COMPREHENSIVE ANALYSIS OF POPs AND OTHER CHEMICALS IN SOIL USING A SIMULTANEOUS ANALYSIS DATABASE FOR GC/MS

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Abstract

We have developed a method of comprehensive analysis for simple and quick detection of soil contamination by approximately 1,000 semi-volatile chemicals, such as persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs) and pesticides. We investigated the extraction and clean-up method using 130 model substances with various properties. Qualification and quantification of the subject chemicals was done with a GC/MS database, which does not require reference standards and preparation of calibration curves. The results demonstrate accurate identification and quantification of a wide variety of chemicals, ranging from semi-polar substances to hydrophobes, such as POPs and PAHs; however, some water-soluble or highly polar chemicals could not be analyzed because of low recovery rates. When the method was applied to an environmental standard sample and actual soil samples, the results were consistent with certified values as well as the results of the existing individual analyses, confirming the applicability of the method to soil. This method allows a single analyst to measure concentrations of about 1,000 chemicals contained in five soil samples in just one day; therefore, it is an effective method for an investigation of soil contamination.

Introduction

Since the Soil Contamination Control Law came into effect in Japan (Feb, 2003), soil surveys have been conducted during redevelopment of industrial sites, with findings of contamination increasing. Testing required under this law is limited to regulated substances, such as volatile organic compounds, heavy metals, pesticides and PCBs. In many cases, however, businesses wish to understand, through self-management or land use history, the state of contamination by substances that are not regulated. If, however, no information about the soil exists, there is no way of knowing what types of contaminant there may be. Finding the state of contamination of such soil requires considerable time, manpower and expenses. Even if the state of contamination is known to some extent, the full extent cannot be determined by methods that focus on a limited numbers of chemicals. In this context, we have developed a simple and quick method of comprehensive analysis of soil contaminated by multiple components, and have investigated the effectiveness of this method.

Materials and Methods

(1) Model compounds

From the chemicals registered in a GC/MS database, we selected 130 model compounds including n-alkanes, benzenes, nitro-compounds, amines, phenols, pesticides and PAHs, comprising a wide range of physicochemical properties. We used the GC/MS data for a simultaneous analysis for each of the substance types.

(2) Analytical method

(2)-1. Pre-treatment: The flow of analysis is shown in Fig. 1. Model compounds (2.5 µg each) were added to a soil sample (5 g-dry) placed in a centrifuge tube. The sample then underwent three rounds of supersonic extraction with 10 mL of acetone and centrifugal separation. After 100 mL of 5% saline solution was added, the resulting extract was extracted twice with dichloromethane (15 and 10 mL). The extract was then washed in 100 mL of 5% saline solution, and dehydrated, and added to 10 mL of hexane, which was finally concentrated to 5 mL under a rotary evaporator and a nitrogen stream. With 1 mL of the concentrate loaded into a solid phase cartridge, the first fraction was eluted using 15 mL of 100% hexane, the second fraction using 15 mL of hexane containing 5% acetone, and the third fraction using 20 mL of hexane containing 30% acetone. In addition, the third fraction was processed through activated charcoal to remove pigments. The fractions were concentrated to 1 mL each, to which the internal standards were added to make up samples for GC/MS measurements.

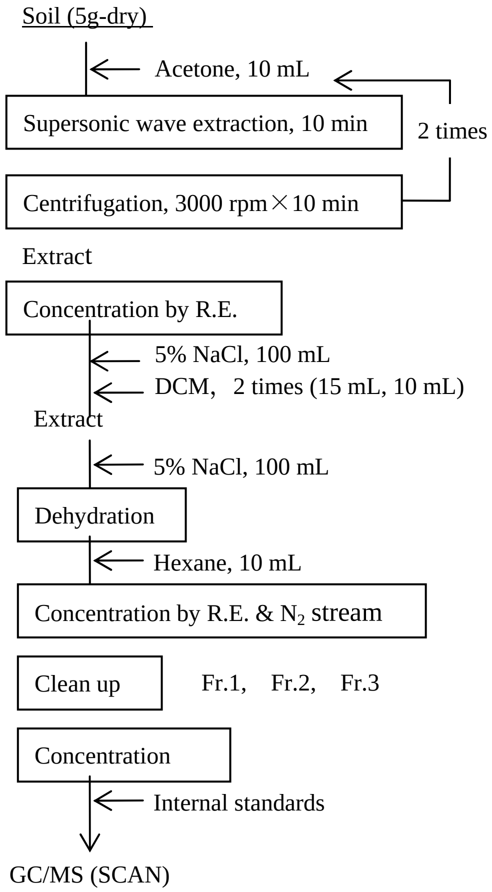

Fig.1 Analysis flow

(2)-2. Measurements: GC/MS measurements were carried out under the conditions specified by the database1). Qualification of the subject chemicals was based on the degree of consistency between the corrected retention time, which was the retention time registered in the database corrected by n-alkanes at the time of the measurements of samples, and the mass spectra, while quantification used the calibration curves registered in the database.

Results and Discussion

(1) Examination of extraction rates with dichloromethane

We suspected that extraction rates of highly polar compounds by liquid-liquid extraction with dichloromethane are low. In order to evaluate what properties of chemicals hinder quantitative extraction with dichloromethane, extractions were performed using dichloromethane after adding the model compounds to 5% saline solution. The extraction rates of chemicals with logPow of less than 1 were less than 5%, confirming the difficulty in extracting chemicals with low logPow.

(2) Examination of clean-up methods

We used three types of solid phases (silica gel, florisil and alumina N (Vac 12cc 2grum; Waters Corporation)), and three types of eluting solutions (hexane-acetone, hexane-dichloromethane and hexane-methanol). Elution of the model compounds was examined in the following solvents:① First fraction: hexane 100%; Second fraction:hexane with 3% polar solvents; Third fraction: hexane with 15% polar solvents; and ②First fraction: hexane 100%; Second fraction: hexane with 5% polar solvents; Third fraction: hexane with 30% polar solvents. Fig. 2 shows the results of the fractionation by a combination of the hexane-acetone solvent composition of ② above and three solid phases, which produced the best recovery rates. The recovery rates for nine chemicals with silica gel, and for amines and phenols in 12 chemicals with florisil were less than 5%. With alumina-N, recovery rates for more than 20 chemicals, including nitrophenols and pesticides, which eluted in the third fraction with both silica gel and florisil, were less than 5%. These results confirmed that a combination of silica gel and hexane-acetone solvents was best suited to a comprehensive analysis of chemicals with a wide range of properties, although it might not be able to recover some highly polar chemicals.

(3) Verification test using actual soil samples

We tested our comprehensive analysis method on two types of soil (sediment) samples.

(3)-1. Commercial environmental standard sample (NIST SRM 1941a): Table 1 shows the measurements taken by the developed method from 5 g of an environmental standard sample containing 67 chemicals with certified concentrations (0.653–1,095 µg/kg), including alkanes, PCBs, pesticides and PAHs. The flow of an analysis to determine certified values measured by NIST is essentially identical to that of the technique of the method presented here. Comparison of the results from conventional methods with those from our new method for those analytes measured with the same column type in both (Table 1, Column (4)) confirms that the accuracy of the developed method is comparable to the conventional methods for individual analysis.

Fig. 2 Results of fractionation using 3 solid phases and hexane-acetone elution solvent

<table>
<tr><th>Solid phase</th><th>First Fr.</th><th>Second Fr.</th><th>Third Fr.</th><th>Recovery less than 5%</th></tr>
<tr><td rowspan="11">Silicagel
Florisil
AluminaN</td><td rowspan="3">Alkanes
Benzenes
Biphenyl
Naphthalenes</td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td colspan="2">PAHs</td><td></td><td></td></tr>
<tr><td></td><td>Nitrobenzenes</td><td></td><td></td></tr>
<tr><td></td><td>Ethers</td><td></td><td></td></tr>
<tr><td></td><td colspan="2">Phthalates</td><td></td></tr>
<tr><td></td><td></td><td>Phosphates</td><td></td></tr>
<tr><td></td><td></td><td colspan="2">Amines</td></tr>
<tr><td></td><td colspan="3">Phenols</td></tr>
<tr><td colspan="4">Pesticides</td></tr>
</table>

Table 1 Result using environmental standard sample

Compounds to intend for	Number of compounds	Measured value/Certified value	
		Average	SD
(1)	57	1.07	0.529
(2)	41	1.21	0.513
(3)	25	0.972	0.286
(4)	14	0.912	0.183

∗Column (1) of the table shows the results after excluding any chemical that was not detected because it was below the detection limit or influenced by matrix components.

∗Column (2) shows the results after further exclusion of any chemical remaining in the Column (1) group because of the detection of blank or possibly vaporization during concentration with a rotary evaporator.

∗Column (3) excluded chemicals remaining in Column (2) which had a certified value of less than 10 μg/kg.

∗Column (4) shows the results of an evaluation performed only on the chemicals measured using the same type of the column (DB-5) as the one used by the analytical technique described in this study.

(3)-2. Soil contaminated with organochlorine pesticides: We used a soil sample which was confirmed to be polluted by six organochlorine pesticides by a conventional (SIM) method. We spiked 0.5 μg of each of the model substances to the soil, and then analyzed by the developed method (Fig. 3). From the comparison between non-spiked and spiked sample, 16 % of the model compounds showed less than 10 % of recovery rates. These were the substances that could not be recovered by liquid-liquid extraction and clean-up. The result confirms that the developed method is capable of analyzing chemicals with medium, weak or no polarity.

Table 2 shows the measurements taken from the contaminated soils with no addition of the model substances using both the developed method and the conventional (SIM) method. The developed method produced satisfactory results: in comparison with the results of the conventional method, contaminants were reliably and consistently identified with our new method, even for those contaminants present at low concentrations.

(4) Effectiveness of the comprehensive analysis method

The results of this study indicate that the developed method cannot detect water-soluble chemicals with logPow of less than 1 and some highly polar chemicals, because the former could not be recovered by liquid-liquid extraction and the latter by clean-up. However, the method satisfactorily identified and quantified hydrophobes, such as chemicals with medium and weak polarity, POPs and PAHs. In order to cover chemicals with a wide range of properties, this comprehensive analysis method has adopted a simpler clean-up procedure rather than individual chemical-specific methods. Owing to its simplicity, an analysis of soil containing a large number of matrix components may produce a positive error as a result of some of the analyses being influenced by interfering substances during the GC/MS measurements. Even in such an event, however, the method can be adapted as necessary to determine the presence of such influences by examining mass spectra or mass chromatograms.

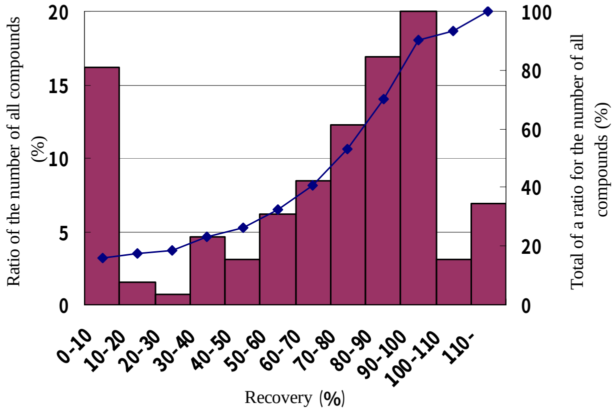

Fig. 3 Results of an analysis by the developed method of the soil sample contaminated by adding 0.5 μg each of the model substances

The objectives of the authors in the development of this comprehensive analysis method were to allow not only 1,000 chemical analysis but a single analyst to perform the entire process, from pre-treatment to quantification, for about five samples at a time in one day, so that as many soil contaminants as possible can be identified simply and quickly. The objectives have been effectively achieved. Moreover, the developed method does not require preparation of calibration curves, eliminating the use of toxic chemicals. This result improved safety, as well as substantially increasing speed and reducing cost. Consequently, the new method is effective for investigation of soil contamination by a wide range of chemicals.

Table 2 Result of analysis using both the developed method and the conventional (SIM) method of the soil sample with no addition of the model substances

Compound	Comprehensive analysis (mg/kg)	Conventional analysis (mg/kg)
α-HCH	0.01	0.01
β-HCH	0.13	0.10
γ-HCH	0.02	0.03
δ-HCH	0.03	0.03
Aldrin	0.004	0.007
Dieldrin	0.05	0.03

Reference

1) K.Kadokami，K.Tanada，K.Taneda，K.Nakagawa, *J.Chromatogr.A.*,1089(2005)