingredient is performed after gas chromatographic separation by means of nitrogen and phosphorous selective detection according to the indicated conditions. Quantitative evaluation is made by means of an integrator via determination and comparison of peak areas of standard solutions with the peak areas of the analytical solutions (external standard method). Each solution is analysed twice and the respective mean value is used for the calculation.	
3.1.2 Cleanup	-	
3.2 Detection		
3.2.1 Separation method	Gas chromatographic separation is performed using a Hewlett Packard, Ultra 2 column (length: 25 m, inner diameter: 0.20 mm, film thickness: 0.11 µm); Injector: cold injection system, temperature program; Splitless time: 0.00 min to 2.00 min; Injection volume: 1 µl; Carrier gas: helium, head pressure: 1.8 bar; Total flow rate: 45 ml/min (RT); Oven temperature: T1 = 100 °C, t1 = 0.5 min, rate-1 = 25 °C/min; T2 = 250 °C, t2 = 2.0 min, rate-2 = 25 °C/min; T3 = 275 °C, t3 = 0.1 min	
3.2.2 Detector	Nitrogen and phosphorous selective detector (300 °C)	
3.2.3 Standard(s)	External standard (dichlofluanid)	
3.2.3 Interfering substance(s)	Substances of the adsorption material	
3.3 Linearity		
3.3.1 Calibration range	The detector linearity was checked at an injection concentration ranging from 0.226 mg/l to 0.904 mg/l (see table A4_2-1).	
3.3.2 Number of measurements	Single measurement of four concentrations (see table A4_2-1).	
3.3.3 Linearity	Correlation coefficient: 0.985361	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of pure active substance 4.2 **Analytical methods on:** (a) soil; **(b) air;** (c) water; (d) animal and human body fluids and tissues	
3.4 Specifity: interfering substances	The adsorption systems did not show any chromatographic blank values. No significant interferences were detected at the retention time of dichlofluanid in any of the control samples (Tenax-blank value and XAD-2-blank value).	
3.4 Recovery rates & Standard deviations at different levels	The recovery rates were checked by spiking adsorption tubes with active ingredient (dissolved in n-butylacetate). The solvent was removed by sucking through air (2 l/min) for approx. 10 minutes. Subsequently the adsorption tubes were exposed to defined climatic conditions (e.g. in a refrigerator). After a short equilibration phase (approx. 20 min) air, which was climate-controlled accordingly, was sucked through the adsorption tubes over a period of 6 hours at a rate of 2 l/min. The mean recovery rates were in the range of 87% to 98%. Range of data, fortification levels and climatic conditions are given in table A4_2-2a and table A4_2-2b.	
3.4.1 Relative standard deviation	Relative standard deviations are 1.7% to 11.1% depending on the type of adsorption material, the amount of active ingredient and the climatic conditions (see table A4_2-2a and table A4_2-2b).	
3.5 Limit of determination	The lower limit of determination was 0.003 mg a.i./m^3 air.	
3.6 Precision		
3.6.1 Repeatability	See recovery rates (point 3.4)	
3.6.2 Independent laboratory validation	Not data	

Section A4 (4.2) **Annex Point IIA, IV.4.2**	**Analytical Methods for Detection and Identification** Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of pure active substance 4.2 **Analytical methods on:** (a) soil; **(b) air;** (c) water; (d) animal and human body fluids and tissues	
	4 APPLICANT'S SUMMARY AND CONCLUSION	
4.1 Materials and methods	A method for the gas chromatographic determination of dichlofluanid in air is performed. For sampling air is sucked through Tenax or XAD-2 adsorption tubes with a rate of 2 l/min during a period of 6 hours. The adsorbed active ingredient is extracted with n-butylacetate and determined after gas chromatographic separation by means of a nitrogen and phosphorous selective detector.	
4.2 Conclusion	This method allows the determination of dichlofluanid in air in a concentration range of 0.003 mg a.i./m^3 (= lower limit of determination) to 0.835 mg a.i./m^3, whereby two different, equivalent adsorption systems are available. The systems were validated at different climatic conditions. It was shown that the active ingredient neither at low nor at high concentrations, temperatures and air humidities was desorbable with air.	
4.2.1 Reliability	2	
4.2.2 Deficiencies	Yes, No purity mentioned of the test substance; Determination of linearity was performed by single measurement of 4 concentrations instead of duplicate measurement or, alternatively, measurement of 5 concentrations, each as single measurement; Only 3 or 4 determinations of the recovery rate were performed for each fortification level instead of at least 5 (for repeatability);	
	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	
Date	06/01/2005	
Materials and methods	Study was not carried out to GLP. The Company state that the study did not follow any official guidelines in 2.1, however the study was carried out to a method described in SANCO/825/00 rev.6 (20/06/2000), guidance document on residue analytical methods. The study sets out the criteria for a value of limit of determination of 0.003 mg ai/m^3	
Conclusion	GLP was not compulsory at the time the study was performed. The study demonstrates full methods of analysis. The study meets the criteria it was set to achieve, and it also demonstrates robustness when slight changes to the operating parameters (temperature	
Reliability	2	
Acceptability	Acceptable	
Remarks	UK CA agrees with the applicant's summary and conclusions.	

Section A4 (4.2) Annex Point IIA, IV.4.2	Analytical Methods for Detection and Identification Specify where appropriate, e.g. isomer of a.s., metabolite of a.s., impurity of a.s., matrix 4.1 for the determination of pure active substance 4.2 **Analytical methods on:** (a) soil; **(b) air;** (c) water; (d) animal and human body fluids and tissues	
	COMMENTS FROM...	
Date	*Give date of comments submitted*	
Results and discussion	*Discuss additional relevant discrepancies referring to the (sub) heading numbers and to applicant's summary and conclusion.* *Discuss if deviating from view of rapporteur member state*	
Conclusion	*Discuss if deviating from view of rapporteur member state*	
Reliability	*Discuss if deviating from view of rapporteur member state*	
Acceptability	*Discuss if deviating from view of rapporteur member state*	
Remarks		

Table A4 2-1: Linearity of detector response of dichlofluanid

External standard concentration [mg/l]	Measured areas
0.2259	8590
0.4518	19337
0.5873	23076
0.9036	42451

Table A4 2-2a: Recovery rates for adsorption on Tenax

	Climatic conditions		Recovery rate [%]	Relative standard deviation [%]
	°C	RH [%]		
0.003 (*)	20	30	94.8 (88.6 – 103)	8.1
0.003	35	80	92.5 (90.1 – 95.6)	2.8
0.04	20	30	87.4 (81.0 – 97.4)	8.4
0.04	35	80	93.4 (80.0 – 102.3)	11.1
0.835 (**)	35	80	98.2 (96.5 – 100.1)	1.7

Results were obtained from 4 tests ((*) = 3 tests) each for determination of the recovery rate
RH = relative air humidity
(**) The second adsorption layer contained less than 5% active ingredient (referred to the lowest quantity of active ingredient added)

Table A4 2-2b: Recovery rates for adsorption on XAD-2

	Climatic conditions		Recovery rate [%]	Relative standard deviation [%]
	°C	RH [%]		
0.003	20	30	94.0 (85.0 – 98.3)	5.1
0.003	35	80	93.3 (86.7 – 97.9)	5.1
0.04	20	30	94.5 (83.8 – 101.7)	8.8

0.04 (*)	35	80	88.5 (85.1 – 93.2)	4.8
0.835 (**)	35	80	93.9 (90.6 – 95.9)	2.4

Results were obtained from 4 tests ((*) = 3 tests) each for determination of the recovery rate
RH = relative air humidity
(**) The second adsorption layer contained less than 5% active ingredient (referred to the lowest quantity of active ingredient added)

Section 4.3 **Annex Point IIA4.2(d)**	**Analytical Methods for Animal and Human body fluids and tissues**	
	JUSTIFICATION FOR NON-SUBMISSION OF DATA	Official use only
Other existing data [...] **Limited exposure [...]**	**Technically not feasible [ ]** **Scientifically unjustified [ ]** **Other justification [X]**	
Detailed justification:	According to the TGD, Data Requirements for Active Substances and Biocidal Products, ECB, February 2008 p. 33 analytical methods for animal and human body fluids and tissues must be submitted where the active substance is classified as toxic or highly toxic. Dichlofluanid is classified Xn - harmful. Therefore no respective analytical method is required for this active.	
Undertaking of intended data submission [ ]	–	
	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	
Date	03/05/11	
Evaluation of applicant's justification	The applicant's case is acceptable.	
Conclusion	Applicant's case is acceptable.	
Remarks	Applicant's case is acceptable.	
	COMMENTS FROM OTHER MEMBER STATE *(specify)*	
Date	*Give date of comments submitted*	
Evaluation of applicant's justification	*Discuss if deviating from view of rapporteur member state*	
Conclusion	*Discuss if deviating from view of rapporteur member state*	
Remarks		

Section A4 (4.3) **Annex Point IIIA IV.I**	**Analytical methods for Determination of Residues in /on Fish and Shellfish** Method for the determination of dichlofluanid in fish and shellfish	
	JUSTIFICATION FOR NON-SUBMISSION OF DATA	**Official use only**
Other existing data [ ] **Limited exposure [X]**	**Technically not feasible [ ] Scientifically unjustified [X]** **Other justification [ ].**	
Detailed justification:	*Reference: Schwab (2011). Dichlofluanid – Analytical methods for residues in fish and shellfish – marine waters. Currenta Analytics, Product Safety, Chempark 51368 Leverkusen, Germany. Report: 2011-03-22. Unpublished.* According to the expert statement of Schwab a method for determination of dichlofluanid residues in fish and shellfish is not justified: The bioaccumulation of ^{14}C labelled Dichlofluanid in fish yielded BCF values between 61 (edible parts) and 72 (non-edible parts), certifying a very low potential for bioaccumulation. As the substance is known to degrade in aqueous solutions, a semi-static study was conducted to ensure constant exposure concentrations throughout the test duration. Nevertheless, hydrolysis could not completely be avoided yielding a certain fraction of N,N-dimethyl-N'-phenyl-sulfamide (DMSA) in the exposure medium. As the selected detection method was not able to discriminate between the concentration of the parent and DMSA, the determined BCF values attest a very low potential to accumulate. Several studies are available investigating the abiotic degradation of dichlofluanid under laboratory as well as environmental conditions. Hydrolysis (method: OECD 111) at pH7 yielded a degradation half life of 28h (20°C) and of only 1.45 h (pH 8.2, 20°C) in artificial seawater. The latter one is most relevant, since dichlofluanid is supported for marine/estuarine antifouling paints under BPD. Further studies using natural waters and water/sediment systems also showed fast hydrolysis with half-lifes in the order of 2 h up to 6 h. All studies provide evidence that dichlofluanid rapidly degrades in aquatic media. This fact is supported by environmental monitoring data. No dichlofluanid was detected in water samples taken in Greek marinas up to the Limit of Detection of 3ng/L. Based on the facts presented above – firstly the non-achievement of a relevant exposure level in aqueous media due to rapid hydrolysis and secondly the absence of a potential to bioaccumulate – significant concentrations in fish and shellfish can be excluded. Thus, the need to develop a validated analytical method to determine dichlofluanid residues in fish and shellfish is scientifically not justified.	
Undertaking of intended data submission [ ]	–	
	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	

Section A4 (4.3) Annex Point IIIA IV.I	Analytical methods for Determination of Residues in /on Fish and Shellfish Method for the determination of dichlofluanid in fish and shellfish
Date	03/05/11
Evaluation of applicant's justification	The applicant's case is acceptable.
Conclusion	Applicant's case is acceptable.
Remarks	Applicant's case is acceptable.
	COMMENTS FROM OTHER MEMBER STATE *(specify)*
Date	*Give date of comments submitted*
Evaluation of applicant's justification	*Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Remarks	

Section A6 (6.15.1) Annex Point IIIA VI.4	Food and Feeding stuffs	
	JUSTIFICATION FOR NON-SUBMISSION OF DATA	Official use only
Other existing data [ ] **Limited exposure [ ]**	**Technically not feasible [ ] Scientifically unjustified [x]** **Other justification [x].**	
Detailed justification:	Please refer also to Schwab (2011). The main PT 21 use of **dichlofluanid** is in antifouling paints for application on underwater parts of ship hulls. For such uses information on residues in food and feeding stuffs is not foreseen according to the TNsG. However, use of the active in biocidal products for marine or estuarine aqua-culture, where production of food for human consumption takes place, is also possible. Due to the inherent characteristics of the active substance food residues are not expected from its use in aqua-culture products. After possible release of **dichlofluanid** from such products into surrounding water the substance will hydrolyse very fast. Its half-life (t1/2) in artificial seawater was determined to 1.45 hours (Feldhues 2006). Further studies using natural waters and water/sediment systems also showed fast hydrolysis with half-lifes (t1/2) in the order of 2 up to 6 h (Hardy (2005), Scholz (1997). Further more, the bioaccumulation of ^{14}C labelled **dichlofluanid** in fish yielded BCF values between 61 (edible fish fraction) and 72 (non-edible fish fraction) (Grau (1991)), certifying a very low potential for bioaccumulation. As the substance is known to degrade in aqueous solutions, a semi-static study was conducted to ensure constant exposure concentrations throughout the test duration. Nevertheless, hydrolysis could not completely be avoided yielding a certain fraction of **DMSA** in	

Section A6 (6.15.1) Annex Point IIIA VI.4	Food and Feeding stuffs	
	the exposure medium. As the selected detection method was not able to discriminate between the concentration of the parent substance and **DMSA**, the determined BCF values comprised the accumulation of both substances. In summary, the BCF values as reported by Grau (1991) represent a worst case value, overestimating the accumulation of **dichlofluanid** itself, but considering the simultaneous accumulation of the degradation product **DMSA**. The determined BCF values attest a very low potential to accumulate. Further degradation of **dichlofluanid** in the aquatic environment is mainly via **DMSA** to **N,N-dimethylsulfamide** (**N,N-DMS**)*. Log P_{OW} values for **N,N-DMS** ranged from -0.8 (pH5 , 20°C) to -0.9 (pH 9, 20°C) (Eyrich (2007b). Thus, also **N,N-DMS** does not seem to have potential for accumulation in fish for human consumption. To summarize, due to the fast hydrolysis of **dichlofluanid**, the low accumulation potential of the parent as well as its metabolites no residues in fish or shellfish are expected from dichlofluanid uses in aqua-culture. *: Information on **N,N-DMS** was provided for the authorisation of wood preservative JJT 3581 Primer (folder Doc I; Doc 03_Addendum_RA_N,N-dimethylsulfamide_May 2009.doc) and also for Dichlofluanid/PT 7 Annex I listing (Folder: Addendum_dimethylsulfamide).	
Undertaking of intended data submission [ ]	-	
	Evaluation by Competent Authorities	
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted	
	EVALUATION BY RAPPORTEUR MEMBER STATE	
Date	03/05/11	
Evaluation of applicant's justification	The applicant's case is acceptable. The applicant's case is acceptable. Although dichlofluanid has a log Pow > 3 and therefore bioaccumulation potential is indicated, its half-life in water is less than 12 hours and this mitigating property suggests that no accumulation is likely, backed up by the evidence discussed in the case outlined by the applicant. DMSA has a log Pow < 3 therefore no indication of accumulation potential - monitoring would probably not be useful.	
Conclusion	Applicant's case is acceptable.	
Remarks	Applicant's case is acceptable.	
	COMMENTS FROM OTHER MEMBER STATE *(specify)*	
Date	*Give date of comments submitted*	

Section A6 (6.15.1) **Annex Point IIIA VI.4**	**Food and Feeding stuffs**
Evaluation of applicant's justification	*Discuss if deviating from view of rapporteur member state*
Conclusion	*Discuss if deviating from view of rapporteur member state*
Remarks	