

# Extraction and gas chromatographic determination of chlorinated solvents in contaminated soil

Tomaso C Gerbino, Sandro Nadotti and Paolo Castello

Laboratorio Chimico, Castalia SpA, Via Borzoli 79A/r, I-16161 Genoa (Italy)

(Received May 26th, 1992)

---

## ABSTRACT

The performance of a simple and reliable extraction method for the analysis of chlorinated solvents in soil was evaluated. The gas chromatographic analysis of the final extracts dissolved in acetone showed that the tested compounds (tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane and 1,2-dichloroethane) can be recovered with an efficiency ranging between 70 and 90% over a wide concentration range in the sample. The method can be used for *in situ* analysis of polluted areas, dumping sites, sediments and sands.

---

## INTRODUCTION

The contamination of the environment by halogenated methanes, ethanes and ethenes has been widely investigated owing to the mutagenic effect of some of these compounds [1–4]. The methods used for the determination of these compounds in water samples can be grouped into three different classes: liquid–liquid extraction [5–7], static headspace [8–11] and purge and trap [12–13]. The final concentrated extracts are analysed by gas chromatography (GC) with specific electron-capture and Hall detectors that exhibit a very high sensitivity to these compounds.

The extraction of halogenated compounds from soil samples is carried out with water when their expected concentration is below 1 mg/kg and with methanol (followed by dilution of the extract with water) when the expected concentration is higher [14]. The aqueous solution is then analysed using the methods mentioned above.

The use of the headspace methods with solid samples has also been reported [15–19]. They require

dedicated instruments and a series of replicate samplings in order to apply the so-called multiple headspace extraction. The procedures can therefore hardly be applied in field analyses. A large number of analyses carried out during the decontamination of a site polluted by tetrachloroethylene showed that the application of the described methods is complicated by the wide range of concentrations existing in the samples, which makes it difficult to predict the dilution needed to maintain the injected sample within the linearity range of the detector used. Further, the use of concentration methods for the preparation of liquid extracts that must be strongly diluted for GC analysis is time consuming and may result in unacceptable errors.

The purpose of this paper is to present a simple and reliable method for the analysis of contaminated soil for chlorinated industrial solvents.

## EXPERIMENTAL

Soil samples were obtained from a site (Alessandria, Italy) contaminated by tetrachloroethylene discharged from metal-plating and degreasing operations. The soil samples were drilled and collected from various depths in the contaminated area and were transferred into amber-glass jars which were

---

Correspondence to: Dr T. C. Gerbino, Laboratorio Chimico, Castalia SpA, Via Borzoli 79A/r, I-16161 Genoa, Italy.

closed with PTFE-lined caps and transported to the laboratory in an ice-filled cooler

A reference soil sample was taken from unpolluted area in the same site, dried at 105°C for 24 h, crushed, passed through a 0.075-mm sieve and used for the preparation of the recovery samples

### Chemicals

Stock standard and working standard solutions were prepared by dissolving aliquots of tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, 1,2-dichloroethane (Aldrich, Steinheim, Germany) in pesticide-grade acetone (Merck, Darmstadt, Germany) and diluting with organic-free, deionized, distilled water (Millipore, Bedford, MA, USA)

The normal precautions appropriate for handling volatile analytes were employed [12] and the working standards were checked against certified standards (Supelco, Bellefonte, PA, USA) and reprepared when the deviation was greater than 1%

In recovery studies an accurately weighed 3-g sample of clean reference soil was placed in a glass flask with a ground-glass stopper, then 100 µl of dilute aqueous standard were added with a microsyringe and the flask was stored for 12 h at 4°C to minimize the losses due to evaporation and to allow the chlorinated hydrocarbons to be absorbed by the soil. Possible inhomogeneity of the distribution in the sample is of minor importance because all the spiked amount (3 g) is subjected to the analytical procedure

### Analysis

The analyses were carried out with a Varian (Palo Alto, CA, USA) Model 3600 gas chromatograph equipped with a nickel-63 (8 mCi) electron-capture detector

A glass column (3 m × 1/4 in. I.D.) packed with 10% SP-2100 on 80–100-mesh Supelcoport (Supelco) was used at 60°C with pure nitrogen as the carrier gas at a flow-rate of 30 ml/min. The on-column injector was maintained at 70°C and the detector at 300°C

The pH values of aqueous soil extracts [20] were measured with an Orion Research Model 701 digital pH meter and the total organic carbon was determined by the wet combustion method [20]

### Procedures

The halogenated compounds are extracted from 3 g of soil with 60 ml of acetone–water (5:1) in a 100-ml stoppered flask and agitated for 2 h on a shaker. The flask is then allowed to stand in the dark at room temperature for 24 h. The losses of volatile analytes in the extraction are minimal, as the problem may arise when the partition is between the headspace and water, where the compounds are rather insoluble. The presence of the acetone layer where the compounds are highly soluble strongly reduced the losses due to evaporation and to liquid–headspace partition

An aliquot of clear upper layer (12 ml) is transferred into a 20-ml vial and 2 g of NaCl are added to separate the water layer from the acetone containing the compounds to be determined [21,22]

A 2-ml volume of the acetone layer is taken, dried with anhydrous CaCl<sub>2</sub> and stored in vials with PTFE-lined caps at 4°C for further GC analysis, 3 µl of this solution are injected on to the column

Series of samples spiked with different analyte concentrations were run in duplicate. Analysis of contaminated soils for tetrachloroethylene was performed in accordance with the procedure described above

The recovery of the extracted compounds was determined by comparing the peak area from the analysis of extracts with the peak area on the calibration graph corresponding to the concentration calculated from 100% recovery of the compound in the organic layer

### RESULTS AND DISCUSSION

Tables I–IV show that the recovery of the compounds is greater than 80% (except for 1,2-dichloroethane) and seems to be independent of the concentration in the analysed soil. The lower recovery observed for 1,2-dichloroethane is probably due to the greater volatility of this compound. The lack of a quantitative recovery may be explained by the losses due to handling volatile analytes, but this situation reflects what may happen in authentic samples of contaminated soil, and it is therefore important to follow the same procedure (times, temperatures, volumes) in the calibration and in the analysis in order to minimize the fluctuations

The incomplete recovery of the compounds is al-

TABLE I

RECOVERY OF TETRACHLOROETHYLENE (B P 121°C)  
ADDED TO REFERENCE SOIL AT DIFFERENT LEVELS

Amount added ( $\mu\text{g}/\text{kg}$ )	Recovery (%)	
	Replicate 1	Replicate 2
54	95	91
108	81	83
162	89	93
540	92	87
1080	86	88
1540	76	84
3080	88	84
5400	84	91
Mean $\pm$ S D	87.0 $\pm$ 4.9	

so due to the different partition coefficients between the aqueous and organic layers and to the mutual miscibility of the two solvents [23]. The salting-out effect due to the addition of NaCl increases the recovery to an extent that depends on the solubility in the two layers [24].

The practical detection limit is about 10  $\mu\text{g}/\text{kg}$  for tetrachloroethylene, 100  $\mu\text{g}/\text{kg}$  for 1,1,1-trichloroethane and trichloroethylene and 1 mg/kg for 1,2-dichloroethane, owing to the different responses of the detector to these molecules [25].

The overall linearity of the method also depends on the linear dynamic range of the electron-capture

TABLE III

RECOVERY OF 1,1,1-TRICHLOROETHANE (B P 74°C)  
ADDED TO REFERENCE SOIL AT DIFFERENT LEVELS

Amount added ( $\mu\text{g}/\text{kg}$ )	Recovery (%)	
	Replicate 1	Replicate 2
40	74	70
80	76	87
120	99	99
400	76	85
800	74	80
1200	77	78
2400	84	88
4000	88	88
Mean $\pm$ S D	82.6 $\pm$ 8.6	

detector, which is a function of the analysed compound and generally ranges within 2-3 orders of magnitude [25]. When the detector signal is above the linear range, a plateau region is observed on the sensitivity plot, an apparent concentration lower than the true value is found and the correct quantitative analysis requires a suitable dilution of the extract. If the concentrations of the various compounds differ widely, two or more samples with different dilution factors should be injected in order to detect each compound within its linearity range.

The high recovery and satisfactory reproducibility over a wide concentration range, from a few  $\mu\text{g}/$

TABLE II

RECOVERY OF TRICHLOROETHYLENE (B P 87°C)  
ADDED TO REFERENCE SOIL AT DIFFERENT LEVELS

Amount added ( $\mu\text{g}/\text{kg}$ )	Recovery (%)	
	Replicate 1	Replicate 2
44	83	78
88	91	82
176	89	83
438	81	84
876	86	90
1314	96	94
2628	84	86
4380	79	90
Mean $\pm$ S D	86.0 $\pm$ 5.2	

TABLE IV

RECOVERY OF 1,2-DICHLOROETHANE (B P 57.2°C)  
ADDED TO REFERENCE SOIL AT DIFFERENT LEVELS

Amount added ( $\mu\text{g}/\text{kg}$ )	Recovery (%)	
	Replicate 1	Replicate 2
3750	62	56
7500	61	68
11 250	81	78
37 500	67	75
75 000	89	91
150 000	83	88
300 000	77	78
375 000	69	64
Mean $\pm$ S D	74.0 $\pm$ 10.7	

TABLE V

REMOVAL OF TETRACHLOROETHYLENE FROM CONTAMINATED SOILS AS FUNCTION OF EXTRACTION TIME, WITH pH AND TOC VALUES OF THE SOILS EXAMINED

Sample No	Depth (m)	pH	TOC (mg/kg)	Amount extracted ( $\mu\text{g}/\text{kg}$ )		
				2 h	24 h	48 h
1	1-1.40	7.76	3201	2245	5089	5239
2	2-2.40	8.00	1656	2305	4742	4775
3	3-3.40	7.66	4505	9922	28 228	26 884
4	4-4.40	7.38	3954	13 423	34 182	38 354
5	5-5.40	7.70	2878	6106	7549	7388
6	6-6.40	7.73	618	149	646	684
7	7-7.40	8.61	873	681	1238	1375
8	8-8.40	7.71	691	76	173	170
9	9-9.50	7.83	564	16	67	70

kg to hundreds of mg/kg, show that the method can be used for the extraction of chlorinated compounds from soil polluted in different environments and therefore containing variable amounts of contaminants, *e.g.*, spill-over of solvents from chemical plants, reclaimed areas contaminated by industrial wastes and dumping sites. The experiments with soil samples spiked with known amounts of standards showed that the extraction is virtually complete after 2 h of extraction on a shaker.

It has been reported [26] that the sorbed compounds in contaminated soil may be highly resistant to desorption. The slow release of trichloroethylene from contaminated soil requires an extended equilibration time for extraction, the equilibrium steady state is reached within 24 h [27,28].

Table V reports the recovery efficiency for tetrachloroethylene from various samples of contaminated soil as a function of extraction time and confirms that the equilibrium between the extracted tetrachloroethylene and that still retained in the soil is complete within 24 h. This behaviour does not depend on the pH and total organic carbon (TOC) values (Table V), which has been correlated with the sorption of organic compounds in soils and sediments [29-31]. This is expected for pH as a change in pH should not affect the desorption of non-polar tetrachloroethylene.

It has been well documented that there is a linear relationship between soil organic carbon and partition coefficients, but when the organic content is low (about 0.1%), the organic fraction is not a valid

predictor of the sorption of organic compounds and other sorbent properties, such as specific surface area and cation-exchange capacity, may control the adsorption of non-polar organic compounds.

The available literature data [28] and the experimental results confirm that a 24-h extraction time is preferred in order to ensure the complete recovery of the halogenated compounds from contaminated soil.

#### CONCLUSIONS

The suggested method permits the determination of chlorinated compounds in polluted soil to be carried out in a short time and with high and reproducible recoveries. The compounds can be analysed over a wide range of concentrations without the problems connected with the extraction methods obtained by modifying the procedures used for the analysis of liquid samples and without requiring dedicated instruments such as for multiple head-space extraction.

The simplicity of the procedure permits its application in field conditions mainly when a rapid analysis is necessary to evaluate the performance of remedial measures by conventional treatment or biological techniques, and is independent of variable soil parameters such as pH and TOC.

Further experiments are in progress in order to evaluate whether the proposed method can be applied to the analysis of sites that have been contaminated for many years ( $\geq 10$  years), where the ha-

logenated compounds may be strongly adsorbed. It has in fact been reported [27,29,32] that the recovery and efficiency may depend on the age of the polluted sample

## REFERENCES

- 1 M Mercier, M Laus and J de Garlache, in M Kirsch-Volders (Editor), *Mutagenicity, Carcinogenicity and Teratogenicity of Industrial Pollutants*, Plenum Press, New York and London, 1984
- 2 International Agency for Research on Carcinogens, *Some Halogenated Hydrocarbons*, Monograph No 20, IARC, Lyon, 1979
- 3 V F Simmon and R G Tardiff, in R L Jolly, H Gorcher and D H Hamilton Jr (Editors), *Water Chlorination 2*, Ann Arbor Sci Publ. Ann Arbor, MI, 1978, p 471
- 4 S Kanitz, G Castello, T C Gerbino, G Gallelli and V Patrone, *Tec Sanit*, 23 (1985) 859
- 5 J P Mieux, *J Am Water Works Assoc*, 69 (1977) 60
- 6 J J Richard and G A Junk, *J Am Water Works Assoc*, 69 (1977) 62
- 7 H Norin and L Ronberg, *Water Res*, 14 (1980) 1397
- 8 E A Dietz, Jr and K F Singley, *Anal Chem*, 51 (1979) 1809
- 9 S L Friant and I H Suffet, *Anal Chem*, 51 (1979) 2167
- 10 J Drozd and J Novak, *J Chromatogr*, 165 (1979) 141
- 11 G Castello, T C Gerbino and S Kanitz, *J Chromatogr*, 247 (1982) 263
- 12 US Environmental Protection Agency, *Method 601, Purgeable Halocarbons*, 40 CFR, Part 136 43261, *Fed Regis* 49, No 209 (1984)
- 13 T A Bellar and J J Lichtenberg, *J Am Water Works Assoc*, 66 (1974) 739
- 14 US Environmental Protection Agency *Test Methods for Evaluating Solid Waste (SW 846), Method 5030*, Office of Solid Waste and Emergency Response, Washington, DC, 1986
- 15 M J Charles and M S Simmons, *Anal Chem*, 59 (1987) 1217
- 16 B Kolb, P Pospisil and M Auer, *Chromatographia*, 19 (1984) 113
- 17 B Kolb and P Pospisil, *Chromatographia*, 10 (1977) 705
- 18 B Kolb, *Chromatographia*, 15 (1982) 587
- 19 M R Milana, A Maggio, M Denaro, R Feliciani and L Gramiccioni, *J Chromatogr*, 442 (1991) 205
- 20 Societa Italiana della Scienza del Suolo, *Metodi Normalizzati di Analisi del Suolo*, Edagricole, Bologna, 1985
- 21 S G Heuser and K A Scudamore, *J Sci Food Agric*, 20 (1969) 566
- 22 Report by Panel on Fumigant Residues in Grain, *Analyst (London)*, 99 (1974) 570
- 23 D C Legget, T F Jenkins, and P H Hyares, *Anal Chem*, 62 (1990) 1355
- 24 T F Jenkins and P H Hyares, *Anal Chem*, 62 (1991) 1341
- 25 G Castello, T C Gerbino and S Kanitz, *J Chromatogr*, 351 (1986) 165
- 26 S H Steinberg, J J Pignatello and B L Sawhney, *Environ Sci Technol*, 21 (1987) 1201
- 27 J A Smith, C T Chiou, J A Kammer and D E Kile, *Environ Sci Technol*, 24 (1990) 676
- 28 S G Pavlositathis and K Jaglad, *Environ Sci Technol*, 25 (1991) 274
- 29 J W Hamaker and J H Thompson, in C A I Goring and G L Hammer (Editor), *Organic Chemicals in the Soil Environment*, Marcel Dekker, New York, 1972, p 49
- 30 S W Karickhoff, D S Brown and T A Scott, *Water Res*, 13 (1979) 241
- 31 R P Schwarzenbach and J Westell, *Environ Sci Technol*, 5 (1981) 1360
- 32 W J Weder and T C Voice, *Water Res*, 17 (1983) 1433