Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 66 (2005) 249–252

Talanta

www.elsevier.com/locate/talanta

Prediction of solvents extraction—the organochlorine pesticides in soil using solubility parameter

Yin Hai Lang[a,*], Zheng Mei Cao[b], Xin Jiang[c]

[a] *College of Environmental Science and Engineering, Ocean University of China, Qingdao 266003, China*
[b] *Institute of Environment Science, Qingdao 266003, China*
[c] *Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China*

Received 15 October 2004; received in revised form 19 November 2004; accepted 19 November 2004
Available online 24 December 2004

Abstract

Prediction of the optimal extraction solvent based on the solubility parameter to extract the typical organochlorine pesticides from Jiangxi red soil was reported in this paper. Hildebrand solubility parameters, including dispersion coefficient (δ_d), polarity (δ_p) and hydrogen bonding (δ_h), of extraction solvents (including hexane, dichloromethane, hexane/methanol (4:1, v/v), hexane/acetone (1:1, v/v), hexane/dichloromethane (1:1, v/v) and organochlorine pesticides were calculated using group contribution method. The solvents, such as hexane/methanol (4:1, v/v) and hexane/acetone (1:1, v/v) were selected as ideal extraction solvents to extract *o,p*′-DDT *o,p*′-DDE and *o,p*′-DDD with high recoveries (>82%), furthermore, these solvents can be used to extract α-endosulfan, Endrin and HCB with the reliable recoveries (>75%). The estimated finding by solubility parameters was supported by the results of soxhlet extraction.

Keywords: Solubility parameters; Soxhlet extraction; Organic solvents; Organochlorine pesticides

1. Introduction

Organochlorine pesticides, such as HCHs, DDTs, HCB, Endrin, are widely used to control diseases and improve the yield of crop in agriculture [1,2]. The production and usage of organochlorine pesticides has been banned in China since 1980s [3]. However, the noticeable residues of these compounds are still detected in soil for their high persistence [2].

For example, the concentration of HCHs range from 0.18 to 0.25 mg kg^{-1} and DDTs range from 0.22 to 0.27 mg kg^{-1}. For detection of the organochlorine pesticides in soil, different extraction methods and analytical techniques have been developed recently [4]. Selection of effective extraction solvents is an important part of extraction approaches. Hildebrand solubility parameter provides an easy numerical method of rapidly predicting the extent of interaction between materials, particularly liquids and polymers [5–7]. The most well known practical use of the solubility parameter has been applied to select solvents in rubber, plastic and paint manufacturing, as well as describing the solubility of some solutes in supercritical fluids and predicting effective extraction solvent for the extraction process [8,9].

In this paper, Hildebrand solubility parameter was applied to select the solvents for simultaneous extracting the typical organochlorine pesticides in Jiangxi red soil. Furthermore, the performance of extraction solvents predicted with solubility parameter was evaluated by experiment of soxhlet extraction.

2. Materials and methods

2.1. Reagents and sampling

The mixtures of six organochlorine pesticides in hexane were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

---

* Corresponding author. Tel.: +86 532 8643667; fax: +86 532 2032058.
E-mail address: yhlang@ouc.edu.cn (Y.H. Lang).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.11.018

Deionized water was obtained from a Mili-Q system (Millipore, USA). Hexane, methanol, dichloromethane and acetone were supplied by TEDIA (USA). All glasswares used in the study were washed with liquid soap and rinsed properly with distilled water, and then baked in the oven at 100 °C for 12 h.

Red soil obtained from Jiangxi, China, was used in the study. Soil sample was air dried and sieved with 2 mm sieve to remove debris and coarse particles. The main characteristics of soil are pH 5.5, clay 16.0% and organic matter 0.43%. Soil samples were prepared by spiking standard solutions to get final concentrations (100 ng g^{-1}). The soils were shaken in an orbital shaker to homogenize and evaporate the solvent at room temperature.

2.2. *Chromatographic conditions*

Gas chromatographic analyses were performed with a Hewlett Packard 6890 gas chromatograph equipped with a ^{63}Ni electron capture detector and HP 7683 autosampler. The column used was HP 5 (30 m × 0.32 mm i.d. × 0.25 μm film). The split/splitless injector and detector temperatures were set at 220 and 280 °C, respectively. The carrier gas was nitrogen. The initial oven temperature was kept at 60 °C for 1 min, which was increased to 140 °C at 20 °C min^{-1}, held for 5 min, and then raised to 280 °C at 12 °C min^{-1} and kept for 4 min. The detector's linearity for direct injection (1 μl) of standard solutions was checked and detector calibration curves were obtained. Pesticides quantification was performed by external standard method.

2.3. *Analytical method*

Concentration of organochlorine pesticides in the spiked red soil was determined using soxhlet extraction procedure. A 15 g amount of soil sample was placed into a thimble filter and the organochlorine pesticides were extracted with following solvents for 24 h: hexane, dichloromethane, hexane/methanol (4:1, v/v), hexane/acetone (1:1, v/v), hexane/dichloromethane (1:1, v/v), respectively. After the extraction, the extract was preconcentrated to 1 ml on a rotary evaporator. Anhydrous sodium sulfate was added to the silica gel cartridge prior to the clean-up procedure. The extract was then added to the column and eluted with 8 ml of dichloromethane/hexane (1:99, v/v) and collected in a 25 ml pear shaped flask. Finally, the elution was concentrated by a rotary evaporator and further concentrated with a gentle nitrogen stream to 100 μl.

3. Results and discussion

3.1. *Calculation of Hildebrand solubility parameter for solvents and analytes*

Hildebrand solubility parameter of solvents and analytes can be divided into three components: dispersion coefficient (δ_d), polarity (δ_p) and hydrogen bonding (δ_h) [10]. Many empirical correlations for predicting the solubility parameters have been mentioned [7,11]. An earlier developed method for calculating the solubility parameters in terms of energy unit using group contributions theory. The method for measuring the solubility parameters of the solvents and analytes was previously reported [12,13]. The values calculated by the empirical correlations were reported almost the same as those obtained experimentally [8]. Fraction parameters for solvents and analytes can be calculated by following main equations and plotted on a triangular graph.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2, \qquad f_d = \delta_d^2 \frac{100}{(\delta_d^2 + \delta_p^2 + \delta_h^2)},$$

$$f_p = \delta_p^2 \frac{100}{(\delta_d^2 + \delta_p^2 + \delta_h^2)}, \qquad f_h = \delta_h^2 \frac{100}{(\delta_d^2 + \delta_p^2 + \delta_h^2)}$$

The calculated values for dispersion coefficient (δ_d), polarity (δ_p), hydrogen bonding (δ_h), total Hildebrand solubility parameter (δ) and fractional parameters for the solvents, mixtures of solvents and analytes were showed in Table 1.

The position of the solvents and analytes in a triangular graph was presented in Fig. 1. In this plot, the

Table 1
Hildebrand solubility parameter of individual components and fractional parameters for solvents and analytes

	Dispersion coefficient		Polarity		Hydrogen bonding		Total Hildebrand solubility parameter
	δ_d ($J^{1/2}$ $cm^{-3/2}$)	f_d	δ_p ($J^{1/2}$ $cm^{-3/2}$)	f_p	δ_h ($J^{1/2}$ $cm^{-3/2}$)	f_h	δ_t ($J^{1/2}$ $cm^{-3/2}$)
Hexane	14.90	100	0.00	0	0.00	0	14.90
Dichloromethane	18.20	81.18	6.30	9.73	6.20	9.42	20.20
Hexane/methanol (4:1, v/v)	14.94	89.59	2.46	2.43	4.46	7.98	15.78
Hexane/acetone (1:1, v/v)	15.20	85.47	5.20	10.00	3.50	4.53	16.44
Hexane/DCM (1:1, v/v)	16.55	93.34	3.15	3.38	3.10	3.28	17.13
HCB	28.70	50.08	28.30	48.69	4.50	1.23	40.56
Endrin	12.54	52.92	10.43	36.61	5.58	10.48	17.24
α-Endosulfan	15.37	45.53	16.02	49.46	5.10	5.01	22.78
o,p′-DDT	23.46	84.00	9.80	14.66	3.12	1.49	25.60
o,p′-DDE	24.97	89.01	8.28	9.79	2.90	1.20	26.47
o,p′-DDD	21.60	86.68	7.80	11.30	2.82	1.48	23.20

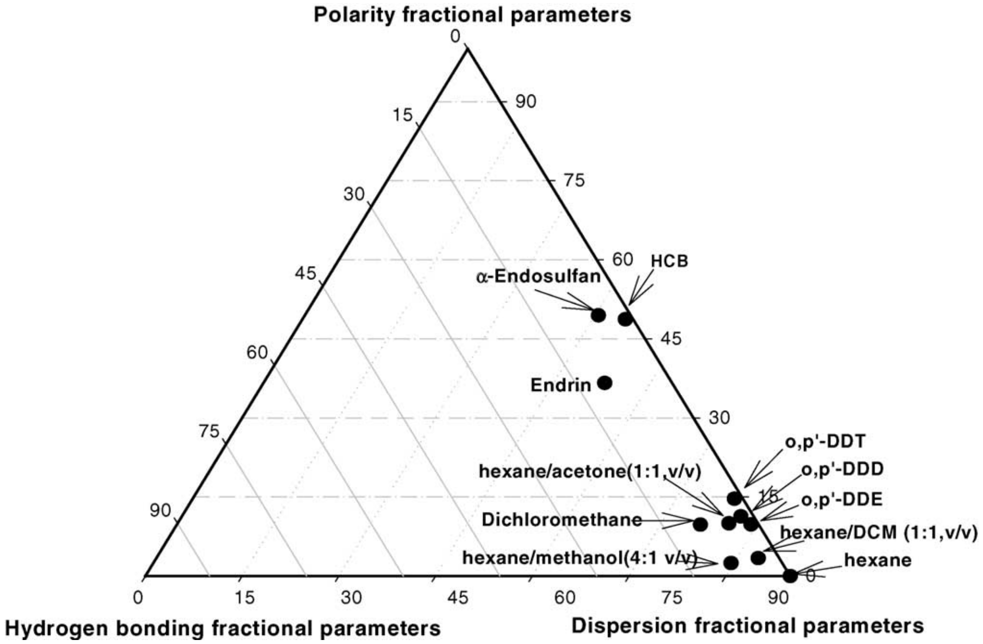

Fig. 1. The fractional parameters graph of three solubility scales of solvents and analytes.

position of dichloromethane, hexane/methanol (4:1, v/v), hexane/acetone (1:1, v/v), hexane/dichloromethane (1:1, v/v) is near to the position of *o,p*′-DDT, *o,p*′-DDE and *o,p*′-DDD and is far away the position of α-endosulfan, Endrin and HCB. It is well known that GC-μECD is high sensitive to halogenated organic compounds. Halogenated solvents were avoided to use in organochlorine pesticides analysis. Therefore, hexane/methanol (4:1, v/v) and hexane/acetone (1:1, v/v) were predicted to be the ideal solvents for simultaneous extraction organochlorine pesticides in soil.

3.2. Effect of solvents on the extraction of organochlorine pesticides in soil

Extraction organochlorine pesticides from soil is very complicate process affected by many factors, such as characters of soil matrix, the physical–chemical properties of organochlorine pesticides, selection of different solvents, the interaction of analytes with soil matrix and aged time of analytes with soil. In this study, five extraction solvents, namely hexane, dichloromethane, hexane/methanol (4:1, v/v), hexane/acetone (1:1, v/v) and hexane/dichloromethane (1:1,

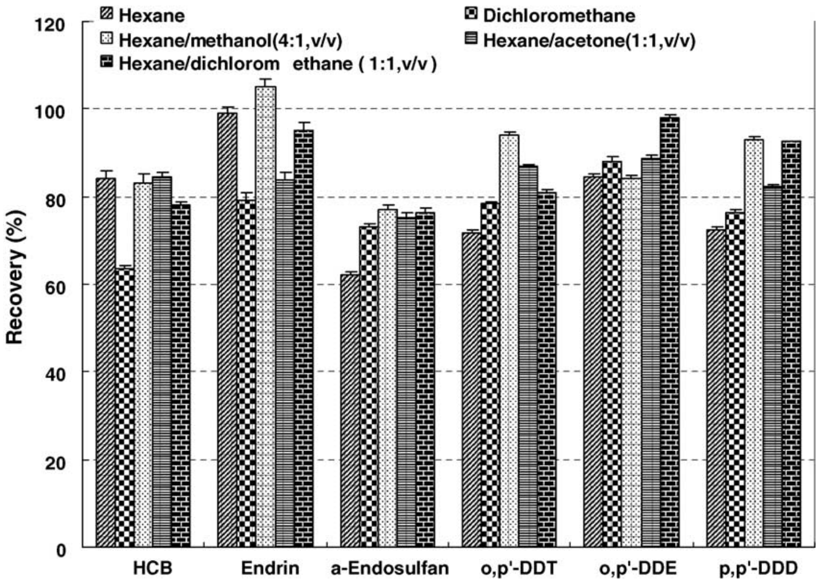

Fig. 2. Effect of five solvents on the extraction organochlorine pesticides in red soil of Jiangxi.

v/v), were selected to simultaneous extraction organochlorine pesticides in Jiangxi red soil with soxhlet extraction (Fig. 2). It is observed that the higher recoveries of *o,p*′-DDT, *o,p*′-DDE and *o,p*′-DDD are obtained with hexane/methanol (4:1, v/v) (ranged from 84.0 to 94.0%) and hexane/acetone (1:1, v/v) (ranged from 82.2 to 88.9%). It would also be found that the recoveries of α-endosulfan, Endrin and HCB obtained with hexane/methanol (4:1, v/v) and hexane/acetone (1:1, v/v) are higher than 75%, which are suited to environmental analysis. The data of soxhlet extraction experiment has been confirmed the prediction conclusion with Hildebrand solubility parameter.

4. Conclusion

The solubility parameters, including dispersion coefficient (δ_d), polarity (δ_p) and hydrogen bonding (δ_h), of extraction solvents, such as hexane, dichloromethane, hexane/methanol (4:1, v/v), hexane/acetone (1:1, v/v) and hexane/dichloromethane (1:1, v/v), and organochlorine pesticides were estimated using group contribution method, and then prediction the optimal extraction solvents to extract the typical organochlorine pesticides from the Jiangxi red soil. The solvents, namely hexane/methanol (4:1, v/v) and hexane/acetone (1:1, v/v), were selected as ideal extraction solvents to extract *o,p*′-DDT, *o,p*′-DDE and *o,p*′-DDD with high recoveries (>82%), furthermore, these solvents can be used to extract α-endosulfan, Endrin and HCB with the reliable recoveries (>75%). The results of soxhlet extraction have confirmed the finding of solubility parameters prediction. Optimization of the selection of the solvents to extraction organochlorine pesticides in soil depends on many environmental factors. Prediction of extraction solvents with Hildebrand solubility parameter may be limited by the interaction of analytes with soil matrix or the formation of high-octane covalent binding, in particular the extraction bonding pesticides from soil. However, Hildebrand solubility parameter provides a simple method for preliminary predicting the extraction solvents in environmental analysis and will be a subject in further development of extraction techniques.

Acknowledgements

The authors thank Dr. Dieter Martens for valuable technical assistance.

References

[1] E.C. Voldner, Y.F. Li, Sci. Total Environ. 160 (1995) 201–210.
[2] K.L. Willett, E.M. Ulrich, R.A. Hites, Environ. Sci. Technol. 32 (1998) 2197–2207.
[3] Y.F. Li, D.J. Cai, A. Singh, Arch. Environ. Contam. Toxicol. 35 (1998) 688–697.
[4] J.R. Dean, Extraction Methods for Environmental Analysis, Wiley, Chichester, UK, 1998.
[5] J.H. Hildebrand, R.L. Scott, The Solubility of Nonelectrolytes, third ed., Reinbold, New York, 1950.
[6] J.H. Hildebrand, J.M. Prausnitz, R.L. Scott, Regular and Related Solutions: The Solubility of Gases Liquids and Solid, Van Nostrand Reinhold, NY, 1970.
[7] C.M. Hansen, Prog. Org. Coat. 51 (2004) 77–84.
[8] N.O. Elbashir, S.M. Al-Zahrani, M.I. Abdul Mutalib, A.E. Abasaeed, Chem. Eng. Process. 41 (2002) 765–769.
[9] A.E. Bozdogan, Polymer 44 (2003) 6427–6430.
[10] C.M. Hansen, The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient, Denish Technical Press, Copenhagen, 1967.
[11] R. Wisniewski, E. Smieszek, E. Kaminska, Prog. Org. Coat. 26 (1995) 265–274.
[12] A.F.M. Barton, The Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, Florida, 1983.
[13] D.W. van Krevelen, Properties of Polymers: Their Estimation and Correlation with Chemical Structure, fourth ed., Elsevier, New York, 1991.