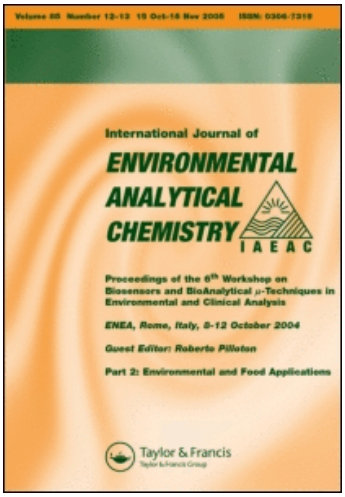

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Ion chromatography as a tool for the investigation of unsymmetrical hydrazine degradation in soils

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Ion chromatography as a tool for the investigation of unsymmetrical hydrazine degradation in soils

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A new procedure for the determination of 1,1-dimethylhydrazine (UDMH) in soil samples was developed. This involves the distillation of UDMH from an alkaline suspension of soil and ion chromatographic analysis of the distillate. The separation was performed on a silica cation-exchanger column with ammonium acetate buffer solution as mobile phase and amperometric detection at +1.2 V. Hydrazine (Hy) and methylhydrazine (MH), which are decomposition products of UDMH, can be determined simultaneously. The limits of detection in aqueous solutions were 0.2, 0.5 and 1 $\mu g\,L^{-1}$ for Hy, MH and UDMH, respectively. The developed technique was used for investigating the behaviour of UDMH in spills of rocket fuels on soils. It was found that the addition of 4 $kg\,m^{-2}$ UDMH resulted in a 0.02% residue one year after the soil treatment. The vertical migration of UDMH in soil was less than 50 cm.

Keywords: Ion chromatography; Soil analysis; 1,1-Dimethylhydrazine; Degradation

1. Introduction

Ion chromatography was first introduced in 1975 [1], and since that time the technique has grown in usage at a surprising rate [2]. The reasons for this are clear; this analytical method offers the only simple, reliable and inexpensive means for the simultaneous separation and determination of inorganic and organic ions in complex mixtures [3, 4].

1,1-Dimethylhydrazine (UDMH) is a xenobiotic compound harmful to the environment and human health [5]. One of the primary ways UDMH enters the environment is from its use as rocket fuel [6]. Another significant source of UDMH contamination is the application of the outlawed plant growth regulator daminozide. A reliable

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evaluation of UDMH's danger to the environment involves the examination of its fate in overland ecosystems, which is not possible without sensitive and specific analytical methods.

Earlier spectrophotometric techniques have been used for the determination of UDMH [7, 8]. However, their usage has decreased with the development of more selective chromatographic methods. Gas chromatography (GC) has been proposed for UDMH determination in fruits [9–11] and soils [12, 13]. GC has also been used for indirect determination of daminozide in food when preliminary alkaline hydrolysis of daminozine to UDMH takes place [14–19]. The application of GC necessarily involves a derivatization step due to the high polarity of hydrazines. Also, UDMH cannot be directly determined by reverse-phase liquid chromatography; its weak retention is the other reason why derivatization should be used. LC determination of UDMH has been performed by derivatization with 5,7-dinitrobenzofurazan [20], salicylaldehyde [21] or 4-nitrobenzaldehyde [22].

Derivatization is an additional labor-intensive step of sample preparation that increases time of analysis and decreases precision, so methods with direct determination are preferable. Hydrazines can be determined directly by ion chromatography (IC) with amperometric detection [23, 24]. Separation on cation exchangers in contradiction with reversed phases leads to higher-capacity factors for hydrazines. Using amperometric detection, it is possible to obtain a sensitivity of 10^{-6}% without any preconcentration step.

This article describes an approach for the determination of UDMH in soils using IC with amperometric detection. Compared with existing methodologies, the technique is straightforward and involves a minimum sample preparation.

2. Experimental

2.1 *Chemicals*

Samples of 1,1-dimethylhydrazine (99%), methylhydrazine (99%) and hydrazine sulphate were obtained from Aldrich (Steinheim, Germany). All other reagents employed in this study were of high-purity or analytical grade. Standard solutions of hydrazines ($1\,g\,L^{-1}$) were prepared in 1 M H_2SO_4 and could be stored in the dark at 4°C for six months. Working solutions were prepared in various concentrations by dissolving the standard solutions with 10 mM H_2SO_4.

2.2 *Instrumentation*

The liquid chromatograph employed was a modular system consisting of an LC-10ADvp pump (Shimadzu, Japan), a Reodyne Model 7125 sample injector (Reodyne, USA) with a 0.25 mL sample loop, and a Tsvet-Yauza amperometric detector (Chimavtomatika, Russia) with glassy carbon working electrode. The separation of hydrazines was performed on a stainless steel column 4×100 mm packed by Nucleosil 10 SA (10 μm). The flow rate was $1\,mL\,min^{-1}$. Unless otherwise mentioned, ammonium acetate buffer (pH 5.4) was used as mobile phase, and the applied potential was +1.2 V (DC mode).

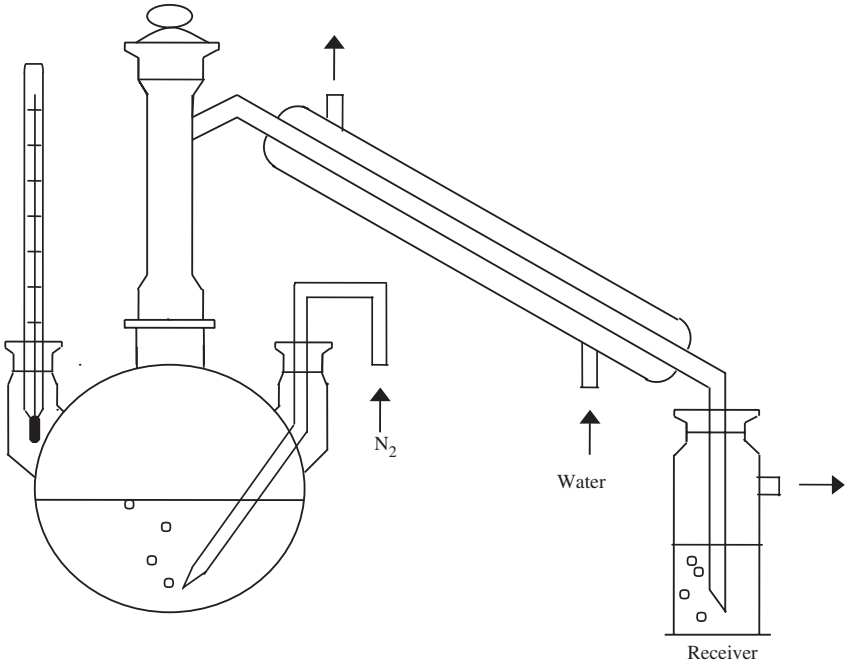

Figure 1. Scheme of instrument for the extraction of 1,1-dimethylhydrazine from soils.

2.3 *Sample preparation*

The design of the device for sample preparation is shown in figure 1. A 10 mL aliquot of 10 mM sulphuric acid was placed into the receiver of samples. A weighted soil sample (5 g) was placed in a round-bottom 250 mL flask. A 40 mL aliquot of solution containing of sodium sulphide (40 g L^{-1}) and appropriate amount of NaOH was added into the flask. A stream of nitrogen was used to eliminate oxygen and to mix the contents of the flask. The flask was heated to provide a moderate speed of the distillation and to prevent breakthrough of the flask contents in the refrigerator and the receiver. The distillation was finished after the complete removal of the liquid from the flask. Then, the contents were poured into a 100-mL volumetric flask and filled with deionized water. The stream of nitrogen was then switched off, and the contents of the receiver were poured into a 100 mL volumetric flask and filled with deionized water. An aliquot of the solution (2 mL) was filtered through a 0.45 μm filter to remove any solid particles and injected directly into the chromatograph for the determination of UDMH and its decomposition products.

2.4 *Ion chromatography*

A calibration curve was prepared by injection of eight working solutions of UDMH over a concentration range of 0.004–2.0 mg L^{-1}. Peak areas were plotted against concentrations in the UDMH working solutions.

The LOD was calculated as the concentration of compound required to produce the response that was three times greater than baseline noise from an unfortified soil sample.

Quantitation was performed by comparing the peak areas of UDMH in the sample with those of the calibration solution. The amount of UDMH in the sample was calculated as the average of two replicate analysis.

2.5 *Recovery*

The matrix effect on UDMH recovery was investigated for 25 soil samples that differed from each other in terms of chemical, physico-chemical properties and granulometric composition, and represent a variety of topsoils in areas of rocket drops. Clean soils were analysed as mentioned earlier. The samples were spiked with 250 μg of UDMH after addition of alkaline Na_2S solution.

2.6 *Repeatability*

Recovery studies were performed at a fortification level of 50 mg kg^{-1} by adding 250 μg of UDMH to six portions of clean sod-podzolic loamy soil samples that were analysed on the same day.

2.7 *Field-experiment procedure*

A field experiment was conducted in the southern taiga zone, in forested interfluve occupied by sod-shallow-podzolic soils (*Albeluvisols* according to the World Reference Base for Soil Resources). The forest cover in this area was dominated by birch–spruce associations with an admixture of pine and the herbaceous cover being represented by cereals, oxalis, and other grasses. A series of plots, 20 by 20 cm, were established in similar soil and lithological conditions. Clean UDMH was applied to the plots at a rate of 4 kg UDMH m^{-2}. Soil samples were taken 1, 3, 30, 90, and 365 days after treatment. After the plots had been sampled, the soil was cleaned of the residual UDMH.

2.8 *Sampling procedure*

Soil samples, to 90-cm depth, were separated into 0- to 5-, 5- to 10-, 10- to 15-, 15- to 20-, 20- to 30-, 30- to 40-, 40- to 50-, 60- to 70-, and 80- to 90-cm sections. To minimize the influence of any localized non-uniformity and contamination of subsoil samples by topsoil, the upper four samples within the 0–20 cm range were collected by taking the whole soil material from the 20 by 20 cm plot. The deeper samples were obtained as undisturbed vertical cores by using a hand soil auger (Clements Instruments Co., USA). Additional sampling was carried out to measure the soil water contents.

3. Results and discussion

3.1 *Optimization of sample preparation*

The initial stage of any analysis of soils is the extraction of UDMH from a solid to a liquid phase. Trace amounts of heavy and transition metals, fulvic- and hydroxy-acids

Table 1. Effect of soil type and extraction solvent composition on recovery data (%).

	NaOH solution (%)	
Soil type	0.02	50
Sod-Podzolic	30	92
Southern Chernozem	60	74
Meadow Chernozemic Solonetz	90	102
Solonchak	90	90
Chernozemic Meadowish Solonetz	68	70

Table 2. Comparison of parameters of UDMH peak between different eluents[a].

Eluent composition	Retention time (t_R) (min)	Relative peak height	Relative peak area	Efficiency (N) ($TP\,m^{-1}$)
50 mM CH_3COONa	12.23	0.6	0.99	14,000
75 mM CH_3COONa	8.44	0.8	0.85	14,800
50 mM CH_3COOK	8.41	0.9	0.9	19,200
50 mM CH_3COONH_4	8.57	1	1	22,000
25 mM $(NH_4)_2HPO_4$	8.42	0.9	0.94	22,000

[a] Mobile phase pH 5.4, flow rate 1 mL min^{-1}, potential +1.2 V.

contained in soils prevent the full extraction and determination of 1,1-dimethylhydrazine. These substances are capable of forming various complexes with UDMH and of promoting its decomposition. For the analysis of soils, alkaline distillation for UDMH recovery from soil suspension was proposed. This procedure was based on the use of 10% solution of sodium sulphide as an extracting agent. Sulphide ions forms strong insoluble complexes with transition metals and thus eliminate their negative influence. Besides, sodium sulphide, being a strong reducing agent, prevents the oxidation of UDMH during the analysis.

Sulphide-ion oxidation on glassy carbon electrode is observed under conditions used for hydrazines determination, and its excess in the distillate could mask their peaks. Therefore, the composition of the extraction solution was modified in order to prevent a penetration of sulphide into the distillate by decreasing the Na_2S concentration to 40 g L^{-1} and using a more alkaline pH by adding NaOH. Two levels of NaOH concentration were studied: 0.02% (50 mM) and 50% solutions. The first case ensures just a pH value where H_2S cannot be formed and reach the receiver. The 50% NaOH solutions were used earlier for distillation of UDMH from food samples. It was found that a more concentrated solution provides a more significant recovery, in the 70–102% range (table 1), especially for sod-podzolic soils where recovery was significantly improved from 30% to practically full extraction. The greater extraction ability of the 50% NaOH solution is likely to be the result of hydrolysis of chemical bonds of UDMH and soils.

3.2 *Optimization of IC determination*

The mobile phase composition is an important parameter in liquid chromatography from the viewpoint of both separation and detector response. IC demands the use of

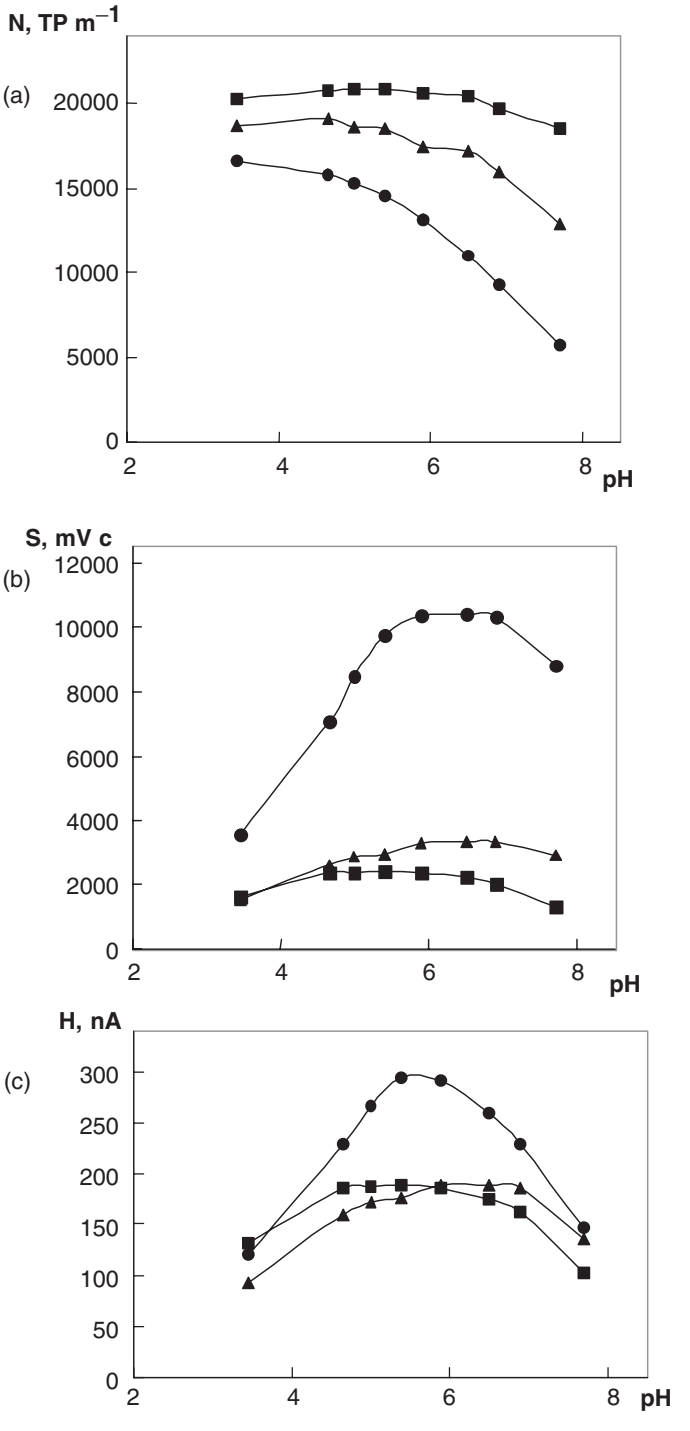

Figure 2. Dependence of efficiency (a), peak areas (b), and peak heights (c) for hydrazine (0.05 mg L^{-1}; —■—), methylhydrazine (0.1 mg L^{-1}; —▲—) and 1,1-dimethylhydrazine (0.4 mg L^{-1}; —●—) upon pH of eluent. Separation condition: 50 mM $(NH_4)_2HPO_4$, adjusted with H_3PO_4.

Table 3. Effect of the mobile phase pH on parameters of hydrazine peaks[a].

Analyte	t_R (min)	k'[b]	$\alpha_{N_2H_4}$[c]	N (TP m^{-1})	R_s[d]
pH 6.9					
Hy	4.33	2.26	1.00	28,500	–
MH	5.51	3.12	1.39	21,300	1.67
UDMH	11.14	7.38	3.27	10,900	4.07
pH 5.3					
Hy	4.30	2.24	1.00	35,000	–
MH	5.30	2.99	1.33	27,000	1.43
UDMH	8.80	5.6	2.50	22,000	3.69

[a] Mobile phase 25 mM $(NH_4)_2HPO_4$, pH adjusted with H_3PO_4, flow rate 1 mL min^{-1}, potential +1.2 V.
[b] Capacity factor.
[c] Selectivity.
[d] Resolution was calculated according to the formula $R_s = 2(t_2 - t_1)/(w_1 + w_2)$, where t – retention time ($t_2 > t_1$) and w – width of the peak.

acidic buffers as eluents in order to convert hydrazines to the corresponding cation forms. Non-electroactive salts such as acetates, phosphates, citrates and perchlorates should be chosen for amperometric detection. Consequently, the effects of buffer type and pH on sensitivity and separation efficiency were investigated.

Table 2 shows that sodium acetate decreases the efficiency of separation, and as a result, the peak height and sensitivity of the UDMH determination also decrease. All other investigated eluents did not show any significant differences.

The pH of the mobile phase affects more significantly the chromatographic behaviour of UDMH. The dependences of peak area, peak heights and efficiency as functions of pH for ammonium phosphate eluents are shown in figure 2. The separation efficiency worsens with increasing pH particularly when the pH is >6. Moreover, the retention times of hydrazines also increase. These facts are probably accounted for by silanol activity, which rises with increasing pH. As a rule, additional interaction with silanol besides greater retention leads to a decrease in separation efficiency.

The maximum peak area was achieved in the pH range 6–7. The result is in agreement with those described in previous studies [24]. Only the non-protonated form of hydrazines can be oxidized, providing a detector response. The competing reaction of protonation decreases the peak area in more acidic solutions. However, the peak height is the more preferable parameter for the optimization of the system sensitivity. Thus, the optimal area with a maximum peak height of UDMH is obtained at about 5.3–5.9 pH units. This is a compromise between peak area and separation efficiency.

As shown by the data in table 3 and figure 3, a mobile phase with pH 5.3 can provide not only the best sensitivity but also the separation of a mixture of UDMH and its decomposition products hydrazine and methylhydrazine.

3.3 *Selection of electrode potential*

Maximum sensitivity is achieved by appropriate choice of electrode potential. The examination of dynamic voltamperograms (figure 4) showed that peak heights of hydrazines rise by increasing the potential value to +1.2 V and achieve a plateau where a maximal amount of substances is oxidizing. It was this potential value that

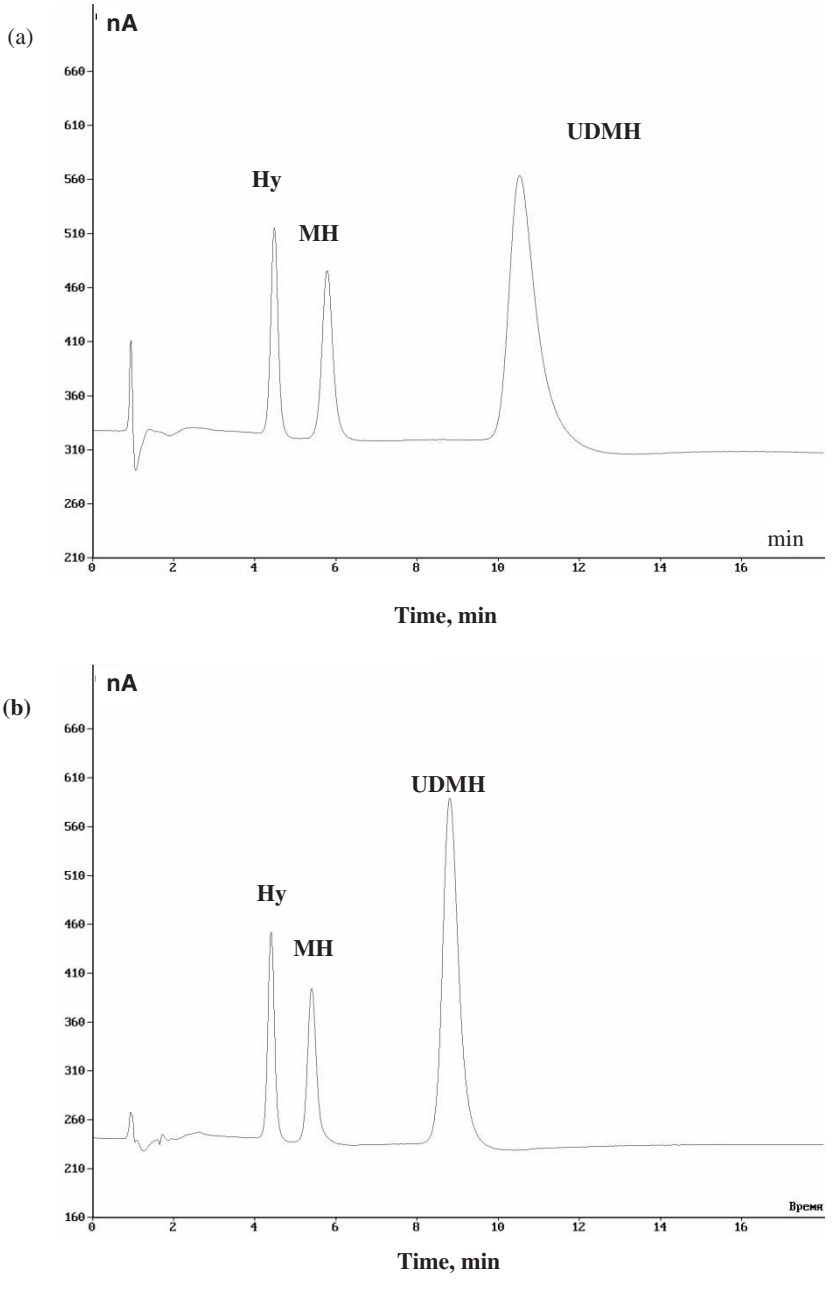

Figure 3. Influence of pH of eluent on the separation of hydrazines: (a) 50 mM CH_3COONH_4, pH 6.9; (b) 50 mM CH_3COONH_4, adjusted with CH_3COOH to pH 5.3.

was chosen as the optimum for the detection. Increasing the potential requires more time for electrode equilibration. Furthermore, at a potential higher than 1.4 V, the mobile phase is likely to begin oxidize, causing not only an increase in baseline current but a decrease in hydrazine signal due to competitive reactions.

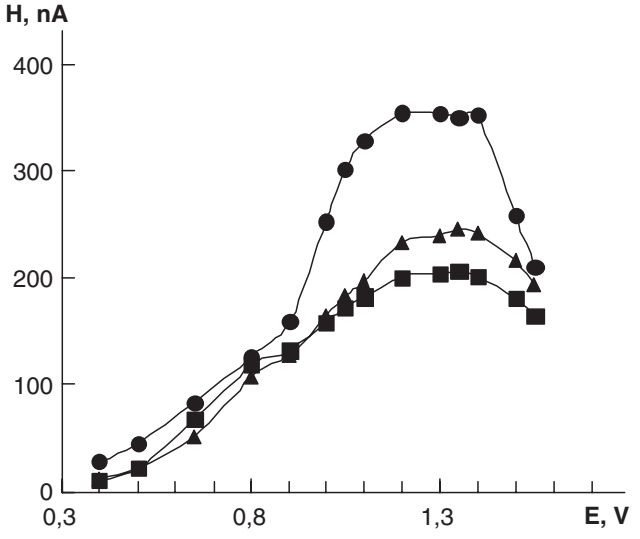

Figure 4. Dependence of hydrazine response as a result of the applied potential.

3.4 *Quantitation parameters*

Linearity of response was observed in the range investigated, corresponding to 0.08–40 $\mu g\,kg^{-1}$ of UDMH in soil. The correlation coefficient (r^2) was 0.9994 and the intercept zero. The precision of five injections of 8 $\mu g\,L^{-1}$ UDMH solution was 8% RSD.

The LODs of IC-AD in aqueous solutions were 0.2, 0.5 and 1 $\mu g\,L^{-1}$ for Hy, MH and UDMH, respectively. The LOD of UDMH of the present method is comparable with the LODs obtained by GC analysis [12, 13], but these methods require an additional prior derivatization step.

The repeatability of the soil sample analysis at a fortification level of 5 $mg\,kg^{-1}$ showed that the average recovery was 92% with a precision of 13% RSD. A typical chromatogram of the soil extract is shown in figure 5.

3.5 *Transformation of UDMH in sod-podzolic loamy soil*

A 1-year-long field experiment demonstrated a high potential of the developed approach for studying UDMH transport and sustainability in soils (table 4). Only 4.3% of the added UDMH was observed in soil 1 day after treatment. The maximum concentration of UDMH found in the upper 0–5 cm layer of the soil was 6720 $mg\,kg^{-1}$. This amounted to 98.5% of the total applied UDMH. For the 5–10- and 10–15-cm layers, the UDMH levels were 90 and 312 times lower than those of the upper layer, respectively. Almost no UDMH was identified in soil deeper than 40 cm. Therefore, rapid UDMH losses appear to be a result of its volatilization from the soil surface immediately after the treatment.

Further studies revealed a clear decline in rates of UDMH removal from the treated soil. Samples collected 3, 10, 30, and 90 days after treatment contained 4.4, 1.1, 1.0,

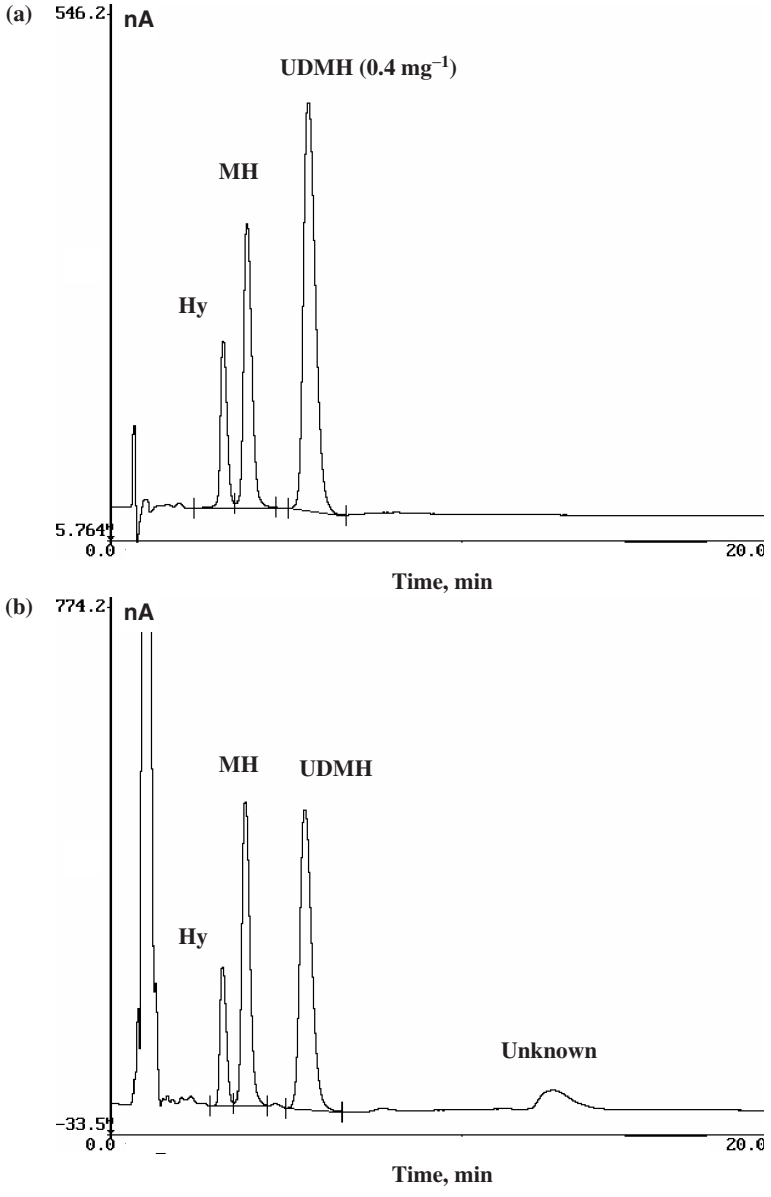

Figure 5. Chromatograms obtained from the soil analysis: (a) standard solution; (b) soil extract.

and 0.2% of applied UDMH, respectively. Finally, 1 year after treatment, the residual soil contamination was reduced to less than 0.02% of the initial value. It is reasonable to say that oxygen and oxidized forms of polyvalent elements are the most important limitations of UDMH residence time in the soil profile.

It should be noted that UDMH did not show a capacity for intensive downward flow through the soil profile. Despite the most indicative UDMH diffusion recorded in the plot sampled 3 days after soil treatment, the highest UDMH levels were observed

Table 4. UDMH depth distribution in soil profile ($mg\,kg^{-1}$).

	Sampling time (days after treatment)					
Depth (cm)	1	3	10	30	90	365
0–5	6700	5300	1500	1400	160	18
5–10	70	480	55	60	60	5.9
10–15	22	330	11	6.2	12	2.5
15–20	7	160	11	18	15	0.17
20–30	1.1	1.9	1.2	52	7	0.5
30–40	0.1	1.3	1.1	23	0.9	5.6
40–50	0[a]	4.7	0.6	0.3	0.16	1.6
60–70	0	0	0.5	0	0.3	0
80–90	0	0	0.3	0	1.9	0

[a] Less than the LOD.

in the subsurface horizon during the entire experimental period. Free water infiltration in soil profile following precipitation had little or no effect on the UDMH vertical movement.

The acid reaction of the subsurface soil horizon and its enrichment with organic matter are favourable for the generation of UDMH's cationic form that proved to be strongly adsorbed by negatively charged soil colloidal constituents. This factor is an important restriction to UDMH transport down into the soil profile. Among the factors mobilizing UDMH in soil, UDMH-containing water moving through the root channels and burrows of soil fauna was distinguished in contrast to relatively insignificant frontal water diffusion. This is why in some cases UDMH was found at a depth of up to 90 cm, although in most cases all the detectable contaminant was redistributed within the upper 50 cm layer.

The hydrazine anomaly found at a depth of about 40 cm results from the relatively higher sorption capacity of this horizon, which is rich in fine particles. Since accumulated soil colloids provide not only additional adsorption sites for UDMH but also a decrease in soil permeability, this soil layer serves as a barrier for hydrazine-bearing solutions.

4. Conclusion

This work has demonstrated the robustness of the application of ion chromatography for the determination of UDMH. The approaches used are simple and convenient, and meet the sensitivity requirements. The optimized chromatographic conditions and a technique for the sample preparation can be applied for stability studies of hydrazine compounds and their behaviour in the natural environment, or for the analysis of samples with the purpose of outlining sources of UDMH pollution. Field experiments under specified UDMH loading rates were successively employed to simulate the hydrazine's dynamics and depth distribution in sod-podzolic soil.

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