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One-step Extraction and Sensitive Measurement of Polar and Non-Polar Pollutants Simultaneously in Soil Using Modified Ultrasonic Technology with *in situ* Derivatization

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A simple low-cost ultrasonic extraction procedure has been developed for determination of polar aromatic acids, polar phenols and nonpolar pesticides simultaneously in soil. This procedure was accomplished by *in situ* derivatization as well as elevated temperature, increased power and dispersing intimate contact of solvent with samples. Combined with GC/NCI/MS method, the sensitivity was improved remarkably because of the enhanced electronegativity of derivatized products of herbicide and phenols as well as the intrinsic electronegativity of organochlorine. The method presented here showed that the modified ultrasonic extraction method can be a robust preparation methodology for both polar and nonpolar organic contaminants which can be applied to solid sample pre-treatment extensively.

Keywords: Ultrasonic extraction, Herbicide, Phenols, Organochlorine, Polar, Non-polar, NCI, Soil.

INTRODUCTION

There is a long-lasting desire for simultaneous determination of polar and non-polar contaminants in soil, but unfortunately many difficulties need to overcome, including both extraction and instrumental determination. It is well known that many polar contaminants such as chlorinated acidic herbicides is not amenable for GC analysis, but many non-polar contaminants such as organochlorine is just suitable for GC analysis. This contradiction was solved by Famigliani *et al.*¹, which was based on a special-designed instrument named LC/direct-EI-MS. Many analytical scientists has developed derivatization method for GC analysis. Polarity of phenols or others can be reduced through esterification², this work has paved the way for simultaneous determination. Likewise, polar and non-polar compounds require different extraction methods. In previous work, we reported the first simultaneous extraction method for polar and non-polar compounds with accelerated solvent extraction (ASE)³. However among the extraction instruments, accelerated solvent extraction is the most expensive one, maybe it is not available in many labs.

Ultrasonic cleaner is a common mini type machine which is available in most labs. In most cases, ultrasonic extraction has long been considered not as rigorous as other extraction methods for soils/solids⁴, especially when it comes to multi-component analysis in soil. In order to improve the ultrasonic extraction efficiency, many approaches were being undertaken by analytical scientists⁵⁻⁷. Up to now, there is no example for

simultaneous ultrasonic extraction for polar and non-polar organic compounds. *in situ* derivatization or in-cell derivatization is a great idea which has made much progress in the way to simultaneous analysis of polar and non-polar organic compounds. The conception of *in situ* derivatization was firstly put forward by Hawthorne *et al.*⁸, which is by adding polar substance and derivative reagent into non-polar CO₂. Recent years, *in situ* derivatization was applied to many polar chemicals⁹⁻¹³.

The aim of the research was to find a simple way to obtain enough extraction efficiency of polar and non-polar analytes in soil together. To the best of our knowledge, it is the first time that ultrasonic extraction and derivatization was synchronized. It is the first robust ultrasonic extraction method for polar and non-polar compounds all together. With this extraction method, no expensive instruments and multi-step derivatization process are required. All the equipment we utilized in the pretreatment was an ultrasonic cleaner and all we should do is to add specific volume reagent to the soil and then one-step ultrasonic extraction is enough to accomplish the pretreatment. So this methodology can be named accelerated ultrasonic extraction (AUE). Combined with the GC/NCI/MS method we have developed before¹⁴⁻¹⁵, a perfect multi-targets determination scheme for was demonstrated in this work.

EXPERIMENTAL

The soil used in this experimental study was collected from North China Plain (Clay) and Gansu Loess Plateau (Loess and sandy soil). The samples were air-dried and ground to

pass a 1.7 mm sieve (U.S.10 mesh). The ground samples were stored in capped glass jars.

In preparation of the spiked samples, the known amount of soil (either clay, loess, or sandy soil) which was spiked with known volume of herbicides, phenols and organochlorine standards, was added to a bottle, in order to make it homogenized, a little amount of CH_2Cl_2 was necessary to help the standard to disperse into the soil.

The analytical standards of herbicide acids were procured from Dr. Ehrenstorfer. Phenols and organochlorine standards were purchased from chemical service. Acetone, *n*-hexane, toluene were purchased from merk. 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr) was attained from J&K Chemical Ltd. Ethylenediaminetetraacetic acid tetrasodium salt (Na_4EDTA) was purchased from Shijiazhaung Jieke chemical Factory. Potassium Carbonate and quartz sand were purchased from Tianjin Damao Chemical reagent Factory.

Pre-dispersal and pre-chelation: Prior to extraction, a certain amount of quartz sand was added to the spiked soil in a mortar, after mixing, Na_4EDTA (about 5 %) and pure water (over 20 %) was added to the mortar and the volume of water was large enough to entirely immerse the soil. Then the samples were evaporated overnight. A general optimized procedure was to weigh 4 g sample, 2 g quartz and 0.2 g Na_4EDTA into a mortar, the mixture was homogenized well and 1 mL pure water was added slowly until slurry was formed, chelate and evaporate the sample for over 12 h after drying, the sample was re-ground to about 10 mesh.

Ultrasonic one step extraction with *in situ* derivatization procedure: The procedures of ultrasonic extraction and *in situ* derivatization were carried out simultaneously in the specific derivatization bottle which was fixed in the ultrasonic cleaner. The derivatization bottle with PTFE stopper was purchased from Bei Jing Xinweier Glass Factory. The ultrasonic cleaner (KQ-700DV) was attained from Kun Shan Ultrasonic Instruments Co., Ltd. The developed operation was as followed. The ultrasonic cleaner was preheated to 65 °C. Prepared sample and 4 mL acetone were added to derivatizing bottle, after shaking gently, PFBBr (30 %) 200 μL and K_2CO_3 (30 %) 100 μL were added to the bottle successively. The bottle was then capped and placed in the preheated ultrasonic cleaner, the power wattage was adjusted to over 560 watts. The extraction and derivatization time was 40 min. If necessary, the extract can be purified by clean-up procedure provided by Environmental Protection Agency (EPA) 363 °C¹⁶, the supernatant liquor was limpid, the supernatant liquor can be filtrated through the filter (0.22 μm) and then be capped in the GC vial directly for analysis.

Instrumentation: The gas chromatographic system consisted of a gas chromatograph GC-2010 equipped with an autosampler AOC 20 is, a split/splitless injector and a mass spectrometer equipped with a negative chemical ion source (NCI), (Shimadzu Corporation). A DB-5MS capillary column (J&W Scientific) was used, with the dimensions of 30 m length, 0.25 mm i.d. and 0.25 μm film thickness. The injection port liner used was of a packed single taper type and kept at 230 °C. The GC/MS ion source and transfer line temperatures were 200 and 230 °C, respectively. The analysis was conducted in

NCI and selected ion monitoring (SIM) modes using methane (purity 99.999 %) as a reagent gas. The ion source pressure was set at about 1.0 Pa and system vacuum pressure was better than 2×10^{-3} Pa. The ions monitored were as Table-2 for the 2,3,4,5,6-pentafluorobenzyl bromide derivatives of the analytes. The GC oven temperature started from 90 °C for 1 min and was ramped at 30 °C/min to 200 °C and then was ramped at 10 °C/min to 300 °C held for 2 min.

RESULTS AND DISCUSSION

In order to monitoring the recoveries of three types of compounds simultaneously, first of all, a set of GC/NCI/MS method was developed. It is well known that the GC-MS with NCI is amenable to both the derivatized polar compounds of PFBBr¹⁴ and the organochlorine respectively. To merge the two determination processes is not a difficult problem. After derivatization the polarity of the 3 categories of organic compounds became concordant because of esterification, the high electronegativity of those was obtained because of the introduced element-fluorine, in this case, the whole monitoring process can be integrated into one temperature-programming of GC and one mass spectra acquisition of NCI MS detector. The optimized parameters were listed in Table-1.

Potential of ultrasonic technology: Traditional ultrasonic technology usually served as a rinse or clean-up enhancer. As a extraction method, it often suffered from instability and low recovery, especially for polar organic compounds. As a matter of fact, much potential or many parameters can be implemented to this technology, such as dispersal intimate contact of solvent, boosted power, elevated temperature, derivatization reaction and chelating impetus.

Optimization of ultrasonic extraction parameters: The traditional ultrasonic method failed to make good use of temperature, dispersing agent and derivatization. So in present research, elevated temperature and other possible approaches which have potential to improve the efficiency, have been investigated and evaluated.

In this paper, the extraction temperature as well as the derivatization temperature was investigated from 30-70 °C, the data showed that 65 °C is suitable for extraction and derivatization. The ultrasonic power was studied in the range of 300-700 watts (300 is the recommended temperature⁴ of EPA 3550c and 700 is the maximum power of the ultrasonic cleaner). Experiment showed that 560 watts can significantly improve the recovery of extraction as well as the derivatization efficiency. The extraction time as well as the derivatization time was evaluated from 10-50 min. Part of the data was listed in Table-2.

Derivatization reagent PFBBr and catalyst K_2CO_3 was chosen according to Zhang *et al.*¹⁵, the volume of PFBBr was optimized in the range from 50-500 μL . The quantity of K_2CO_3 was investigated from 50-200 μL . The experiment showed that the maximum recovery was attained by using 200 μL of PFBBr (30 %) and 100 μL of K_2CO_3 (30 %).

Dispersing reagent is another factor which is easy to be overlooked. To ensure intimate contact of the sample matrix with the extraction solvent is the fundamental condition, to blend appropriate quartz sand can help the extraction solvent

TABLE-1
ESTABLISHED MONITORING PARAMETERS OF GC/NCI/MS

Compounds	Retention time (min)	Molecular weight of derivatized compound	Quantitative ion (<i>m/z</i>)	Reference ion (<i>m/z</i>)
α -BHC	4.73	-	71	35, 73
β -BHC	4.97	-	35	71,73
γ -BHC	5.07	-	35	71,73
δ -BHC	5.37	-	71	35, 73
2,4,6-Trichlorophenol	5.52	376	197	195
3,5-Dichlorobenzoic	5.98	370	189	191,193,190
MCPP	6.06	394	213	215,214,216
Dicamba	6.65	384	203	205,159,161
MCPA	6.76	400	219	221,175,177
2,3,4,6-Tetrachlorophenol	6.79	412	231	229,233
Dichloroprop	6.85	380	199	201,200,202
2,4-D	7.29	414	233	235,237,234
<i>p,p</i> -DDE	7.70	-	35	37
2,4,5-TP	7.82	400	219	221,223,220
Pentachlorophenol	7.90	448	267	269,271,270
2,4,5-T	8.32	420	239	240,241,242
<i>p,p'</i> -DDD	8.37	-	35	37
<i>p,p'</i> -DDT	8.98	-	35	37
2,4-DB	9.06	428	247	249,161,167

TABLE-2
RECOVERIES WITH DIFFERENT ULTRASONIC AND EXTRACTION TIME AND DIFFERENT POWER

Compound	Recovery (%)							
	Extraction time (min)				Power (watt)			
	10	30	40	50	280	420	490	560
α -BHC	32.5	85.1	92.1	105.2	22.3	75.1	82.1	102.2
β -BHC	38.7	92.7	90.7	92.5	28.7	93.7	93.8	92.5
γ -BHC	56.9	102.5	93.7	107.1	36.2	92.5	91.2	108.1
δ -BHC	60.1	91.7	87.9	99.6	50.1	81.7	97.3	107.6
2,4,6-Trichlorophenol	30.5	59.8	89.8	97.8	22.1	49.9	81.9	99.9
3,5-Dichlorobenzoic	50.2	77.2	81.3	89.7	86.2	93.3	100.4	105.1
MCPP	61.8	79.1	89.6	90.3	75.3	96.6	102.3	106.3
Dicamba	60.3	79.7	88.8	87.6	89.3	91.9	98.1	104.0
MCPA	36.9	71.4	94.6	93.8	42.6	73.2	106.4	98.2
2,3,4,6-Tetrachlorophenol	20.5	30.6	79.8	77.8	10.5	53.6	85.8	109.8
Dichloroprop	45.7	68.5	91.2	93.1	54.5	87.3	90.2	107.2
2,4-D	29.8	59.6	102.8	97.4	28.8	69.6	89.8	82.1
<i>p,p</i> -DDE	48.7	69.9	89.9	107.2	38.7	67.1	95.3	112.2
2,4,5-TP	45.1	69.4	91.6	93.2	51.6	86.3	103.5	100.9
Pentachlorophenol	10.2	59.2	81.5	84.7	20.2	69.1	91.5	99.7
2,4,5-T	26.9	66.1	99.2	106.6	24.1	69.1	86.6	93.2
<i>p,p'</i> -DDD	50.6	85.8	100.5	97.8	70.6	82.1	105.5	107.4
<i>p,p'</i> -DDT	56.5	97.2	98.1	95.6	76.2	92.2	97.1	94.6
2,4-DB	28.1	78.6	99.6	96.7	31.5	68.6	93.8	102.1

and derivatization reagent to further intimate contact with the analytes in the sample especially for some complex soil.

Roles of Na₄EDTA and quartz sand: In this paper, the special function of Na₄EDTA was discovered that not only does the Na₄EDTA play the role of complexation or chelation¹⁵, but also it help to precipitate the particulate matter and purify the extract. To some extent, Na₄EDTA played the role of flocculating reagent and dispersed quartz sand played the role of condensation nucleus. In order to extract clearer liquid, NaCl, Na₂SO₄, Na₄EDTA, quartz sand was added separately and conjunctly. The appearance of extract showed that addition of Na₄EDTA and quartz sand can help clean the extract significantly, for most of the soil sample, after simple filtering

with 0.22 μ m organic filter (Tian Jin Autoscience Corporation), extract can be injected into the GC-MS directly. If without the addition of them, the extracted liquid was just translucent even dark and muddy, in this case, cleanup procedure must be carried out. The theory of this phenomena can be explained as precipitation or flocculation.

Evaluation of main method parameters: Method quality parameters were evaluated according the following operation. 6 g quartz sand samples were spiked with herbicides, phenols and organochlorine standard in the range from 2.5 to 200 μ g/kg, the procedure of AUE and determination was the same as that of real samples. Correlation coefficient was calculated according to the response intensity of NCI mass detector respectively,

TABLE-3
MAIN QUALITATIVE PARAMETER OF THE DERIVATIZATION PRODUCT, CORRELATION COEFFICIENT AND LODs

Compound	Linear range ($\mu\text{g}/\text{kg}$)	Correlation coefficient (r^2)	LODs ($\mu\text{g}/\text{kg}$)
α -BHC	2.5-200.0	0.997	0.25
β -BHC	2.5-200.0	0.996	0.33
γ -BHC	2.5-200.0	0.997	0.29
δ -BHC	2.5-200.0	0.995	0.21
2,4,6-Trichlorophenol	2.5-200.0	0.993	0.69
3,5-Dichlorobenzoic	2.5-200.0	0.993	0.05
MCPP	2.5-200.0	0.996	0.19
Dicamba	2.5-200.0	0.994	0.19
MCPA	2.5-200.0	0.999	0.09
2,3,4,6-Tetrachlorophenol	2.5-200.0	0.989	0.61
Dichloroprop	2.5-200.0	0.999	0.25
2,4-D	2.5-200.0	0.995	0.18
<i>p,p</i> -DDE	2.5-200.0	0.998	0.65
2,4,5-TP	2.5-200.0	0.998	0.08
Pentachlorophenol	2.5-200.0	0.991	0.79
2,4,5-T	2.5-200.0	0.992	0.13
<i>p,p'</i> -DDD	2.5-200.0	0.997	0.51
<i>p,p'</i> -DDT	2.5-200.0	0.996	0.58
2,4-DB	2.5-200.0	0.998	0.47

TABLE-4
RECOVERIES OF DIFFERENT MATRIX WITH DIFFERENT CONCENTRATION

Compound	Loess		Sandy soil		Clay	
	Average recovery (%, n = 7)	RSD (%)	Average recovery (%, n = 7)	RSD (%)	Average recovery (%, n = 7)	RSD (%)
α -BHC	82.1	3.5	85.6	2.9	80.9	3.2
β -BHC	82.5	5.3	97.3	1.5	78.5	2.8
γ -BHC	73.9	3.2	94.7	2.7	78.3	3.9
δ -BHC	82.1	1.7	100.8	1.9	87.5	3.2
2,4,6-Trichlorophenol	93.8	8.2	85.4	6.1	75.6	7.4
3,5-Dichlorobenzoic	80.5	5.2	103.9	5.7	73.2	5.8
MCPP	87.6	5.8	95.8	4.2	69.9	4.8
Dicamba	81.6	6.1	101.6	2.8	75.5	6.9
MCPA	93.6	6.3	109.9	3.7	67.2	3.3
2,3,4,6-Tetrachlorophenol	75.3	7.1	89.3	5.0	76.4	6.3
Dichloroprop	81.2	5.5	93.7	4.3	85.3	5.6
2,4-D	92.8	6.3	93.3	5.6	75.4	6.1
<i>p,p</i> -DDE	79.9	3.8	98.8	1.7	79.7	3.7
2,4,5-TP	90.6	8.1	107.0	4.2	85.2	4.6
Pentachlorophenol	71.5	7.3	95.1	5.2	76.1	6.5
2,4,5-T	91.2	5.7	90.1	3.2	87.9	5.6
<i>p,p'</i> -DDD	103.2	3.6	109.0	1.5	81.6	4.8
<i>p,p'</i> -DDT	92.1	2.1	100.6	3.4	93.8	4.7
2,4-DB	95.7	6.6	97.3	3.1	74.4	7.5

r^2 ranged from 0.989 to 0.999. 4 g real sample was spiked with 2.5 $\mu\text{g}/\text{kg}$ standard, the limits of detection (LODs) were calculated as the compound concentration giving a signal-to-noise ratio of 3 ($S/N = 3$), Values ranged from 0.05 to 0.79 $\mu\text{g}/\text{kg}$. The overall result of the evaluation as well as the main qualitative parameters can be seen in Table-3.

Application to real samples: Recovery studies were carried out by applying the optimized AUE method to the extraction of a series of different matrix real sample spiked at 25 $\mu\text{g}/\text{kg}$ and these initial concentration were taken into account to calculate the recoveries. As can be seen in Table-4, the recoveries were between 67.2 and 109.9 % in all cases. The precision was also evaluated and the relative standard deviation (RSD) values were lower than 8.2 %.

Comparison between different extraction methods with contaminated soils: The method was validated with real contaminated soils from a farmland. In order to further identify the compounds, both the newly-established AUE and existing accelerated solvent extraction (ASE) method¹⁵ was used as a comparison. Results are consistent with each other approximately. Furthermore, the contaminated soils with spiked standards was extracted and detected, the result was showed in Table-5.

Conclusion

We have developed a prototype for simultaneous one-step extraction of different polar compounds which was based on a novel extraction approach, named as accelerated ultrasonic

TABLE-5
RESULTS OF REAL CONTAMINATED SOILS WITH DIFFERENT EXTRACTION METHODS AND THEIR
CORRESPONDING RECOVERY RESULTS WITH SPIKED STANDARDS

Compound	Result of sample-1(μg/kg)		Result of sample-2 result of sample-1 (μg/kg)		Samples spiked with 50.0 (μg/kg)	
	With AUE	With ASE	With AUE	With ASE	Sample-1 AUE	Sample-2 AUE
α-BHC	-	-	-	-	42.3	46.4
β-BHC	-	-	-	-	39.1	41.6
γ-BHC	-	-	-	-	46.2	53.4
δ-BHC	-	-	-	-	37.9	39.4
2,4,6-Trichlorophenol	11.1	13.6	-	-	59.9	54.2
3,5-Dichlorobenzoic	-	-	-	-	45.9	44.7
MCPP	-	-	-	-	48.9	50.3
Dicamba	-	-	-	-	45.4	44.4
MCPA	-	-	14.2	16.7	48.2	69.8
2,3,4,6-Tetrachlorophenol	-	-	-	-	49.0	45.3
Dichloroprop	-	-	-	-	47.9	45.8
2,4-D	70.2	76.1	-	-	118.1	51.6
p,p'-DDE	-	-	-	-	48.1	46.3
2,4,5-TP	-	-	-	-	47	49.9
Pentachlorophenol	-	-	-	-	46.5	42.8
2,4,5-T	-	-	-	-	49.3	49.3
p,p'-DDD	-	-	-	-	48.6	49.0
p,p'-DDT	-	-	-	-	42.7	46.1
2,4-DB	-	-	-	-	46.7	42.2

extraction (AUE). Quantitatively recoveries can be attained with the elevated temperature, enhanced power, additional dispersal and chelation. Combined with developed GC-NCI-MS method, a satisfied recoveries, precisions and LODs were achieved, the reliability of the method was demonstrated through a broad range of soil samples.

It is a rapid procedure that all samples pretreatment can take place in the little specific derivatization bottle which was fixed in the ultrasonic cleaner. Since dozens of derivatization bottles can be fixed in the ultrasonic cleaner all together, so the procedures for extraction and derivatization of dozens of samples can be accomplished simultaneously in less than 1 h. To our best of knowledge, it was the first simplest method which integrated extraction and derivatization together with the most common ultrasonic technology. This pioneering undertaking has made it possible that the simultaneous determination of polar and non-polar organic pollutants can be achieved in each lab.

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