



Analysis of Acid Organic Compounds in Soil by Complexation Coupled with *in situ* Derivatization

LI ZHANG, CHENLING ZHANG, JIANYE GUI, YONGTAO ZHANG*, XIAOYA LI, GUOXING ZHAO and LAISHENG TIAN

Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, No. 92 Zhongshan dong Road, Zhengding 050803, P.R. China

*Corresponding author: Tel./Fax: +86 311 88017401; E-mail: icpzytws@126.com

Received: 7 January 2014;

Accepted: 29 April 2014;

Published online: 10 January 2015;

AJC-16604

A method that *in situ* derivatization and extraction of acidic organic compounds in soil was developed with Na₄-EDTA as complexing agent and 2,3,4,5,6-pentafluoro-benzyl bromide as derivatization agent. Derivatization products were sensitively determined by gas chromatography-negative chemical ionization mass spectrometry. Acidic organic compounds reacted with Na₄-EDTA (carbonyl group) to form a complex compound, so that the polarity was reduced. On complexation, derivatization and extraction of acidic organic compounds in 4 g soil were performed in 4 mL acetone by the use of ultrasonic technique. Derivatization and reverse reaction of complexation reinforced each other. It was more effectively under action of ultrasonic, so a single extraction within 40 min could get preferable recovery. Soil matrix would not affect complexation and *in situ* derivatization when total organic carbon content was lower than 3 %. In the optimal conditions, the calibration curves showed good linearity in a wide range of 5-200 µg/kg with correlation coefficients higher than 0.99. The detection limits (S/N = 3) were less than 1 µg/kg. The spiked recoveries of different concentrations ranged from 75 to 107 % with relative standard deviations of 8-13 %. This method was suitable for acid organic compounds detection in soil, solid and plant samples.

Keywords: Complexation, Soil, Aromatic acids, Gas chromatography-negative chemical ionization mass spectrometry.

INTRODUCTION

Acid organic compound is one organic compound with high polarity, whose strong polar characteristics make it difficult to extract. King¹ proposed the extraction and separation method based on reversible complex reaction. The main detaching objects are organic Lewis acid or Lewis base. The present reports²⁻⁴ were more about polar organic compounds complexing extraction research in dilute solution, whose complexing agent was usually neutral and acid phosphorus-containing complexing agent. As for acid organic compounds, derivatization was used to realize detection of gas chromatography. Since it is difficult to control derivatization reagent amount and complex matrix in large volume solvent, the main technical report^{5,6} in related reports is extraction first and derivatization followed; and combination of both the steps do simplify the analysis routine. Ultrasonic extraction⁷⁻¹², a traditional and classical extraction technology, has advantages of no pollution, high efficiency and short time. However, ultrasonic technique is relative difficult to extract polar organic compounds. This method focuses on the combination of complexing force, derivatization force and ultrasonic force to ensure high extraction efficiency and makes ultrasonic extraction a method of the low cost, most efficient, easy and require, less time.

This method adopted combination of complexation, derivatization reaction and ultrasonic extraction, together with negative chemical ionization mass spectrometry, with Na₄-EDTA as complexing agent, pentafluoro-benzyl bromide as derivatization agent, achieved high accuracy detection of acid organic compounds in soil.

EXPERIMENTAL

Gas chromatography-Mass spectrometry (GC-MS QP 2010, Shimadzu Corporation) equipped with negative chemical ionization; CNC ultrasonic cleaner (KQ-700DV, Kunshan city Ultrasonic Instrument Co., Ltd.), nitrogen analyzer, mortar, silica gel column.

Acetone, pentafluoro-benzyl bromide (99.5 %), Na₂-EDTA, Na₄EDTA, potassium carbonate, quartz sand carboxylic acid: dalapon, 3,5-dichloro-benzoic acid, dicamba, MCPA, chloramben; phenolic acid: 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachloro-phenol, pentachlorophenol (all purchased from Dr. Ehrenstorfer company).

Chromatography and mass spectrometry conditions: HP-5MS chromatograph column (30 m × 0.25 mm × 0.25 µm); The oven temperature started at 90 °C and was heated to 200 °C at 30 °C/min and then was heated to 300 °C at 10 °C/min (hold

for 2 min); sample inlet temperature: 230 °C; splitless; inlet volume: 1 µL.

Negative chemical ionization; reaction gas: methane; ionization energy: 70 eV; ion source temperature: 200 °C; selected ion monitoring.

Sample pretreatment: 4 g soil sample, 2 g quartz sand, 0.2 g Na₄-EDTA and 1 mL purified water, were thoroughly mixed in mortar and then placed at normal temperature to evaporate moisture (approximately 24-36 h). The mixture was transferred in a derivatization bottle with 4 mL acetone, 200 µL 2,3,4,5,6-pentafluorobenzyl bromide solution (30 %) and 100 µL K₂CO₃ solution (30 %). The bottle was then capped and placed in a ultrasonic chamber, with temperature 65 °C, power wattage 490 watts and time 40 min.

One milliliter supernatant fluid was transferred to a concentrated bottle, condensed to nearly dryness with nitrogen flow. It was dissolved with 1 mL *n*-hexane and was again condensed to nearly dryness. It was dissolved with 3 mL *n*-hexane, transferred to a silica gel column, washed with 3 mL *n*-hexane-toluene (9:1, v/v) and eluted by *n*-hexane-toluene (1:9, v/v). Then the elute was condensed to 1 mL, filtered with a 0.2 µm membrane and analyzed by GC-NCI-MS.

RESULTS AND DISCUSSION

Complexation conditions: Carboxylic acids and phenol compounds all belong to Lewis acids and the complexing agent should be Lewis base¹. In this study, Na₂-EDTA and Na₄-EDTA were employed as complexing agent. These two compounds formed negative charge group in water, making the electron-donating ability stronger. Four spiked soil samples (50 µg/kg) were pretreated according to four different methods and the recovery result was showed in Table-1. Since dissolution of Na₄-EDTA in water is much easier than Na₂-EDTA, it is more suitable for chelating extraction.

Extraction and derivatization conditions: Since it required a large volume solvent in Soxhlet extraction, extraction after shaking and accelerated solvent extraction, it was difficult to control the derivatization reagent amount in simultaneous extraction and derivatization. Ultrasonic technique do simplify the *in situ* derivatization of compounds in soil. In this study, extraction and derivatization of chemical compounds in 4 g soil (complexation system was about 6.3 g) was conducted in 4 mL solvent.

To cope with negative chemical ionization, 2,3,4,5,6-pentafluorobenzyl bromide was employed as derivatization reagent. According to EPA method 8151A, usage amount of 2,3,4,5,6-pentafluorobenzyl bromide (30 %) and K₂CO₃ (30 %) were appropriately increased to 200 and 100 µL. Good derivatization effects were achieved at 60-70 °C. The efficiency reached maximum in 35-45 min, which was far shorter than 180 min static derivatization in EPA 8151A. It proved that ultrasonic technology promoted derivatization. With the increased extraction power, the extraction and derivatization time would decrease and the efficiency would increase at the same time. However, excessive extraction power made extraction matrix complicated and the detection difficult. It was concluded that 490 W was the most suitable extraction power. Derivatization and extraction reaction was set at 65 °C for 40 min to avoid solution loss and extract matrix complexity.

Interaction of complexation and derivatization: Spiked experiments of four schemes (seven samples each project, with concentration 20 µg/kg) was conducted in the study. As is shown in scheme A of Table-2, it was not possible of *in situ* derivatization without complexation reaction. The recovery result of scheme B was low since complexation reaction and derivatization were carried out sequentially. In scheme C, simultaneous derivatization and complexation reaction promoted each other, thus single extraction within 40 min could get the same excellent extraction efficiency as scheme D (EPA8151A). Meanwhile, it stated that simultaneous derivatization and reverse reaction of complexation could enforce the *in situ* derivatization and extraction.

Influence of total organic carbon (TOC) on recovery: Both complexation and derivatization were reactions between special functional groups, so other compounds except those with carboxyl and hydroxyl groups in soil would not react with complexing reagent and derivatization reagent. Total organic carbon content study was carried out in the range of 0.20-4 %. When TOC content was lower than 3 %, soil matrix had no effect on recovery. When TOC content was higher than 3 %, phenol recovery would decrease obviously. Therefore, it was necessary to know the sample sources. In the normal case, TOC content of agriculture and forestry soil samples was lower than 2 %. As to these samples TOC content higher than 3 %, sample scale should be lessened appropriately.

Qualitative parameters negative chemical ionization: After derivatization, fluorine introduction with strong

TABLE-1
CAPABILITY CONTRAST BETWEEN DIFFERENT COMPLEXING CONDITIONS

Compound	Recovery (%)			
	Soil	Soil mixed with Na ₄ -EDTA	Soil mixed with Na ₂ -EDTA and 1 mL water	Soil mixed with Na ₄ -EDTA and 1 mL water
Dalapon	13.3	24.1	103.7	106.8
2,4-Dichlorophenol	10.4	19.6	89.4	87.6
2,4,6-trichlorophenol	15.2	17.1	91.0	92.4
3,5-dichlorobenzoic acid	13.5	22.3	95.8	91.5
Dicamba	18.1	24.1	98.7	94.6
MCPA	12.2	13.6	106.4	99.2
2,3,4,6-tetrachlorophenol	16.4	17.8	92.3	94.3
Pentachlorophenol	17.7	23.4	86.6	88.8
Chloramben	17.1	19.8	104.4	100.1

Derivatization was conducted after complexation reaction

TABLE-2
CONTERINFLUENCE OF COMPLEXATION AND DERIVATIZATION

Compound	Scheme-A		Scheme-B		Scheme-C		Scheme-D	
	Recovery (%)	RSD	Recovery (%)	RSD	Recovery (%)	RSD	Recovery (%)	RSD
Dalapon	12.9	14.6.3	72.8	9.7	106.8	8.7	97.6	10.1
2,4-Dichlorophenol	10.4	12.3	66.2	13.1	87.6	9.2	86.4	11.2
2,4,6-trichlorophenol	15.2	11.2	66.4	12.4	92.4	7.3	88.4	10.4
3,5-dichlorobenzoic acid	13.5	9.8	69.8	8.6	91.5	7.6	93.6	9.4
Dicamba	18.1	12.0	71.4	10.1	94.6	7.9	90.1	8.1
MCPA	12.2	9.6	76.3	8.8	99.2	8.4	100.6	9.7
2,3,4,6-tetrachlorophenol	16.4	13.1	68.8	11.4	94.3	9.6	88.4	10.8
Pentachlorophenol	17.7	10.6	74.7	11.6	108.8	9.7	100.5	8.4
Chloramben	17.1	9.7	80.1	10.0	100.1	6.8	92.7	8.0

Scheme-A: *in situ* ultrasonic assisted derivatization without complexation. Scheme-B: Derivatization after ultrasonic assisted extraction. Scheme-C: Simultaneous extraction and derivatization with complexing and derivatization agents. Scheme-D: According to EPA 8151 A method

TABLE-3
MAIN QUALITATIVE PARAMETERS OF THE DERIVATIZATION PRODUCTS

Compound	Retention time (min)	Molecular weight of derivatized compound	Quantitative ion (<i>m/z</i>)	Reference ion (<i>m/z</i>)
Dalapon	4.080	322	141	143, 107, 109
2,4-Dichlorophenol	6.340	343	161	163
2,4,6-trichlorophenol	6.835	377	197	195
3,5-dichlorobenzoic acid	7.320	370	189	191, 193, 190
Dicamba	8.143	384	203	205, 159, 161
MCPA	8.230	400	219	221, 175, 177
2,3,4,6-tetrachlorophenol	8.242	412	231	229, 233
Pentachlorophenol	9.498	448	267	269, 271, 270
Chloramben	10.27	434	253	255, 257, 256

electronegativity, made it suitable for negative chemical ionization (NCI) detection. In addition, compounds may produce [M-1] fragments (M for molecular weight) in the soft ionization condition. So these fragments differed from each other, the negative chemical ionization detection mode was more selective and more accurate. Quantitative ions and qualitative ions of compounds were shown in Table-3.

Detection limits, linear range and correlation coefficients: Standard solutions, ranging from 2.5 to 200 µg/kg, were tested after extraction and derivatization; correlation coefficients (r^2) were all higher than 0.990; the limits of detection (LODs, defined as $S/N = 3$) were lower than 0.4 µg/kg.

Recovery and precision: Three levels of matrix and concentrations, 5 µg/kg (TOC content 0.3 %), 25 µg/kg (TOC content 1.1 %) and 100 µg/kg (TOC content 1.8 %), were prepared and tested according to experiment procedure. The spiked recoveries ranged from 75 to 107 % with relative standard deviations of 5-13 %.

Conclusion

In this study, a novel method that complexation coupled with *in situ* derivatization of acidic organic compounds in soil was developed. The potential of ultrasonic extraction was excavated enormously. Derivatization and reverse reaction of complexation reinforced each other under the ultrasonic effect. Therefore single extraction within 40 min could get preferable recovery. In addition, the elute could be analyzed without concentration. The sample pretreatment method combining

with developed GC-NCI-MS method, could satisfy the quantitative determination of acidic organic compounds in soil.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support from the National Natural Science Foundation of China (No. 41102151). Thanks are also due to corresponding author Yongtao Zhang for his support to research work and ZHANG Gui-Qin from Weichai Power Ltd. for the paper translation and polishing.

REFERENCES

1. C.J. King, ed: R.W. Rowseau, Handbook of Separation Process Technology, John Wiley & Sons, New York, pp. 760-774 (1987).
2. L.A. Tung and C.J. King, *Ind. Eng. Chem. Res.*, **33**, 3217 (1994).
3. Y.Y. Yang, J.H. Guo and Y.Y. Dai, *CIESC J.*, **48**, 706 (1997).
4. Y.Y. Huang, J. Zhang and Y.Y. Dai, *Chinese Environ. Chem.*, **18**, 136 (2000).
5. U.S. EPA Method 8151A, National Technical Information Service, Washington, DC (1997).
6. J.Y. Gui, L. Zang, J.X. Qi, Y.T. Zang, H.Y. Zuo, X.Y. Li and L. Zhang, *Chinese J. Anal. Chem.*, **38**, 1177 (2010).
7. J. Chen and J. Pawliszyn, *Anal. Chem.*, **67**, 2530 (1995).
8. M.D. David, S. Campbell and Q.X. Li, *Anal. Chem.*, **72**, 3665 (2000).
9. M.D. Esclapez, J.V. Garcia-Perez, A. Mulet and J.A. Cárcel, *Food Eng. Rev.*, **3**, 108 (2011).
10. J.C. Shen and X.G. Shao, *Anal. Bioanal. Chem.*, **383**, 1003 (2005).
11. P. Tolgyessy, B. Vrana and K. Silharova, *Chromatographia*, **76**, 177 (2013).
12. U.S.E.P.A. Method, 3550B, Ultrasonic Extraction, Washington, DC (1997).