SUMMARY

The test method P-14.087.00 for the determination of the residues of Fenpyroximate (HOE 094552) and M-1 (HOE 112573) in water was to be validated.

Samples of water were spiked with Fenpyroximate (HOE 094552) and M-1 (HOE 112573) at the level of 0.05 µg/l, 0.5 µg/l and 5 µg/l, respectively and analysed for residues of Fenpyroximate (HOE 094552) and M-1 (HOE 112573) by GLC, using a thermionic alkali FID (TID).

The routine limit of determination (lower limit of the practical working range) was 0.05 µg/l for Fenpyroximate (HOE 094552) and M-1 (HOE 112573), respectively.

OBJECTIVES

The purpose of this study were to validate the test method P-14.087.00 for the determination of the residues of Fenpyroximate (HOE 094552) and M-1 (HOE 112573) in water.

For this reason a series of recovery experiments was to be performed by spiking samples of water with Fenpyroximate (HOE 094552) and M-1 (HOE 112573).

TEST SUBSTANCES

Name:	**Fenpyroximate (Hoe 094552)**
Chemical name:	Tert-butyl(E)-4-[(1,3-dimethyl-5-phenoxypyrazol-4-yl)-methyleneaminooxy-methyl]benzoate
Empirical formula:	$C_{24}H_{27}N_3O_4$
Molecular mass:	421.5
Appearance:	Colourless crystals

Name:	**M-1 (Hoe 112573)**
Chemical name:	Tert-butyl(Z)-4-[(1,3-dimethyl-5-phenoxypyrazol-4-yl)-methyleneaminooxy-methyl]benzoate
Empirical formula:	$C_{24}H_{27}N_3O_4$
Molecular mass:	421.5
Appearance:	Colourless crystals

REFERENCE SUBSTANCES

(Data as provided by the supplier)

The reference substances were supplied by HOECHST AG, D-65926 Frankfurt/Main and used for fortification and quantification in this study.

Name:	**Fenpyroximate (Hoe 094552)**
Substance code:	NNI-850
Lot No.:	0AA0004P
Certificate of:	27-Jul-94
Purity:	99.8 %
Storage at test facility:	≤-18°C
Expiry:	25-Aug-96

Name:	**M-1 (Hoe 112573)**
Substance code:	NNI-850Z
Lot No.:	2AA0108Q
Certificate of:	27-May-93
Purity:	98.2 %
Storage at test facility:	≤-18°C
Expiry:	13-Mar-95

TEST METHOD

Test method: P-14.087.00

Title: Gaschromatographische Bestimmung von Fenpyroximate and M-1 in Wasser

Author: R.D. Weeren

Literature: DR. SPECHT & PARTNER, D-20354 Hamburg

Outline of method:

The sample of water is extracted three times with each 50 ml of dichloromethan. The combined organic phases are dried by filtration through a layer of sodium sulfate. The evaporation residue is dissolved in ethyl acetate analysed by gas chromatography using a capillary column and a thermionic alkali FID (TID).

Evaluation:

Concentrations in sample extracts were determined by comparing the detector response (peak height) of the sample with the pertinent detector response obtained from the neighbouring external standard.

Limit of determination: 0.05 µg/l*

* Lower limit of the practical working range: Based on fortification levels in untreated samples worked up concurrently with treated samples. The limit of determination is defined as the lowest fortification level yielding acceptable recoveries (70 % to 120 %) at analysis.

CHROMATOGRAPHIC CONDITIONS

Gas chromatograph:	Hewlett-Packard 5890 with a thermionic alkali FID (TID)
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 ml/min Make-up: helium, 30 ml/min Detector: synth. air, 120 ml/min hydrogen, 3 ml/min
Temperatures:	Oven: initial 150°C, hold for 2 min, with a rate of 7°C/min to 250°C, hold for 8 min Injector: 250°C Detector: 270°C
Injection volume:	4 µl splitless (autosampler)
Recorder:	LINSEIS L 5322 Chart speed 1 cm/min
External standards:	M-1, 0.498 µg/ml Fenpyroximate, 0.502 µg/ml (in ethyl acetate)
Retention times:	M-1, about 13.8 min Fenpyroximate, about 14.4 min

STOCK, FORTIFICATION AND STANDARD SOLUTIONS

Stock solutions:

Stock solution 1: 405 µg/ml Fenpyroximate

40.57 mg Fenpyroximate (99.8 %) were dissolved in acetone and filled up to 100 ml in a volumetric flask.

Stock solution 2: 415 µg/ml M-1

42.26 mg M-1 (98.2 %) were dissolved in acetone and filled up to 100 ml in a volumetric flask.

Fortification solutions:

Fortification solution A: 5.02 µg/ml Fenpyroximate
+ 4.98 µg/ml M-1

0.31 ml of stock solution 1 and 0.3 ml of stock solution 2 were diluted with acetone to 25 ml.

Fortification solution B: 0.502 µg/ml Fenpyroximate
+ 0.498 µg/ml M-1

The fortification solution A was diluted 1:10 with acetone.

Fortification solution C: 0.0502 µg/ml Fenpyroximate
+ 0.0498 µg/ml M-1

The fortification solution A was diluted 1:100 with acetone.

Standard solution:

External standard: 0.502 µg/ml Fenpyroximate
+ 0.498 µg/ml M-1

The fortification solution A was diluted 1:10 with ethyl acetate.

Dilutions were obtained from the stock solutions using an automated HAMILTON^{R} diluter.

FORTIFICATIONS

Samples of water were fortified prior to extraction with 1 ml of fortification solution A, B and C, respectively to obtain a content of Fenpyroximate and M-1 at the level of 0.05, 0.5 and 5 µg/l, respectively.

The fortified samples, along with the corresponding untreated samples, were analysed subsequently according to test method P-14.087.00.

Fortification levels and recovery results are reported on pages 16 and 17.

Representative chromatograms from the analyses are presented in Appendix IV on pages 27 to 32.

Prüfungsvorschrift

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Gaschromatographische Bestimmung von Fenpyroximat umd M-1 in Wasser

1. Geräte

Meßzylinder 1 l

Scheidetrichter 1 l

Rundkolben 250 ml, mit Schliff

Vakuum-Rotationsverdampfer

Spitzkolben 25 ml, mit Schliff

Glastrichter ϕ 10 cm

Gaschromatograph mit Stickstoff-spezifischem Detektor

Hinweis: Sämtliche Geräte sind vor dem Gebrauch mit Aceton zu spülen!

2. Reagenzien

Dichlormethan für Rückstandsanalytik

Ethylacetat für Rückstandsanalytik

Vergleichs-Standardlösung: Fenpyroximat und M-1 z.B. je 0,5 µg/ml in Ethylacetat

Natriumsulfat p.a., wasserfrei (mind. 2 h auf 550°C erhitzt)

Watte, mit Aceton erschöpfend extrahiert

Stickstoff

3. Durchführung der Analyse

3.1 Extraktion

In einem 1 l-Scheidetrichter 1000 ml Wasser mit 50 ml Dichlormethan 5 min ausschütteln. Die organische Phase (unten) abtrennen. Die wäßrige Phase noch zweimal mit je 50 ml Dichlormethan extrahieren.

Die organischen Phasen über einen mit Natriumsulfat beschichteten Trichter in einen 250 ml-Rundkolben filtrieren. Das Natriumsulfat portionsweise mit 20 - 30 ml Dichlormethan und anschließend mit 10 ml Essigsäureethylester nachwaschen. Am Rotationsverdampfer bei 40°C Badtemperatur auf ca. 5 ml einengen.

Den eingeengten Extrakt in einen 25 ml-Spitzkolben überführen, mit insgesamt ca. 10 ml Essigsäureethylester nachwaschen und am Rotationsverdampfer auf etwa 1 ml einengen. Das restliche Lösungsmittel mit Stickstoff abblasen. Den Rückstand in 1,0 ml Ethylacetat aufnehmen.

3.2 Gaschromatographische Bestimmung

Die Lösung aus 3.1 wird gaschromatographisch unter folgenden Bedingungen untersucht:

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Gerät:	z.B. HEWLETT-PACKARD 5890 mit N-FID
Trennsäule:	z.B. 15 m DB-1 Innendurchmesser 0,53 mm Filmdicke 0,15 µm
Gase:	Trägergas: Helium 5 ml/min Make-up: Helium 30 ml/min Wasserstoff: 3 ml/min Luft: 120 ml/min
Betriebstemperaturen:	Ofen 2 min 150°C, mit 7°C/min auf 250°C, 8 min
	Injektor 250°C
	Detektor 270°C
Einspritzvolumen:	4 µl splitless
Vergleichs-Standardlösung:	M-1 0,498 µg/ml Fenpyroximat 0,502 µg/ml (in Ethylacetat)
Bestimmungsgrenze:	M-1 0,05 µg/l Fenpyroximat 0,05 µg/l

4. Auswertung

Die Proben werden gegen einen externen Standard gespritzt und über die Peakhöhen (oder Peakflächen) ausgewertet.

5. Wiederfindungsrate

Die Wiederfindungsrate betrug bei Zusätzen von 0,05 µg/l, 0,5 µg/l und 5 µg/l im Mittel:

Fenpyroximat 97 %,
M-1 94 %.

Quantification

Fenpyroximate / M-1

The recoveries of Fenpyroximate and M-1, respectively, expressed in %, were calculated from the following equation:

$$\text{Recovery } (\%) = \frac{H_{Sa} \cdot C_{St} \cdot V_{End} \cdot 100\ \%}{H_{St} \cdot E \cdot F}$$

H_{Sa}:	Peak height of sample solution, in cm
C_{St}:	Concentration of compound in standard solution, in µg/ml
V_{End}:	Final volume of the sample solution, in ml (1 or 10 ml)
H_{St}:	Peak height of standard solution, in cm
E:	Sample volume, in l
F:	Fortification, in µg/l