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Determination of ethylenethiourea in water by single-step extractive derivatization and gas chromatography–negative ion chemical ionization mass spectrometry

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Abstract

A method for the determination of ethylenethiourea (ETU) in water samples is described that involves a single-step derivatization and extraction by means of phase transfer-catalysed reaction with 3,5-bis(trifluoromethyl)benzyl bromide followed by gas chromatography–electron-capture negative ion mass spectrometric separation and detection. The reaction resulted in three ETU derivatives, identified by GC–Fourier transform spectrometry as the mono-N-substituted form and two forms substituted at the N,N'- and the N,S-positions. Quantification in the multiple-ion detection mode was performed on the abundant $[M-227]^-$ ions of the N,N'-isomer in low-level (<5 μg/l) and at the N,S-isomer in high-level samples (>5 μg/l). The limit of determination in surface water samples was 0.05 μg/l with recoveries ranging between 60 and 110%. The method was applied for confirmation purposes for the presence of ETU as analysed by HPLC with UV detection. In general, a good correlation was found between the results from both methods.

1. Introduction

Ethylenethiourea (2-imidazolidinethione; ETU) is a formulation contaminant and an environmental metabolite of ethylenebis(dithiocarbamate) fungicides (EBDCs). This group forms the most important class for controlling fungal diseases on fruits, vegetables and other agricultural crops. ETU as such is widely used as an accelerator in the production of synthetic rubber [1].

The presence of ETU in the environment or in biological tissues is of major concern, because of its known pathological effects [2]. In terms of its putative carcinogenicity, ETU was classified by the method of the International Agency for Research on Cancer (IARC) into group 2B, i.e., the compound is possibly carcinogenic to humans; sufficient animal but limited or insufficient evidence of carcinogenicity in humans is available [3,4]. Hence, reliable and rapid methods, for screening purposes, are required for the trace determination of residual ETU. In addition, the method should be sensitive, in order to meet the present norms for surface and drinking water as set by the US Environmental Protection Agency (EPA) and individual governments.

The determination of ETU is commonly performed by GC after derivatization. Onley and Yip [5] and Pease and Holt [6] described an

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extraction and subsequent alkylation method with bromobutane. The use of other types of derivatization reagents was described by Newsome [7], e.g., S-alkylation with benzyl chloride and subsequent N-acylation with trifluoroacetic anhydride; Nash [8,9] applied pentafluorobenzoylation of the S-alkylated ETU derivative and King [10], S-alkylation of ETU with *m*-trifluoromethylbenzyl chloride. All these procedures involve a multi-step derivatization/isolation method, using elevated temperatures, as a result of which decomposition of the EBDC residues present may occur. A fast, single-step extractive N-acylation of ETU with dichloroacetic anhydride was described by Singh et al. [11]. Although this derivative may dissociate in the hot GC injector, yields of about 80% were reported with detection limits in water samples down to 0.01 μg/l. GC determination of ETU after derivatization as S-butyl-ETU, S-benzyl-ETU and trifluoroacetylated ETU was optimized by Matisová et al. [12] by using capillary columns without any precleaning [12].

Although GC is still the major technique for the determination of ETU, liquid chromatographic (LC) methods are becoming more frequently used, employing UV or electrochemical detection [13,14]. Hogendoorn et al. [15] described an LC technique with column switching by means of which clean-up and concentration of ETU are performed on-line, facilitating trace level analysis in less than 10 min per sample. Combined with preconcentration of samples, a detection limit of 0.1 μg/l is achievable. LC coupled on-line with mass spectrometric (MS) detection was described by Doerge and co-workers [16,17] and Kurttio et al. [18], using particle beam and thermospray.

In our laboratory, the method described by Hogendoorn et al. [15] was used for the analysis of large series of water samples. Confirmation of the presence of ETU was conducted by LC–diode-array UV detection (DAD). For trace levels <1 μg/l, however, this technique is not sensitive enough. In view of the good results recently obtained for another group of polar pesticides (chlorophenoxy herbicides [19]), we decided to investigate the utility of a single-step extractive derivatization of ETU with a perfluorinated reagent, followed by GC–MS using the electron-capture negative ion chemical ionization (ECNICI) mode. It has been shown that the principle of extractive derivatization with a selected group of perfluorinated reagents is a fast and reliable approach for the sensitive determination of polar compounds. A wide variety of fluorinated reagents are now available that can be used in aqueous media. The advantages of the use of these types of reagents are their moderate stability towards hydrolysis in aqueous systems, improved extraction yields and the formation of stable, volatile derivatives with high electron affinities. Hence, sensitive detection systems such as GC–ECD and the more selective GC–ECNICI-MS can be applied for measurements at low levels.

This paper describes a method that was developed for the trace determination of ETU in ground and surface waters at levels down to 0.05 μg/l. Because of the large series of samples to be analysed, the procedure should be fast and simple with a minimum of sample handling. Several optimization experiments were carried our concerning both extraction and derivatization conditions, and for the selection of the derivatization reagent and the GC–MS conditions. In addition, structure elucidation was performed on the derivatives formed by GC coupled on-line with Fourier transform infrared spectrometry (GC–FT-IR). Finally, method validation was accomplished by comparison with results from the LC–UV method [15].

2. Experimental

2.1. Chemicals and reagents

Ethylenethiourea (ETU), analytical-reagent grade, was obtained from Dr. S. Ehrenstorfer (Amsterdam, Netherlands). [$^2H_7$] Bentazone (bentazone-d_7, 95 atom% deuterium) was synthesized from methyl anthranilate and isopropylsufamoyl-d_7 chloride, as described by Jacquemijns et al. [20]. Diazomethane was syn-

thesized as a saturated solution in cold diethylether, by reaction of a basic aqueous solution with N-methyl-N-nitroso-*p*-toluenesulfonamide [21]. After preparation the solution was stored at −20°C in capped tubes. Tetrahexylammoniumhydrogen sulphate ($THAHSO_4$) was obtained from Fluka (Buchs, Switzerland), pentafluorobenzyl bromide (PFB-Br) from Pierce (Rockford, IL, USA), 3,5-bis(trifluoromethyl)benzyl bromide (3,5-BTFMB-Br) from Aldrich (Bornem, Belgium), sodium hydroxide (NaOH), potassium carbonate (K_2CO_3) and dichloromethane from Merck (Darmstadt, Germany) and acetonitrile from Rathburn Chemicals (Walkerburn, UK). Demineralized water was passed through a Milli-Q reagent water system (Millipore), before use. All chemicals and reagents were used as received.

A 10 m*M* solution of $THAHSO_4$ in dichloromethane was prepared freshly each week. A 10 *M* aqueous solution of NaOH was prepared and cooled to room temperature just before use. Standard solutions of ETU and bentazone-d_7 were prepared in water at concentrations of 18 and 100 μg/l, respectively, and stored at 4°C. For the non-aqueous derivatization of ETU, a solution of 1 g/l of ETU in acetonitrile was used.

2.2. Derivatization

Methylation

To 10 μl of a standard solution of ETU in acetonitrile (1 g/l) were added 500 μl of a saturated solution of diazomethane in diethyl ether. After incubation for 5 min at room temperature, 2 μl of the solution were subjected to GC–MS with electron impact and positive ion chemical ionization.

Non-aqueous alkylation

To 10 μl of a standard solution of ETU in acetonitrile (1 g/l) were added 1 ml of acetonitrile, 50 mg of K_2CO_3 and 10 μl of the derivatization reagent (PFB-Br or 3,5-BTFMB-Br). The mixture was heated for 2 h at 90°C with occasional stirring. After cooled to room temperature, 1 μl of the solution was injected into the GC–MS system.

Phase transfer-catalysed (PTC) derivatization

To 9 ml of ground water sample (with or without sediment residues) were added 50 μl of bentazone-d_7 (100 ng/ml) and 1 ml of 10 *M* NaOH solution with continuously stirring. The mixture was centrifuged at 2500 *g* for 10 min. The clear supernatant was transferred into a clean tube with a PTFE-lined screw-cap. To the mixture were added 3 ml of $THAHSO_4$ in dichloromethane (10 m*M*) and 20 μl of 3,5-BTFMB-Br. The mixture was shaken vigorously for 30 min in a horizontal position at a rate of ca. 250 strokes/min. After phase separation, 1 μl of the clear organic layer was subjected to GC–MS analysis.

2.3. Gas chromatography–mass spectrometry

All GC–MS analyses were performed on a Hewlett-Packard HP5890 gas chromatograph directly coupled to a Finnigan MAT SSQ710 system, with a Digital 5000/25 workstation and ICIS application software. Sample separation was performed on a DB-1701 capillary column (30 m × 0.25 mm I.D., 0.15 μm film thickness) (J&W Scientific, Folsom, CA, USA). The column temperature was programmed from 50°C (held for 1 min) to 200°C at 20°C/min, followed by a second increase to 275°C at 10°C/min, and maintained isothermal at 275°C for 5 min. Samples were injected in the splitless mode (45 s sampling time) at an injector temperature of 180°C. The transfer-line temperature was maintained at 275°C. Helium was used as the carrier gas at a column head pressure of 100 kPa.

The mass spectrometer was operated in the negative ion chemical ionization (NICI) mode. Methane was used as the reagent gas at an optimized source pressure (i.e. 93 Pa CH_4, as estimated from the intensity ratio for the reagent ions $C_2H_3^+$ and $C_2H_4^{+\cdot}$ according to Drabner et al. [22]). For structure elucidation, full-scan spectra were acquired from 50 to 600 u at a rate of 1 scan/s. Quantification was performed using

Table 1
m/z values used for MID quantification of the PFB- and 3,5-BTFMB-Br ETU derivatives under ECNICI conditions

Derivative	Monosubstituted main fragment ion (m/z)	Disubstituted main fragment ion (m/z)
PFB form	101	281
3,5-BTFMB form	101	327

ECNICI with multiple-ion detection (MID) at m/z values as shown in Table 1.

2.4. Gas chromatography–Fourier transform infrared spectrometry

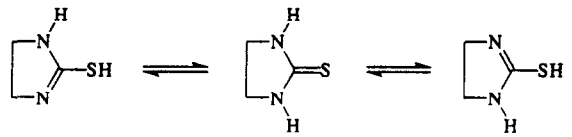
GC–FT-IR was used for identification of the isomeric ETU derivatives. Separations were carried out on a Carlo Erba MEGA 5160 gas chromatograph with a split–splitless injector. The gas chromatograph was equipped with a DB-17 capillary column (J&W Scientific) (15 m × 0.25 mm I.D., 0.15 μm film thickness). The injection volume was 1 μl. Helium was used as the carrier gas. The column temperature was programmed from 50°C (held for 2 min) at 10°C/min to 150°C and then at 20°C/min to 290°C, and maintained isothermal at 290°C for 5 min. The column was connected to a fused-silica transfer line of 150 μm I.D. The transfer line was guided into the FT-IR spectrometer by means of a stainless-steel tube, heated at 250°C. The spectrometer was a Digilab FTS-40 Fourier transform instrument equipped with a Digilab Tracer cryotrapping GC interface and an SPC 3200 computer for data processing. Chromatograms were processed as the Gram–Schmidt plot and as six functional group chromatograms of preselected wavenumber intervals. Spectra were recorded on-the-fly at a rate of 2 scans/s (4 scans co-added). All spectra were recorded at an optical resolution of 8 cm^{-1}.

3. Results and discussion

Preliminary experiments including methylation with diazomethane and anhydrous alkylation with PFB-Br or 3,5-BTFMB-Br were carried out to examine the ability of ETU to react in the aqueous sample with the fluorinated reagents. For this reaction, the analyte should be slightly acidic so that it can form a sufficiently stable ion pair with the catalyst for transport to the organic layer, where it can react with the reagent. For ETU, one might expect slightly acidic properties owing to its keto–thiol tautomerism [23] (Fig. 1).

Methylation of ETU with diazomethane yielded three products that were identified by their EI and PCI mass spectra as a monosubstituted form ($M_r = 116$) and two disubstituted derivatives ($M_r = 130$). Although the isomeric structure of the mono substituted ETU is not well known (N- or S-substitution), the formation of multiple derivatives was indicative of the occurrence of keto–thiol tautomerism of ETU.

Non-aqueous derivatization of ETU with 3,5-BTFMB-Br yielded the corresponding products as with methylation. GC–FTIR analysis of the mixture revealed that the C=S bond was still present in the monosubstituted derivative, indicating a reaction at the NH function. In addition, the N,N'- and N,S-substituted derivatives were also identified by GC–FTIR, the N,N'-isomer eluting earlier than the N,S-isomer (Fig. 2). NCI mass spectra of these ETU derivatives are dominated by an abundant $[M-227]^-$ fragment ion (i.e., loss of one substituted group) at



Ethylenethiourea (ETU)

Fig. 1. Proposed keto–thiol tautomerism of ETU in aqueous solutions.

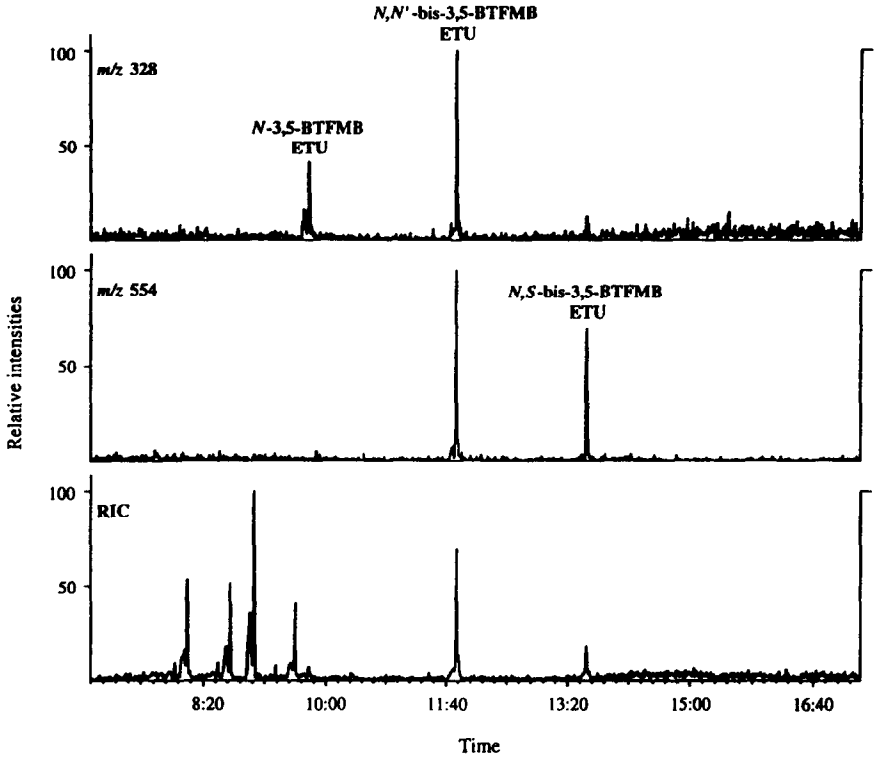


Fig. 2. Ion chromatograms (EI) of the 3,5-BTFMB-Br derivatives of ETU prepared under anhydrous conditions. GC conditions: DB-1701 fused-silica column (30 m × 0.25 mm I.D., 0.15 μm film thickness); temperature programme, 50°C (1 min) to 300°C (5 min) at 20°C/min time in min:s.

m/z 101 and 327 for the mono- and both disubstituted derivatives, respectively.

In contrast to 3,5-BTFMB-Br, the non-aqueous reaction of ETU with PFB-Br resulted in a single derivative containing two PFB groups. This was against expectation, as these reagents normally behave similarly. A corresponding difference in behaviour was also observed with the PTC derivatization of ETU. This mechanistic difference, however, was not investigated further. The NCI mass spectrum of the ETU-diPFB parallels that of the 3,5-BTFMB derivatives, by the loss of one substituent, i.e., $[M-181]^-$ at *m/z* 281.

It is obvious that the detection limit of the method will decrease when multiple ETU compounds are formed during derivatization. The most abundant 3,5-BTFMB derivative (i.e., N,N'-substituted), however, is much more sensitive in NCI than the PFB form, indicating a higher electron affinity. The formation of three derivatives can be considered as an advantage, as it provides an extra feature in compound identification. In addition to the retention time, the presence of the ETU-related satellite peaks on the chromatogram provides an unambiguous identification criterion. Because of the high chemical background in the monosubstituted ion trace (*m/z*, 101), quantification on the disubstituted derivatives (*m/z* 327) was preferred.

3.1. PTC optimization

The pH of the aqueous layer was the most important parameter affecting the reaction kinetics (Fig. 3). Clearly, a strongly alkaline medium (pH > 13) was required in order to obtain high yields. From this, ETU could be considered to

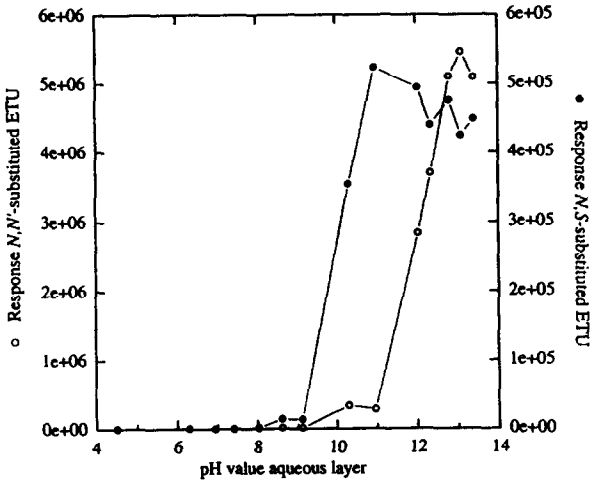


Fig. 3. Influence of the pH of the aqueous layer on the yield of the ETU derivatives. ○ = N,N′-Substituted; ● = N,S-substituted.

be a very weakly acidic compound. Further, the presence of a catalyst was essential, as no ETU derivative was formed in the absence of the catalyst. This indicates the similarity for the reaction with carboxylic acids. Rosenfeld and Crocco [24] did not find any pentafluorobenzyl ester for carboxylic acids, in the absence of a counter ion. This, contrasts with phenolic compounds, which can be alkylated in a similar biphasic system without a counter ion.

Experiments had revealed that no ETU was left in the aqueous layer after the PTC derivatization, indicating complete conversion of the analyte. These experiments were carried out by tenfold dilution of the aqueous layer after PTC derivatization followed by subsequent derivatization of an aliquot of this layer. As a consequence of the extreme alkaline conditions, cloudy precipitates were formed in surface samples. These precipitates were removed by centrifugation prior to the derivatization procedure.

Under the optimum conditions, the reaction proceeded rapidly and was completed within 15 min. Although the PTC extract can be analysed directly with ECNICI-MS, it is expected that GC–ECD measurements at trace levels without further clean-up procedures will be hampered by the high background.

ETU derivatives were found to be stable for at least several days when stored at room temperature. However, the derivatives were slightly sensitive to decomposition during flash heating in the hot GC injector (Fig. 4). The optimum injector temperature was 180°C. Probably, but not investigated here as such an injector was not available on the instrument used, the cold-on-column injection technique is inherently the best choice as it is expected that degradation takes place during the injection and not with the gradually increasing temperature of the GC column.

3.2. GC–analysis

Fig. 5 shows the ion traces of a blank water sample fortified with 0.13 μg/l of ETU. The ETU trace (*m/z* 327) contains several abundant background peaks that were also present when pure water (Milli-Q) samples were analysed. Consequently, the limit of determination is mainly determined by this procedural background.

The occurrence of two disubstituted derivatives of ETU with a yield ratio of ca. 10:1 (Fig. 3) permits an extension of the quantification range in unknown water samples with a constant amount of internal standard. In low-level sam-

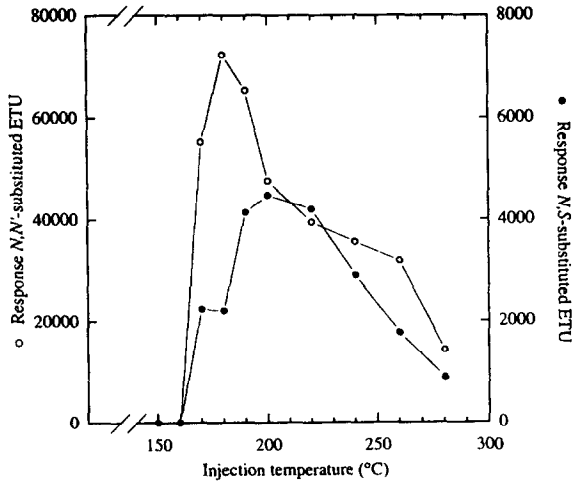


Fig. 4. Influence of the GC injection temperature on the response of the ETU derivatives. ○ = N,N′-Substituted; ● = N,S-substituted.

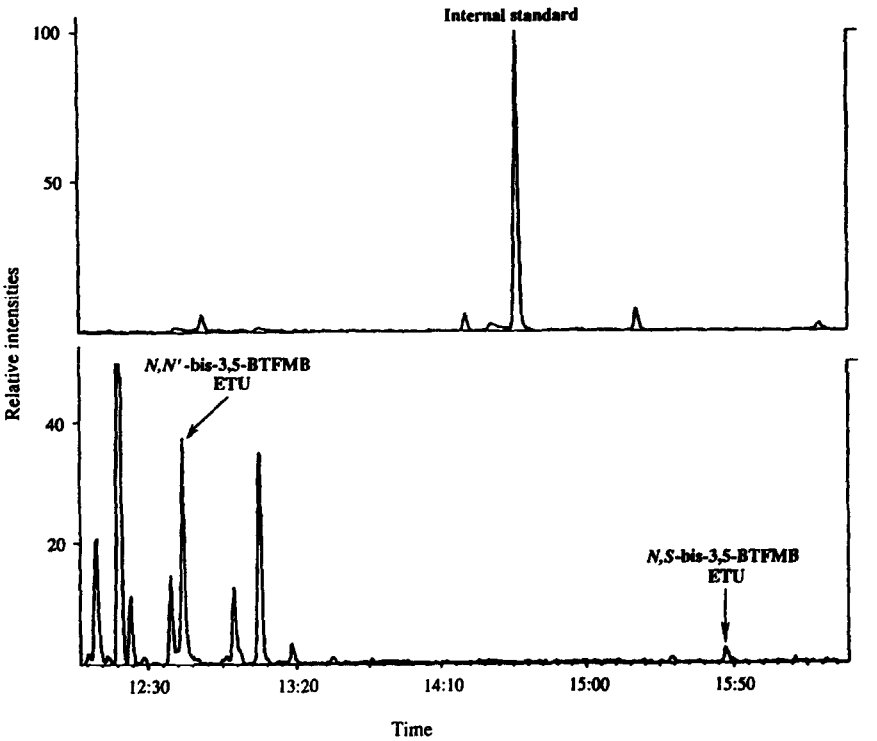


Fig. 5. Ion chromatograms obtained from a water sample fortified with 0.13 μg/l of ETU (lower trace) and the internal standard (upper trace). GC–MS conditions as described under Experimental. Time in min:s.

ples (viz., 0.05–5 μg/l of ETU) quantification can be performed on the most abundant derivative (i.e., the N,N'-substituted compound), whereas in high-level samples (>5 μg/l of ETU) the response ratio of the later eluting, minor N,S-derivative can be used. In the latter samples, the major derivative may readily reach the saturation level of the detector owing to exhausting of the population of the near thermal energy electrons in the NICI source, resulting in a deviation from linearity of the calibration graph (Fig. 6). The calibration graph for the minor derivative was found to be linear up to at least 50 μg/l of ETU.

The reproducibility and recovery of the method were satisfactory. The assay reproducibility was better than 6% (R.S.D., $n = 20$) as determined using duplicate real water samples. The overall recovery of the method was 80 ± 20% on average, as determined in fortified water samples

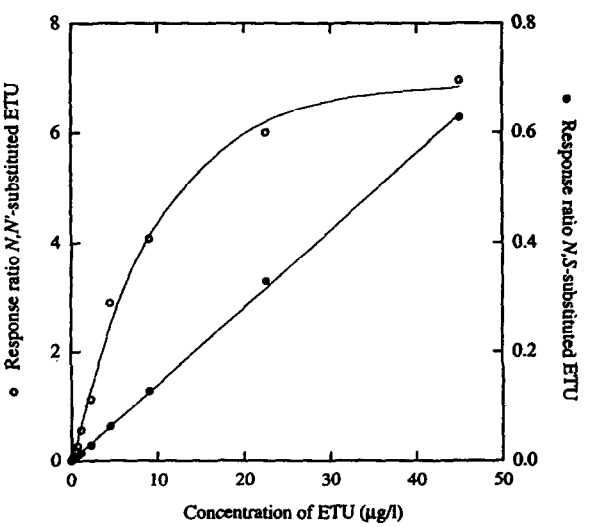


Fig. 6. Calibration graphs for the two forms of disubstituted ETU derivatives. ○ = N,N'-Substituted; ● = N,S-substituted.

in the range 0.5–10 μg/l. Recoveries of added amounts near the determination limit of the method (0.05 μg/l) varied considerably (50–110%). At this level, a slight suppression of the signal of the N,N′-derivative may occur owing to co-eluting compounds with different mass or a slight interference from compounds having the same molecular mass or fragment ions, both originating from the relatively high chemical, procedural background of the method.

3.3. Comparison GC–MS and LC–UV methods

Results of GC–MS and LC–UV analyses of different ground water samples are shown in Table 2. The table gives a random selection of results for a few hundred samples analysed in parallel. One group of results ($n = 5$) concerns false-positive results obtained by LC–UV. The relatively high levels in some samples could not be confirmed by GC–MS. A detailed inspection of the LC method revealed that sample contamination occurred from a rubber seal in the Rotavapor apparatus used for sample concentration. This conclusion is drawn from the GC–MS analysis of the original samples (levels <0.1 μg/l) and the corresponding concentrated samples (Fig. 7). Clearly, this example emphasizes the necessity of independent analysis techniques for tracing false-positive results.

As mentioned before, the comparison of some other results is hampered by the time difference between LC–UV and GC–MS analyses of such samples. Differences in results can be explained by a variable degree of decomposition that was found to occur for ETU when samples are stored for longer periods of time in the refrigerator (group II in Table 2). However, the correlation between results obtained by LC–UV (x) and GC–MS (y) was $y = 1.11x - 0.15$ with a correlation coefficient (r) of 0.989.

In conclusion, in addition to the previously described PTC derivatization of (phenoxy)carboxylic acids, this derivatization technique has

Table 2
ETU concentrations found in some ground water samples of different origins, analysed by LC–UV and GC–MS

Group	Sample No.	ETU (μg/l)		Time between analyses (days)
		LC–UV	GC–MS	
I	1289	0.65[a]	<0.10	
	1290	5.12[a]	<0.10	
	1291	0.23[a]	<0.10	
	1295	0.58[a]	<0.10	
	1299	0.33[a]	<0.10	
II	1281	0.86	0.65	8
	1282	0.22	0.22	8
	1283	0.35	0.40	8
	1287	0.79	0.48	8
	1292	0.27	0.31	13
	1293	1.03	0.75	13
	1294	1.20	0.83	13
	1296	0.31	0.13	13
	944	3.9	4.8	20
	933	1.13	1.15	28
	934	5.9	6.1	28
	1284	0.41	0.62	42
	1285	0.41	0.17	42
	1286	0.56	0.34	42
	932	0.17	0.14	106

[a] False-positive results. See text for details.

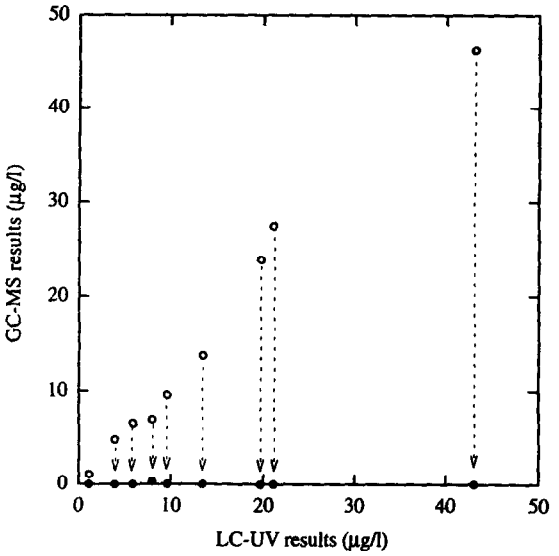


Fig. 7. Comparison of the results for ETU in water samples analysed by GC–MS and LC–UV. ○ = Water samples obtained after concentration on a Rotavapor apparatus as used in the LC–UV method; ● = corresponding original water samples.

been shown to be very useful for the determination of ETU, although it has a completely different class of functional group. The ease of sample preparation in conjunction with the high sensitivity to ECNICI mass spectrometric detection is well suited for routine target compound analysis or confirmation of ETU in surface or ground water. Although the method suffers from a severe procedural background, determination of ETU down to 0.05 µg/l can be easily achieved at unit mass resolution.

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