Method Verification of Soil Volatile Organic Compounds

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Abstract. In this paper, purge-and-trap / gas chromatography-mass spectrometry is used to verify the analysis of six volatile organic compounds in soil, including 1,1-dichloropropene, benzene, and 1,2-dichloroethane. The feasibility of purge and trap / gas chromatography-mass spectrometry for the determination of VOCs in land Engineering was discussed. The results show that in the linear relationship, the response value and concentration of the volatile organic target object show a good linear relationship with a correlation coefficient of 0.9951 to 0.9996; the detection limit is 0.8 to 1.9 μg/kg and the quantification limit is 3.0 to 7.6 μg/kg. The relative standard deviation of 6 volatile organic compounds in precision is: 3.0% to 12.3%; the recovery rate of 6 volatile organic compounds in accuracy is: 112.4% to 127.0%. The verification results show that the linear relationship, detection limit, precision, and accuracy all meet the requirements of "Soil and Sediment-Determination of Volatile Organic Compounds Purge and Trap Gas Chromatography/Mass Spectrometry Method" (HJ605-2011). The purge-and-trap/gas chromatography-mass spectrometry technology can be used to achieve fast, accurate and sensitive detection of target substances, and can meet the detection requirements of trace volatile organic compounds, so it can be applied to environmental testing work such as soil.

1. Introduction
At present, environmental problems are threats and challenges facing the world. With the rapid development of urbanization and industrialization in China, a large number of toxic and hazardous substances in industry and agriculture have entered the soil, surface water, and groundwater, and the situation of environmental pollution has become increasingly severe. Volatile Organic Compounds (VOCs) have the most direct harm to human body and are prone to carcinogenesis in recent years. Volatile organic pollutants are very important environmental pollutants. Some of them are listed as priority pollutants at home and abroad due to their strong "three effects" effect, which has a serious impact on the ecological environment and human health [1-3]. In particular, the occurrence of Changzhou poisonous land and other incidents has accelerated people's consideration of land safety. In order to ensure the safety of land use during the development and utilization of the site, it is necessary to use land engineering, that is, to apply engineering technology to solve land problems, to turn unused
land into usable land or to make efficient use of used land [4]. It is of great significance to judge and evaluate the risk of pollution [5], to effectively and accurately advance risk assessment and remediation, and to prevent land pollution [6], to provide technical support for controlling the migration and transformation of soil pollutants, and improving the ecological environment and land safety. The analysis and detection of soil organic matter pollution parameters require the use of high-resolution, high-sensitivity gas chromatography-mass spectrometry (GC-MS) for the separation, qualitative, and quantitative analysis of complex samples [7]. GC-MS is an instrument that realizes the combined technology earlier in the analysis instrument. It is a mature and widely used qualitative and quantitative analysis and testing technology. Volatile organic compounds need to be combined with purge and trap pretreatment technology to enrich VOCs. After thermal analysis, they are analyzed by gas chromatography mass spectrometry, selected ion mode detection, and external standard method for quantification. Since Bellor and others first proposed the purge-and-trap method in 1974, the technology has been valued by researchers and has been widely used in environmental science, food science, and biological sciences [8-12]. The purge-and-trap sampling technique is the most sensitive analytical method in sample analysis. It has the advantages of less sampling, less interference from the matrix, high enrichment efficiency, and easy online detection. It can be used in combination with GC / MS to target the components were subjected to quasi-deterministic and quantitative analysis [13]. It has been found through practice that the use of purge-and-trap / gas chromatography-mass spectrometry technology can achieve sensitive, fast and accurate detection of target substances, and can meet the detection requirements of trace substances, so it can be applied in land engineering inspection work.

2. Experimental part

2.1. Instruments and reagents

GCMS-QP2020NX Gas Chromatography-Mass Spectrometer (Shimadzu, Japan); Capillary column: 30 m × 0.25 mm, 1.4 μm film thickness (6% Nitrilopropylphenyl 94% dimethyl polysiloxane fixing solution); CDS7000E CDS Purge and Trap Concentrator (CDS, USA); Milli-Q Ultrapure Water Treatment System (Millipore, USA); One Percent Analytical Balance (METTLER TOLEDO, USA); Microinjector: 10 μl, 25 μl, 100 μl, 250 μl, and 500 μ; samplers: disposable plastic syringes or stainless steel special samplers.

Chromatographic grade methanol (Honeywell China Co., Ltd.); CDGG-120788-01-1ml of 59 kinds of VOCs in methanol: ρ = 2000μg/mL (US O2Si, 1mL); CDGG-120016-01 8260 gas in methanol Standard (6 components): ρ = 2000μg/mL (US O2Si, 1mL); CDGG-120004-02 methanol internal standard mixed standard (3 components) isotope standard solution: ρ = 2000μg/mL (US O2Si, 1mL); CDGG-120005-01 3 alternatives in methanol standard: ρ = 2000μg/mL (US O2Si, 1mL); Helium: high purity grade, purity is above 99.999%.

2.2. Sample collection and processing

Before collecting samples, place a clean magnetic stirrer in a 40 ml brown purge bottle, seal, label, and record (accurate to 0.01g). When sampling, use the sampler to take an appropriate amount of sample into the purge sample bottle and seal the sample bottle.

If the content of volatile organic compounds in the sample is initially determined to be less than 200 μg / kg, a 5 g sample is directly measured on the machine. When the initial determination is between 200μg/kg and 1000μg/kg, take 1g sample for direct measurement. For a sample with a preliminary determination of a target content of more than 1000 μg/kg, take about 5 g of the sample from the sample bottle into a pre-weighed 40 mL sample bottle and weigh it (accurate to 0.01 g). Add 10.0 mL of methanol quickly, cap the bottle and shake for 2 min. After standing still, transfer 1 mL of the extract to a 2 mL brown glass bottle. If necessary, the extract can be centrifuged. Use a micro-syringe to measure 10.0 μL to 100 μL of the extraction solution and 10.0 μL substitute to a 40-mL purge bottle. Use an airtight syringe to measure 5.0 mL of blank reagent water as the sample and place it in the sample bottle. Standard 2 μL was measured.
2.3. Instrument Reference Conditions
Purge and trap device conditions: purge flow rate: 40mL/min; purge temperature: 40 °C; preheat time: 2 min; purge time: 11 min; dry blow time: 2 min; pre-desorption temperature: 180 °C; Desorption temperature: 190 °C; Desorption time: 2 min; Baking temperature: 200 °C; Baking time: 8 min; Transmission line temperature: 200 °C.
Gas chromatography conditions: inlet temperature: 200 °C; carrier gas: helium; split ratio: 30: 1; column flow rate (constant flow mode): 1.5 mL / min; heating program: 38 °C/ (1.8 min) → 10 °C/min → 120 °C→ 15 °C/ min → 240 °C/ (2 min).
Mass spectrometry conditions: scanning method: full scanning; scanning range: 35 to 270 amu; ionization energy: 70 eV; electron multiplier voltage: consistent with tuning voltage; interface temperature: 280 °C.

2.4. Calibration curve configuration
Use a micro-syringe to transfer a certain amount of standard use solution and substitute standard solution to blank reagent water, and prepare a mixed standard series with target and substitute concentrations of 5, 20, 50, 100 and 200 μg/L, respectively. Measure 5ml of the above-mentioned mixed standard series into a 40ml purge sample bottle with an air-tight syringe, and the instrument will automatically add 2μL of the internal standard solution to make the internal standard concentration at each point be 50μg / L. Measure from low concentration to high concentration in sequence, record the retention time of the standard series target and corresponding internal standard, and the response value of the quantitative ion (the first or second characteristic ion).

2.5. Qualitative and quantitative analysis of samples
Qualitative analysis of the target: The target is qualitatively determined by its relative retention time (or retention time) and comparison with the mass spectrum of the standard substance.
Quantitative analysis of target: Purge and trap method was used to enrich VOCs. After thermal desorption, it was analyzed by gas chromatography-mass spectrometry, selective ion mode detection, and external standard method for quantification. Calculate according to the response value of the target and the first characteristic ion of the internal standard, and the response value of the quantitative ion (the first or second characteristic ion).

3. Analysis and discussion

3.1. Linear range
A standard curve was drawn using the response ratio of six volatile organic compounds such as 1,1-dichloropropene, benzene, and 1,2-dichloroethane to the internal standard as the ordinate and the concentration ratio as the abscissa. The correlation coefficient of VOC is shown in Table 1.

| Number | Component name            | Linear equation                  | correlation coefficient(R) | method Claim |
|--------|---------------------------|---------------------------------|-----------------------------|--------------|
| 1      | 1,1-dichloropropene      | Y = 4.603116×10^{-3}X-6.432989×10^{-3} | 0.9966                     |              |
| 2      | benzene                  | Y = 1.845031×10^{-2}X+1.100174×10^{-2} | 0.9951                     |              |
| 3      | 1,2-dichloroethane       | Y = 3.227718×10^{-3}X+2.563017×10^{-3} | 0.9982                     | R≥0.99       |
| 4      | Trichloroethylene        | Y = 4.492394×10^{-3}X+1.568692×10^{-2} | 0.9966                     |              |
| 5      | 1,2-dichloropropane      | Y = 5.549971×10^{-3}X-5.197055×10^{-4} | 0.9983                     |              |
| 6      | Dibromomethane           | Y = 2.795584×10^{-3}X+8.480007×10^{-3} | 0.9996                     |              |
Purge-and-trap / gas chromatography-mass spectrometry was used to determine soil and sediment. The response values of internal targets corresponding to six volatile organic compounds, including 1,1-dichloropropene, benzene, and 1,2-dichloroethane, the concentration showed a good linear relationship with a correlation coefficient of 0.9951 to 0.9996. Meet the requirements of "Soil and Sediment Volatile Organic Compounds Purge and Trap/Gas Chromatography-Mass Spectrometry" (HJ605-2011) (correlation coefficient should be greater than or equal to 0.99).

3.2. Determination of method detection limit and determination lower limit
In accordance with the relevant provisions of the HJ 168-2010 Environmental Monitoring and Analysis Method Standards Technical Guidelines. Follow the entire process of sample analysis and testing, repeat 7 blank experiments, calculate the standard deviation of 7 parallel blank experiments, and calculate the detection limit according to formula 1. The data summary table is shown in Table 2.

\[
\text{MDL} = t_{(n-1,0.99)} \times S
\]

In the formula: \(\text{MDL}\) — the detection limit of the method; \(n\) — the number of parallel determinations of the sample; \(t\) — the t-distribution (one-sided) with a degree of freedom of \(n-1\) and a confidence level of 99%; the standard deviation of the \(S\)-n parallel determinations. Among them, when the degree of freedom is 6, the confidence value is 99% and the \(t\) value is 3.143.

| Number | Component name       | 1     | 2     | 3     | 4     | 5     | 6     | 7     | Detect limit | Quantitative limit |
|--------|----------------------|-------|-------|-------|-------|-------|-------|-------|--------------|-------------------|
| 1      | 1,1-dichloropropene  | 9.6   | 10.6  | 10.6  | 10.4  | 10.2  | 10.5  | 10.6  | 1.2          | 4.8               |
| 2      | benzene              | 7.9   | 9.96  | 9.36  | 9.28  | 9.38  | 8.89  | 9.34  | 1.9          | 7.6               |
| 3      | 1,2-dichloroethane   | 6.8   | 6.52  | 6.96  | 6.39  | 6.84  | 6.47  | 7.25  | 1.0          | 4.0               |
| 4      | Trichloroethane      | 5.4   | 5.93  | 6.15  | 5.42  | 5.55  | 4.99  | 5.67  | 1.2          | 4.8               |
| 5      | 1,2-dichloropropane  | 8.4   | 8.79  | 9.37  | 8.70  | 9.14  | 9.11  | 8.80  | 1.1          | 4.4               |
| 6      | Dibromomethane       | 6.8   | 7.31  | 7.13  | 7.22  | 7.18  | 6.87  | 7.56  | 0.8          | 3.2               |

Purge and trap / gas chromatography-mass spectrometry was used to determine soil and sediment. The detection limits of six volatile organic compounds such as 1,1-dichloropropene, benzene, and 1,2-dichloroethane were: 0.8 to 1.9 μg/kg, and the quantification limit is 3.2 to 7.6 μg/kg Meet the "Sweep and Trap / Gas Chromatography-Mass Spectrometry Method for Determination of Volatile Organic Compounds in Soil and Sediment" (HJ605-2011) Claim.

3.3. Method Precision
The laboratory performs a standard addition experiment on soil and sediment for the same sample, and performs the measurement in accordance with all the steps of sample analysis. Each sample is measured 6 times in parallel. The data summary table is shown in Table 3. Calculate the average, standard deviation, relative standard deviation and other parameters of different samples.
Purge-and-trap / gas chromatography-mass spectrometry was used to determine soil and sediment, and the same sample was spiked for 6 times. 1,1-dichloropropene, benzene, 1,2-dichloroethane, etc. The relative standard deviations of the six volatile organic compounds were: 3.0% to 12.6%. It meets the precision requirements of "Soil and Sediment Volatile Organic Compounds Purge and Trap / Gas Chromatography-Mass Spectrometry" (HJ605-2011) (relative standard deviation of the measurement results <15.6%).

3.4. Method accuracy
The laboratory verifies the accuracy of the method through spike experiments. Weigh a sample of 5g, perform the standard addition experiment on the same sample, perform the measurement in accordance with all the steps of the sample analysis, and perform 6 parallel measurements. Calculate the average value, standard deviation, standard addition amount, standard recovery and other parameters of the organic spiked experimental content.

Table 4. Test data of certified reference materials

| Number | Component name    | 1   | 2   | 3   | 4   | 5   | 6   | Standard recovery % | Method Claim |
|--------|-------------------|-----|-----|-----|-----|-----|-----|----------------------|--------------|
| 1      | 1,1-dichloropropene | 105 | 102 | 93.5 | 125 | 123 | 123 | 112                 | 12.4         |
| 2      | benzene           | 114 | 114 | 115 | 129 | 125 | 122 | 120                 | 5.4          |
| 3      | 1,2-dichloroethane | 126 | 131 | 119 | 131 | 122 | 131 | 127                 | 4.3          |
| 4      | Trichloroethylene | 102 | 102 | 102 | 131 | 131 | 120 | 115                 | 12.6         |
| 5      | 1,2-dichloropropane | 123 | 127 | 132 | 126 | 125 | 119 | 126                 | 3.3          |
| 6      | Dibromomethane    | 132 | 129 | 128 | 126 | 123 | 121 | 127                 | 3.0          |

Unit: μg / kg
Determination of soil and sediment by purge-and-trap/gas chromatography-mass spectrometry, standard addition experiments on the same sample, 6 types of 1,1-dichloropropane, benzene, 1,2-dichloroethane, etc. The recovery rate of sexual organics was 112.4% to 127.0%. Meets the accuracy requirements of "Soil and Sediment Volatile Organic Compound Determination Purge and Trap/Gas Chromatography-Mass Spectrometry" (HJ605-2011) (Standard recovery is within 70 to 130%).

4. Conclusion
The laboratory has verified the detection methods of 6 types of volatile organic compounds, such as 1,1-dichloropropane, benzene, 1,2-dichloroethane, etc. in soil and sediment by purge and trap / gas chromatography-mass spectrometry. In the relationship, the corresponding internal standard response value and concentration of the volatile organic compounds show a good linear relationship, the correlation coefficient is 0.9951 to 0.9996; the detection limit is 0.8 to 1.9 μg/kg, and the limit of quantification is 3.2 to 7.6 μg/kg; precision the relative standard deviations of the six volatile organic compounds are: 3.0% to 12.6%; the recovery rate of the six volatile organic compounds in accuracy is: 112.4% to 127.0%. The verification results show that the linear relationship, detection limit, precision, and accuracy all meet the requirements of "Soil and Sediment Volatile Organic Compound Determination Purge and Trap/Gas Chromatography-Mass Spectrometry" (HJ605-2011). The purge-and-trap/gas chromatography-mass spectrometry technology can be used to achieve fast, accurate and sensitive detection of target substances, and can meet the detection requirements of trace volatile organic compounds, so it can be applied to environmental testing work such as soil.

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