Institute of Freshwater Ecology

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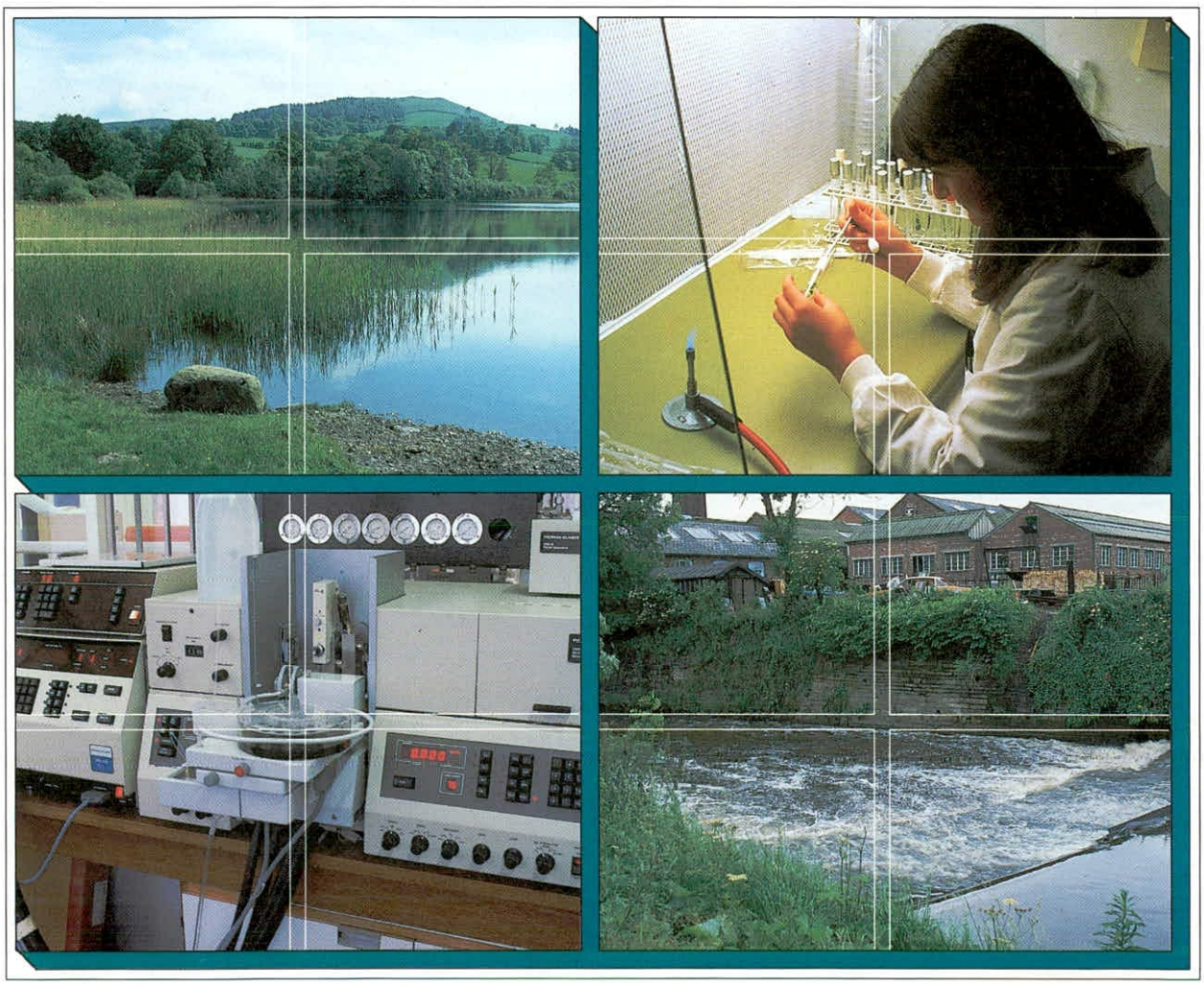

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Analysis of Trifluralin and Deltamethrin in Water, Suspended Solids and Bed-Sediments from ADAS Rosemaund Farm

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Report start date:	12.11.92
Report end date:	18.01.93
Report to:	NRA sub-contract Institute of Hydrology, Wallingford
IFE Report Ref:	RL/T05053k2/1
TFS Project No:	T11053n1

ABSTRACT

The results of the analysis of waters, suspended solids and settled bed-sediments for trifluralin (CAS 1582-09-8) and deltamethrin (CAS 52918-63-5) are presented with information on the partition of trifluralin between the aqueous and solid phases. The proportion of trifluralin transported with the suspended material is seen to be high with several values over 50%. The partition coefficients calculated from the results are variable, indicating either changes in the composition of the particles during a storm or a kinetic influence on the adsorption interaction.

The results for deltamethrin confirm our previous conclusion that this compound is strongly associated with sediment particles with only trace amounts found in the aqueous phase.

CONTENTS

1. INTRODUCTION

The results of the analysis of waters, suspended solids and surface bed-sediments from ADAS Rosemaund Farm (NGR SO 555478) for Trifluralin (CAS 1582-09-8) and Deltamethrin (52918-63-5) pesticides are reported. All samples were collected by the Institute of Hydrology (IH Wallingford) staff on the dates shown in Table 1. Field sampling procedures were those used by IH. All samples were transported to IFE, River Laboratory, as soon as possible after collection. Sediments were frozen after collection and transported frozen. Water and suspended solids were stored by IH prior to transport to IFE. The dates of receipt of all samples at IFE, River Laboratory, are given in Table 1. Records of storage and sample handling at the River Laboratory are not reproduced in full but are available. A summary of the procedures is given in Section 2.

Trifluralin and deltamethrin were analysed using methods tested and described previously (House *et al.*, 1992a). The bed-sediments and suspended solids were soxhlet extracted with dichloromethane (DCM), Kurdena-Danish concentrated, solvent exchanged and analysed by glc/ecd (electron-capture-detector) and GC/MS. The aqueous samples were solvent extracted with DCM, Kurdena-Danish concentrated, solvent exchanged and analysed by glc as described above. Control samples were included in the analysis.

2. METHODS

The IFE codes, sampling times, bottle codes and site descriptions are shown in Table 1.

The bed-sediment samples were already frozen on arrival at the River Laboratory. They were allowed to thaw and IOH 10, 11 and 12 were sieved through a 2 mm stainless steel sieve; samples IOH 14 and 15 did not require sieving. The samples were then frozen overnight and then freeze-dried overnight *ca* 18 h. The samples were lightly crushed and stored under nitrogen gas in the dark at *ca* 5^{0}C prior to analysis. The samples were then extracted and analysed by standard procedures described previously (House *et al.*, 1992a; House & Ou, 1992).

The water samples were stored in the dark at *ca* 5^{0}C and separated as soon as possible after arrival. Full records are available giving storage times and handling of the samples. The water and suspended solids were separated by the procedure described previously (House & Ou, 1992). The water samples were extracted with DCM using as a basis SOP 8/05.03.92 with DCM replacing hexane. The suspended solids were collected on GF/F glass microfibre pads, nominally 0.7 µm pore size: the filters were pretreated to remove organic carbon by heating to 520^{0}C overnight. These filters were found to have the lowest adsorption of a range of organochlorine, pyrethroid and triazine herbicides (House & Ou, 1992). The filters were placed in soxhlet extraction thimbles (pretreated to remove any pesticide residues), frozen overnight and then freeze-dried overnight prior to soxhlet extraction in DCM. The extracts were then concentrated, solvent exchanged using the same methods employed for preparation of the bed-sediments. All weights and volumes were noted to enable the calculation of the suspended solids concentration in µg dm^{-3} in the aqueous phase and µg kg^{-1} (dry weight) for the solids. The volumes of water and masses of the sediments that were separated and then analysed for the pesticides are given in Table 2, together with the calculated concentrations of suspended solids (S/S). The dry masses of settled or bed-sediments are given in Table 2

(samples IOH 10/92 - IOH 15/92). Sample IOH 13/92 was insufficient in quantity for analysis. The mass of sample IOH 10/92 was lower than the other samples.

3. RESULTS

The samples are identified according to their IFE codes given in Table 1. The concentrations of suspended solid are presented in Table 2, together with the volumes of filtered water and dry suspended solids that were separated and subsequently extracted with DCM. As shown, the suspended solid concentrations varied from over 3 g dm^{-3} to 3.1 mg dm^{-3}.

The results of the glc analysis of the water extracts are produced in Table 3 in terms of the concentrations of trifluralin and deltamethrin in the extracts (5% acetone/hexane, volume 2 ml) and the filtered waters. The samples were analysed by glc with ecd and GC/MS using the following ions:

	Target ion	Qualifier ion
	(amu)	
Trifluralin	306	264
Deltamethrin	181	253

The samples were analysed in a series comprising:

1. Standards
2. Solvent (to evaluate injection carry-over)
3. Sample 1 - aqueous
4. Sample 1 - suspended solids
   . . (other samples) . . .
5. Standards

The detectors were calibrated using the average response factors for the series. A typical calibration time for GC/MS is shown in Figure 1.

The concentrations of deltamethrin were too low to be detected by GC/MS without further concentration and isolation of the extracts. The glc/ecd is much more sensitive to deltamethrin with a limit of determination for these samples of *ca* 5 ng ml^{-1} but detection below this to <1 ng ml^{-1} in the extract. Deltamethrin was not detected in many of the samples of water with trace levels, ie ≤0.01 µg dm^{-3}, in some samples. Trifluralin was detected in all the aqueous samples by ecd and GC/MS. The samples containing the highest concentration of trifluralin in the aqueous and sediment phases were quantified by GC/MS (306 amu) (see Figure 2). The other samples were quantified by glc/ecd.

The results from the analysis of the suspended solids are shown in Table 4. Deltamethrin was detected in the first six samples with a typical result from the ecd illustrated in Figure 3.

Results from GC/MS are shown in Figure 4. The relative-retention-times (RRT) of deltamethrin, measured with respect to trifluralin, were within *ca* 0.005 units. Deltamethrin was not detected in samples 7-9. This is not surprising because the detection limit of *ca* 1 ng ml^{-1} in the extract corresponds to ~70 µg kg^{-1} (dry weight) in 30 mg of suspended sediment.

Samples IOH 7-9 all contained <32 mg of suspended solids. For 500 mg of suspended solid extracted, the detection limit is estimated as 4 µg kg^{-1}. No pesticides were determined in the control blank samples and injection carry over was below the limits of detection.

The ion-chromatogram confirming the presence of trifluralin in samples IOH 7-9/92 are given in Figures 5, 6 and 7. The total amounts of trifluralin in the samples IOH 1-9/92 are shown in Table 5, together with the calculated values of the distribution coefficient, K_d. The percentage of trifluralin transported with the suspended solids is substantial and varies considerably between samples. Without information on the organic carbon content of the suspended sediments it is not possible to compare the results with predictions (House *et al.*, 1992a). Previous research (House *et al.*, 1992b) has found that the organic matter content of suspended sediments is often higher than the corresponding surface bed-sediments. The high K_d's of samples 4-9 are particularly interesting. Literature values of between *ca* 100 and 3000 for K_d have been reported. Further, more detailed studies are needed to investigate the reason for the high adsorption on these samples. The adsorption is such that although the suspended solids concentrations are lower for samples 4/92-9/92 than samples 1/92-3/92, the contribution of the suspended solids to the transport, remains significant.

The results for the bed-sediment or settled sediment are given in Table 6 and an example of a chromatogram in Figure 3. Both pesticides were found in all the sediments. The concentrations of deltamethrin were similar to those measured in the suspended solids. The limit of determination for these samples is *ca* 2 µg kg^{-1}. The concentrations of trifluralin are much lower than in the suspended solids. However, when compared with the concentration of other pesticides in river bed-sediments (House *et al.*, 1991, House *et al.*, 1992b), these concentrations are considered to be high. The corresponding field K_d's cannot be calculated without the aqueous concentrations of the pesticides.

4. REFERENCES

House, W.A., Farr, I.S., Orr, D.R. & Ou, Z. (1991) The occurrence of synthetic pyrethroid and selected organochlorine pesticides in river sediments. British Crop Protection Council, No. 47. Pesticides in Soils and Water, University of Warwick, 183-192.

House, W.A. & Ou, Z. (1992) Determination of pesticides on suspended solids and sediments: investigation on the handling and separation. *Chemosphere* **24**, 810-832.

House, W.A., Farr, I.S., Orr, D.R. & Welton, J.S. (1992a) The interaction between pesticides and particles in rivers. Report to DoE, contract PECD/7/7/329, IFE reference RL/T04053h1/5 available from IFE.

House, W.A., Rae, J.A. & Kimblin, R.T. (1992b) Source-sediment controls in the riverine transport of pesticides. British Crop Protection Council, Effects and Fate of Pesticides in the Environment, Brighton, 865-870.

Table 1 Sample codes and field locations

IFE code	Date of collection	Bottle code	Description	Date of receipt at IFE
Water containing suspended solids:				
IOH 1/92	11.11.92	3B	Longlands drain	16.11.92
IOH 2/92	11.11.92	2B	Longlands drain	16.11.92
IOH 3/92	11.11.92	1B	Longlands drain	16.11.92
IOH 4/92	15.11.92	1B	Longlands drain	01.12.92
IOH 5/92	15.11.92	2B	Longlands drain	01.12.92
IOH 6/92	15.11.92	3B	Longlands drain	01.12.92
IOH 7/92	27.11.92	1B	Longlands drain	01.12.92
IOH 8/92	27.11.92	2B	Longlands drain	01.12.92
IOH 9/92	27.11.92	3B	Longlands drain	01.12.92
Surface sediment:				
IOH 10/92	24.11.92	-	IH main site	01.12.92
IOH 11/92	25.11.92	-	MAFF up-stream	01.12.92
IOH 12/92	25.11.92	-	MAFF weir	01.12.92
IOH 13/92	30.11.92	-	IH main site	01.12.92
IOH 14/92	30.11.92	-	MAFF up-stream	01.12.92
IOH 15/92	30.11.92	-	MAFF weir	01.12.92

Note: IOH 1 to IOH 9/92 are *ca* 1 litre samples of water containing suspended solids. IOH 10 to IOH 15/92 are surface sediments. IOH 13/92 contained mainly leaf material with little sediment.

Table 2. Information on the quantity of each matrix extracted by dichloromethane.

Sample code	Vol. water extracted /ml	Mass of sediment /g	S/S concentration mg/dm^{-3}
IOH 1/92	970	1.092	1126
IOH 2/92	970	1.866	1924
IOH 3/92	960	2.991	3116
IOH 4/92	955	0.353	370
IOH 5/92	960	0.567	591
IOH 6/92	960	0.492	513
IOH 7/92	1043	0.033	31.5
IOH 8/92	980	0.027	27.0
IOH 9/92	980	0.003	3.1
IOH 10/92	-	1.328	-
IOH 11/92	-	4.868	-
IOH 12/92	-	4.870	-
IOH 14/92	-	4.867	-
IOH 15/92	-	4.870	-

Note: S/S:- Suspended Solid
Volumes measured to ± 2 ml
Mass measured to ± 0.1 mg

Table 3. Concentration of Trifluralin and Deltamethrin in filtered water samples. C: confirmed by GC/MS. D: quantified by GC/MS and confirmed by ecd.

Sample code	Concentrations			
	Trifluralin		Deltamethrin	
	extract /µg ml^{-1}	sample /µg dm^{-3}	extract /µg ml^{-1}	sample /µg dm^{-3}
IOH 1/92	6.26[D]	12.9	<0.001	<0.002
IOH 2/92	2.84[D]	5.9	<0.001	<0.002
ION 3/92	2.96[D]	6.2	ND	ND
IOH 4/92	0.667[C]	1.4	0.003	0.01
IOH 5/92	0.155[C]	0.32	ND	ND
IOH 6/92	0.153[C]	0.32	ND	ND
IOH 7/92	0.165[C]	0.32	ND	ND
IOH 8/92	0.134[C]	0.27	ND	ND
IOH 9/92	0.180[C]	0.37	ND	ND

Table 4. Concentration of Trifluralin and Deltamethrin in suspended solids. C: confirmed by GC/MS. D: quantified by GC/MS and confirmed by ecd.

Sample code	Concentrations			
	Trifluralin		Deltamethrin	
	extract /µg ml^{-1}	sample /µg kg^{-1}	extract /µg ml^{-1}	sample /µg kg^{-1}
IOH 1/92	0.57[D]	1044	0.01	18.1
IOH 2/92	1.45[D]	1554	0.03	30.2
ION 3/92	2.42[D]	1618	0.05	30.9
IOH 4/92	0.391[C]	2215	ND	ND
IOH 5/92	0.520[C]	1834	0.01	20.8
IOH 6/92	0.273[C]	1110	0.01	21.1
IOH 7/92	0.014[C]	848	ND	ND
IOH 8/92	0.016[C]	1185	ND	ND
IOH 9/92	0.013[C]	867	ND	ND

Table 5. Partition of Trifluralin between aqueous and solid phases in samples IOH 1-9/92. Key: S/S suspended solids.

Sample code	Total amount /µg	% on S/S	K_d /dm^3 kg^{-1}
IOH 1/92	13.7	8.4	80.9
IOH 2/92	8.6	33.6	263
IOH 3/92	10.8	44.8	261
IOH 4/92	2.1	36.9	1582
IOH 5/92	1.3	77.2	5731
IOH 6/92	0.85	64.0	3469
IOH 7/92	0.36	7.7	2650
IOH 8/92	0.30	10.8	4389
IOH 9/92	0.37	0.71	2343

Table 6. Concentration of Trifluralin and Deltamethrin in surface bed-sediments. Values in brackets are standard deviations on triplicate analysis of extracts.

Sample code	Concentrations			
	Trifluralin		Deltamethrin	
	extract /µg ml^{-1}	sample /µg kg^{-1}	extract /µg ml^{-1}	sample /µg kg^{-1}
IOH 10/92	0.013	19.6 (3)	0.013	19.6
IOH 11/92	0.341	140 (2)	0.129	53.0
IOH 12/92	0.193	79.3 (10)	0.091	37.4
IOH 14/92	0.130	53.4 (3)	0.054	22.2
IOH 15/92	0.181	74.3 (1)	0.071	29.2

Legends to Figures

Figure 1. Example of a calibration line for trifluralin in 5% acetone in hexane between 0.1 and 5 μg ml^{-1} with 2 μl injection.

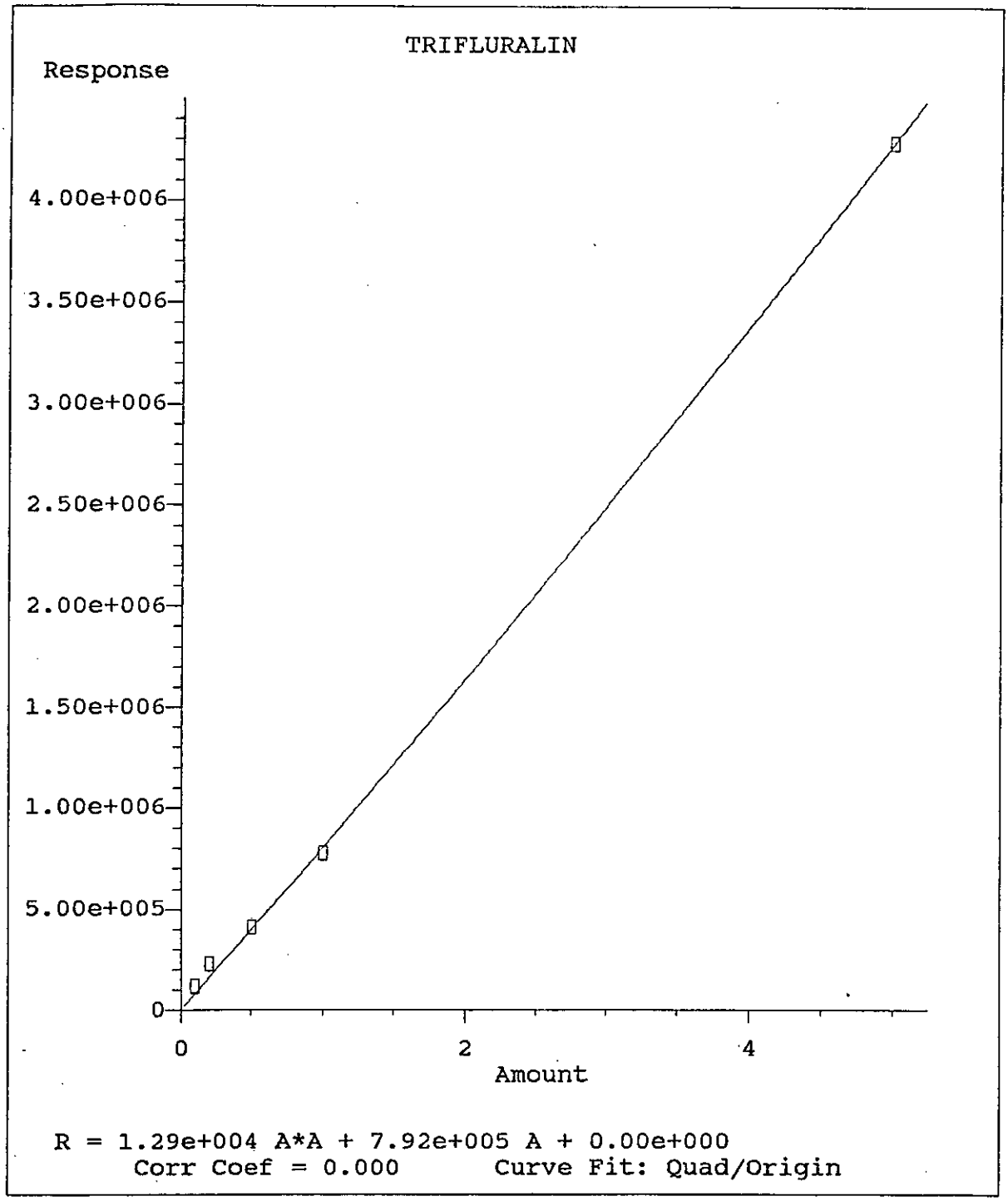
Figure 2 Example of a chromatogram for aqueous sample IOH 3/92. The ion peaks (amu 306 and 264) are shown at a retention time of 11.55 min.

Figure 3 ECD chromatograms for deltamethrin in IOH 2/92 suspended solids and trifluralin in IOH 14/92 sediment. The upper figures show the corresponding 0.1 μg ml^{-1} standard peaks.

Figure 4 Ion-chromatograms for sample IOH 3/92 suspended solids. The absence of peaks for amu = 181 and 253 at RT = 43.5 min for deltamethrin is indicated.

Figures 5,6,7 Ion-chromatograms for samples IOH 7-9 suspended solids show the confirmation of the low concentrations of trifluralin. The RT for trifluralin was 11.33 min. The concentration of trifluralin was measured by glc/ecd (see Table 4) *ca* 0.01 μg ml^{-1} in extract.

Figure 8 glc/ecd chromatogram for IOH 7/92 suspended solids (cf Figure 5 for GC/MS)



Method Name: C:\CHEMPC\METHODS\TRI.M
Calibration Table Last Updated: Mon Jan 11 15:04:33 1993

FIGURE 1

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Method File: tridelt.M
Sample Name: water 3
Misc Info:
ALS vial: 7

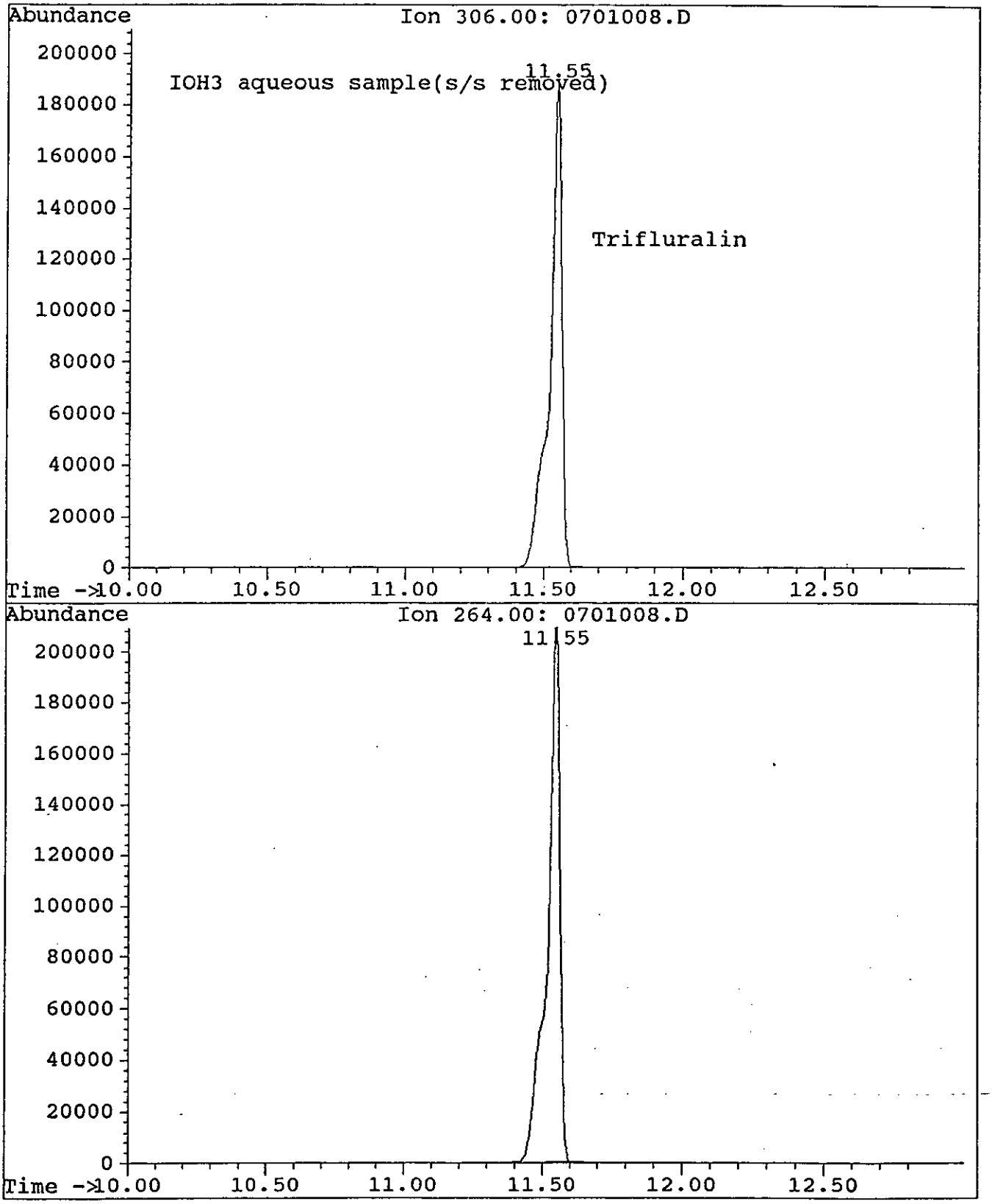

FIGURE 2

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2nd : RUN1__01.D02 0.1 STD W.A. House
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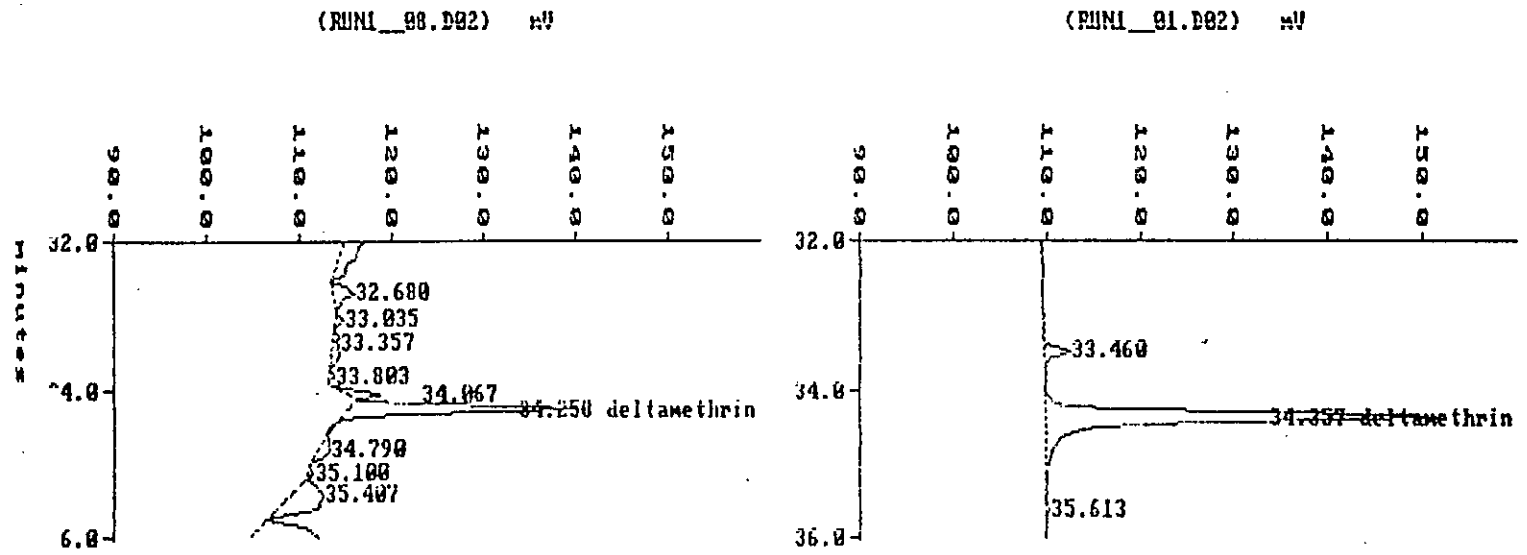

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Collection : 00:25:16 Jan 09 1993 Method : TRI [14:57:54 Jan 08 1993]

2nd : RUN1__01.D02 0.1 STD W.A. House/D. Orr
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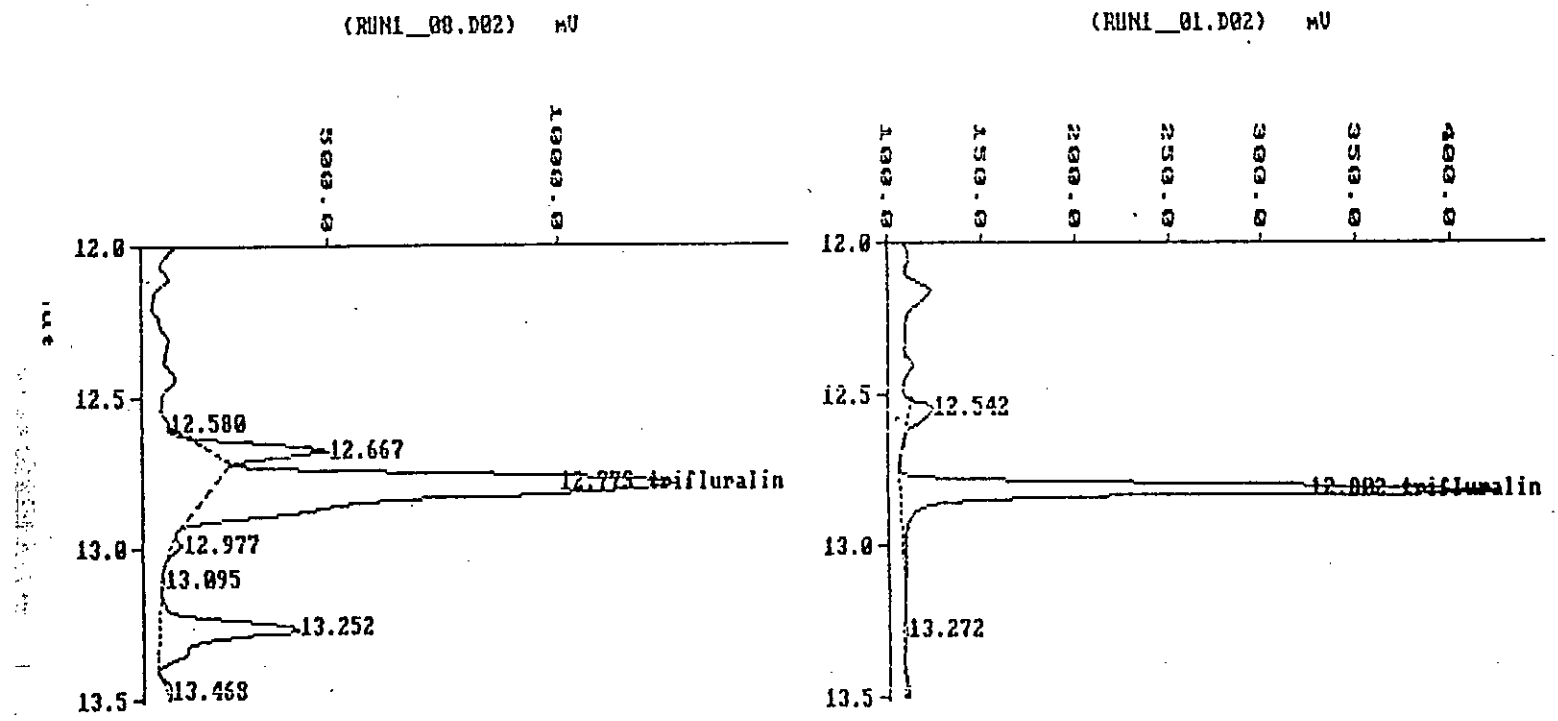

FIGURE 3

File: C:\CHEMPC\DATA\CAL2\0701009.D
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Misc Info:
ALS vial: 7

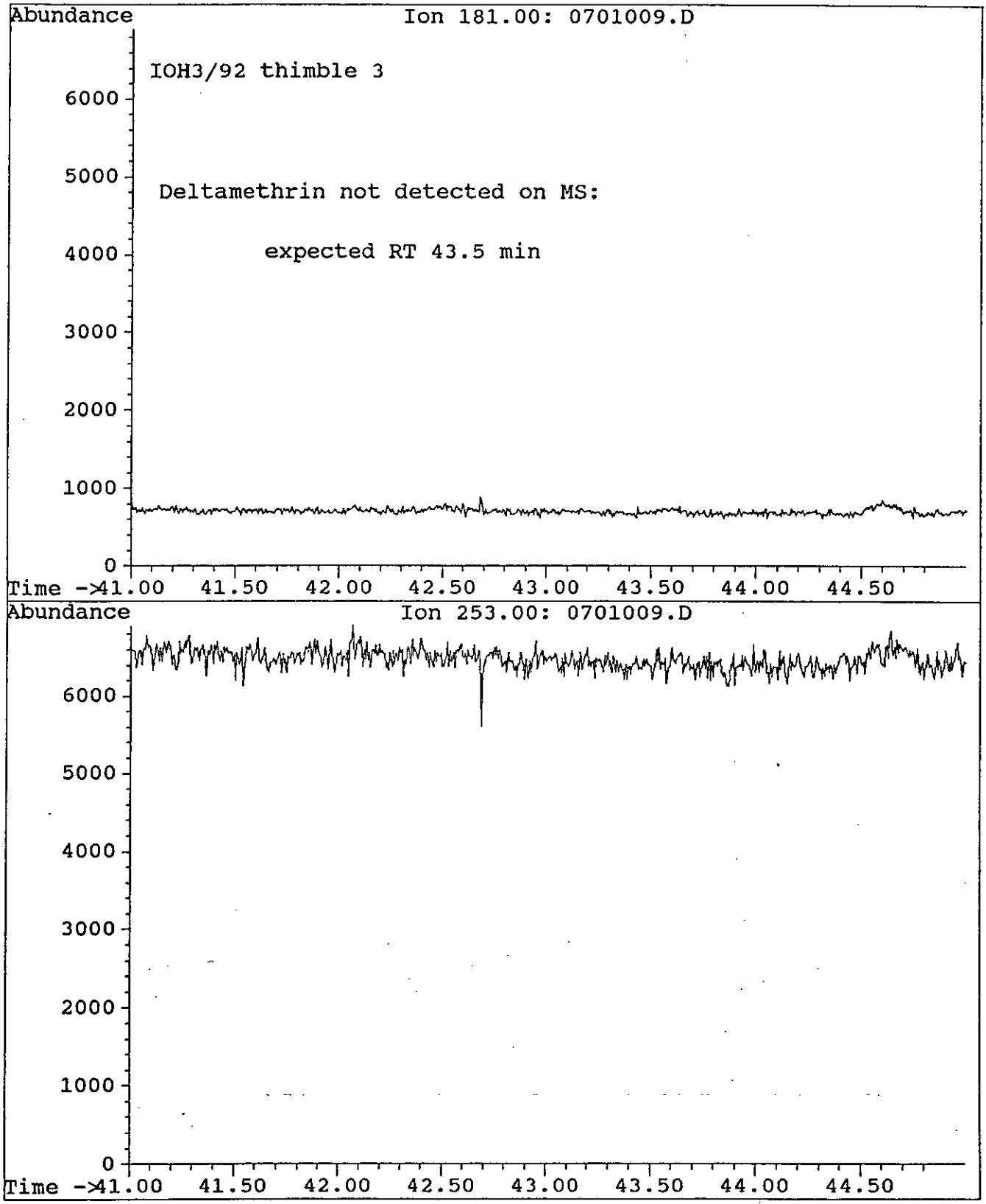

FIGURE 4

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Misc Info:
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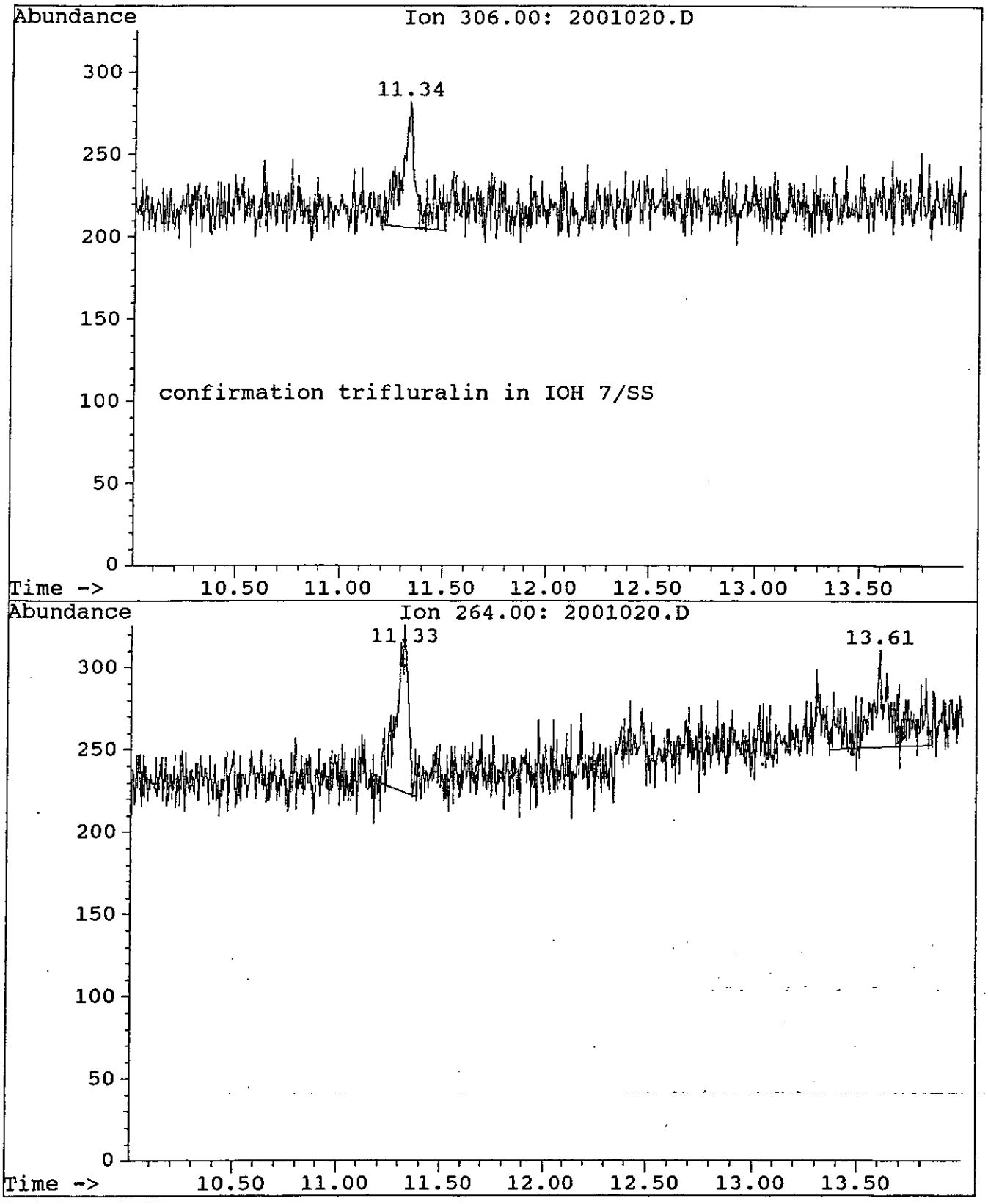

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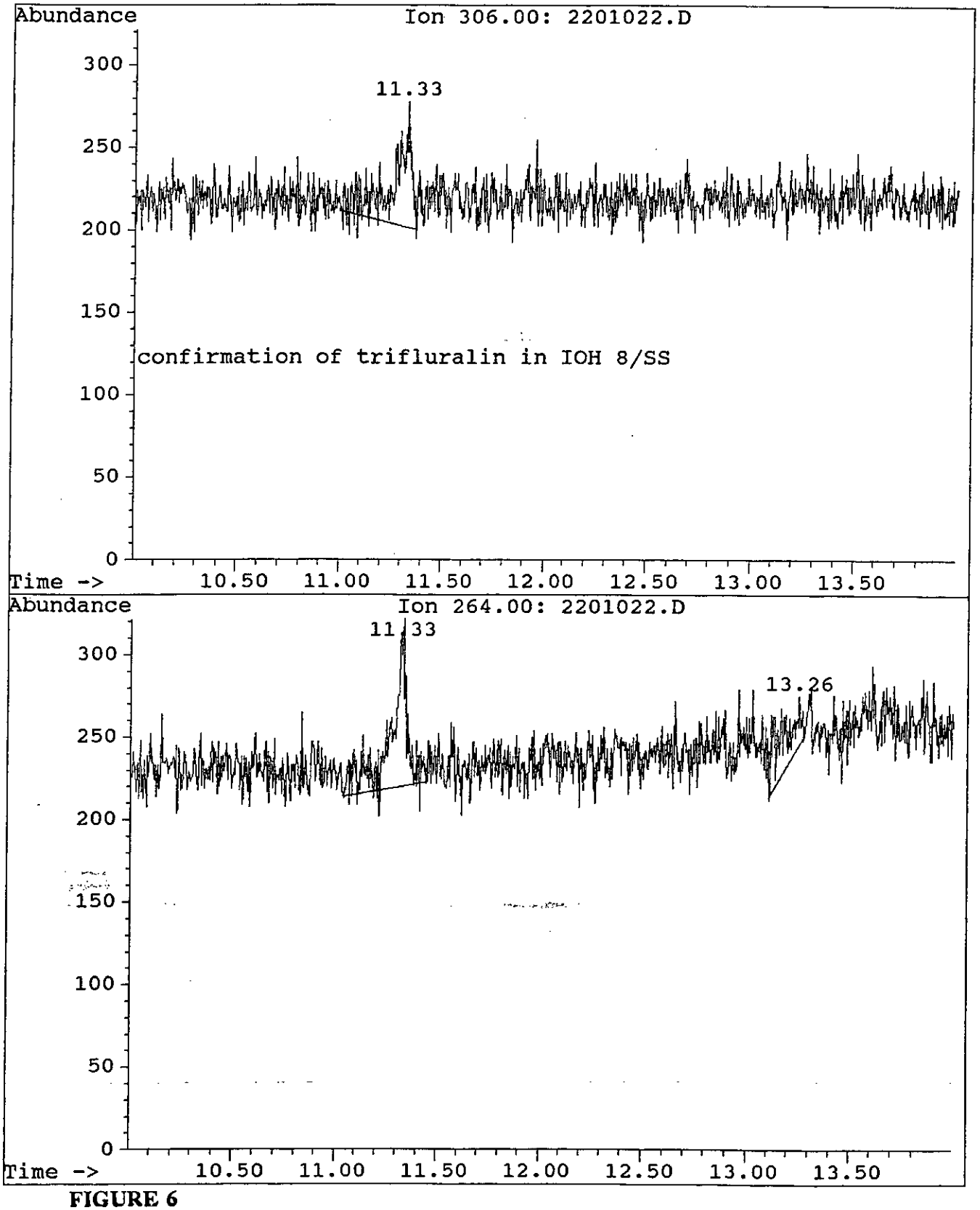

FIGURE 6

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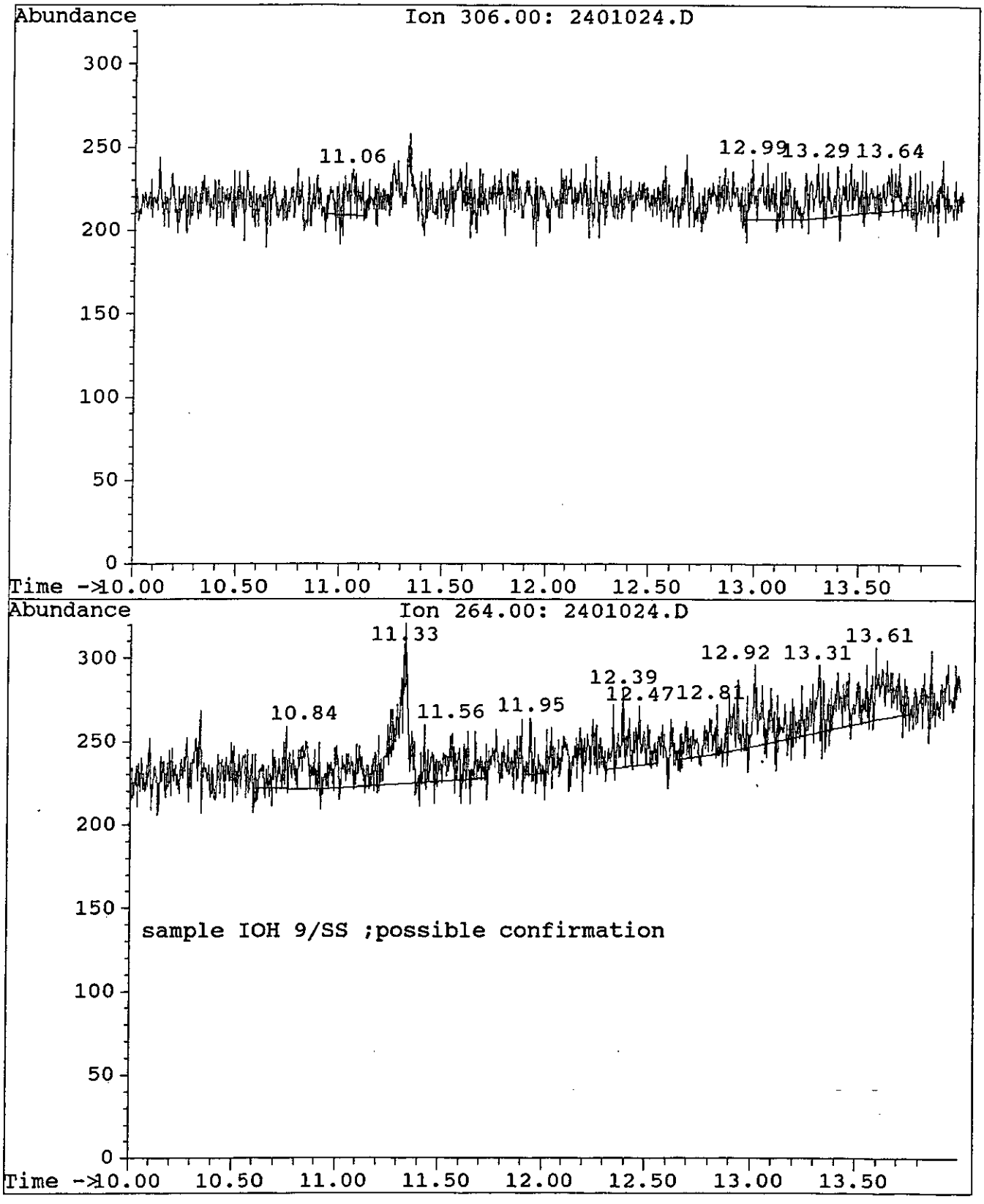
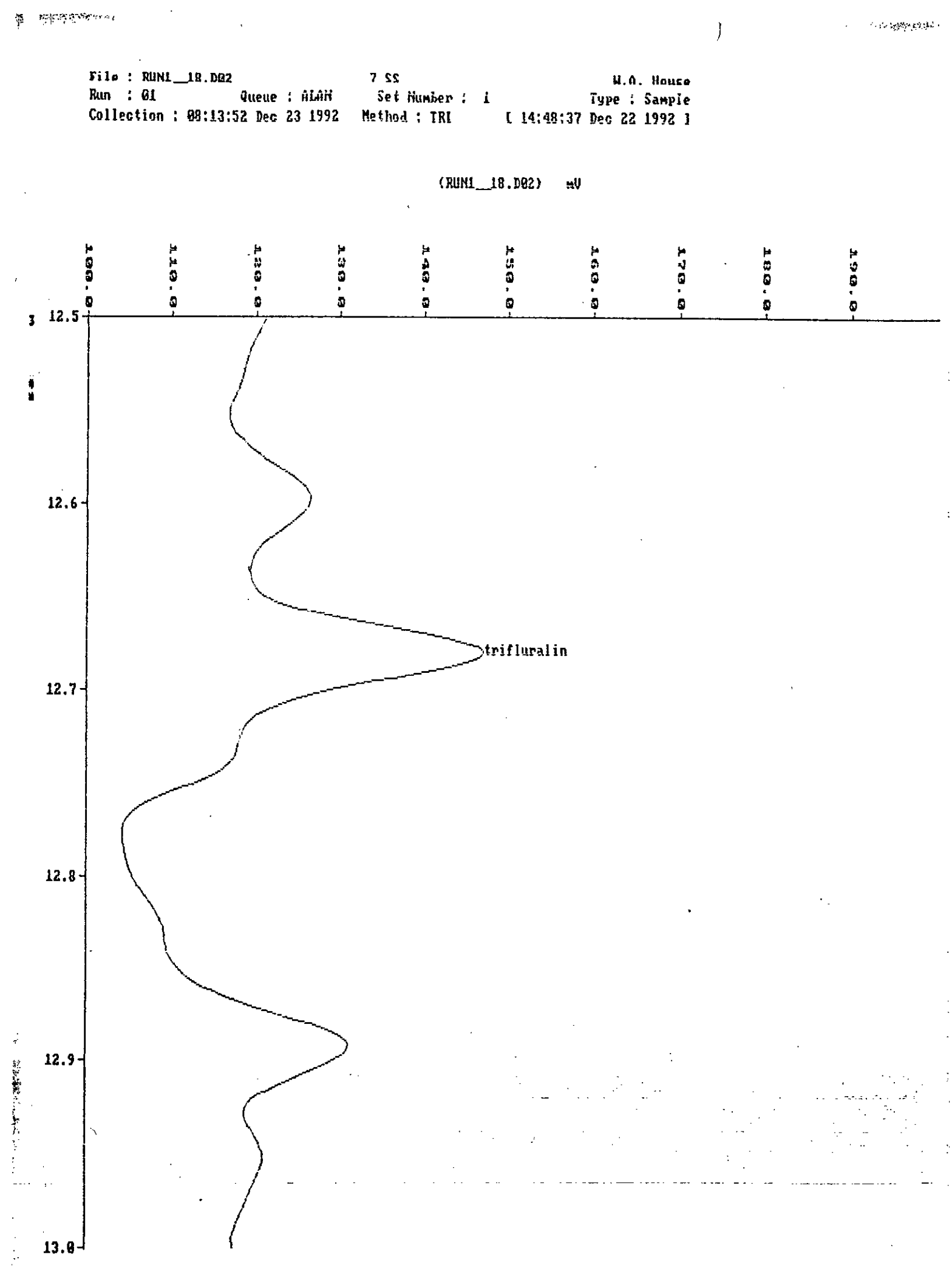


FIGURE 7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100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
12.5
12.6
12.7
12.8
12.9
13.0
trifluralin

FIGURE 8