

Validation Report of Method for Determination of Organochlorine Pesticides in Soil by Gas Chromatography

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Abstract

According to "Determination of Organic Chlorine Pesticides in Soil and Sediment Gas Chromatography" (HJ 921-2017), the determination of organochlorine pesticides in soil is carried out by analyzing the detection limit, precision and accuracy of the measurement. And research shows that the method is accurate and feasible in the laboratory. The results showed that the detection limit of 23 organochlorine pesticides in soil determined by gas chromatography was 0.01~0.06 µg/kg, the limit of quantification was 0.05~0.23 µg/kg, and the relative deviation was 0.00%-7.88%. The recovery rate is 76.7%-96.8%, and the results all meet the requirements of Gas Chromatography Method for the Determination of Organochlorine Pesticides in Soil and Sediments (HJ 921-2017).

Keywords

Gas chromatography; Organochlorine pesticides; Method validation.

1. Introduction

Organochlorine pesticides are organic compounds containing organochlorine elements in the composition used to prevent and control plant diseases and insect pests. It is mainly divided into two categories: benzene as raw material and cyclopentadiene as raw material. The former include the earliest and most widely used insecticides DDT and BHC, as well as the acaricides dicofol, dicofol, etc., and the fungicides pentachloronitrobenzene, chlorothalonil, Daofengning, etc.; the latter Such as chlordane, heptachlor, aldrin, etc. as insecticides. In addition, camphene pesticides, toxaphene and terpene-based borneol-based pesticides that use turpentine as raw materials are also organochlorine pesticides.

Liu Changyun [1] and others established an accelerated solvent extraction (ASE)-gas chromatography-tandem mass spectrometry (GC-MS/MS) method for simultaneous determination of 18 pesticide residues in soil, and the results are in compliance with GB/T 27404-2008 "Laboratory Quality" Control Standard Food Physical and Chemical Testing" requirements; Wei Xiaohua [2] and others established a gas chromatography-triple quadrupole

mass spectrometry multiple reaction (MRM) method for 8 kinds of organochlorine pesticides, and used this method to detect 8 kinds of organochlorine in osmanthus osmanthus volatile oil pesticide. This method has low background interference and high sensitivity, and is suitable for the monitoring of organochlorine pesticides in the analysis of complex matrix samples; Li Xuehua [3] and others used gas chromatography-electron capture detection method to simultaneously determine 26 kinds of organochlorine pesticides (OCPs) in fish. The residual method, during which the target compound in fish meat is extracted by shaking method, purified by gel chromatography cartridge, concentrated and measured on the machine, qualitatively determined by retention time, and quantified by external standard method. It has been successfully applied to the Songhua River Aquatic Biology Pilot monitor.

2. Method

2.1. Main Instruments and Reagent Consumables

Instruments: Gas chromatograph Agilent 7890B, rotary evaporator RE-52AA, nitrogen blowing instrument NK200-1B, one ten thousandth balance BSA224S-CW, ultrasonic cleaner SB-800DT;

Reagents and consumables: chromatographic reagents: n-hexane (C₆H₁₄); acetone (CH₃COCH₃); methylene chloride (CH₂Cl₂);

Analytical reagents: anhydrous sodium sulfate (Na₂SO₄); silicon dioxide (SiO₂).

Standard stock solution: 23 kinds of organochlorine pesticide standard stock solutions (mass concentration 100mg/L).

Others: Nitrogen purity ≥99.999%.

2.2. Principle of the Method

After the organochlorine pesticides in the soil or sediment are extracted, purified, concentrated, and fixed to volume, they are detected by gas chromatography with an electronic capture detector. Qualitatively based on retention time and quantified by external standard method.

2.3. Experimental Steps

Sample collection and storage: Remove the foreign matter in the sample, weigh about 10g (accurate to 0.01g) of the sample in duplicate, one is to measure the dry matter content in accordance with HJ 613, and the other is added with an appropriate amount of anhydrous sodium sulfate, ground and homogenized into quicksand.

Soxhlet extraction: transfer all the samples to a Soxhlet extraction paper sleeve, add 100 ml of acetone-n-hexane (1:1) mixed solvent, extract 16h-18h, and reflux rate is about 3 times/h-4 times/h. Collect the extract after centrifugation or filtration.

Dehydration: Put a layer of glass wool or glass fiber filter membrane on the glass funnel, spread about 5 g of anhydrous sodium sulfate, then filter the extract directly into the concentration device through the funnel, and then use about 5 ml~10 ml acetone- The mixed solvent of n-hexane (1:1) thoroughly washes the container containing the extract, and filters it into the above-mentioned concentration device through a funnel.

Concentration: Concentrate the dehydrated extract to 1 ml below 45°C for purification.

Purification: Wash the magnesium silicate solid phase extraction column with about 8 ml of n-hexane to keep the surface of the adsorbent in the magnesium silicate solid phase extraction column wet. Use a pipette to transfer the concentrated extract to a magnesium silicate solid phase extraction column for 1 min, then discard the effluent. Add 2 ml of acetone-n-hexane (1:9) mixed solvent and let it stay for 1 min. Use a 10 ml small concentrating tube to receive the eluent. Continue to wash the cartridge with acetone-n-hexane (1:9) mixed solvent until it is received. The eluent volume is up to 10ml.

Concentration and constant volume: Concentrate the purified eluate and constant volume to 1.0 ml, and then transfer it to a 2 ml sample bottle for analysis.

Chromatographic conditions: injection port temperature: 220 °C; injection mode: splitless injection to 0.75min and then open the split, the split outlet flow rate is 60 ml/min; injection volume: 1.0 µl. Oven heating program: the initial temperature is 100°C, the temperature is raised to 220°C at 15°C/min, and the temperature is maintained for 5 minutes, and the temperature is raised to 260°C at 15°C/min, and the temperature is maintained for 20 minutes; ECD detector temperature: 280°C. Carrier gas flow in the chromatographic column: 1.0 ml/min; makeup gas: high-purity nitrogen, flow: 20 ml/min.

3. Results

3.1. Linear Range of the Method

Under the conditions of chromatographic analysis required by the method, measure a series of standard solutions of mass concentration. Draw a standard curve with the measured integrated peak area of each organochlorine pesticide as the ordinate and the mass concentration (mg/L) as the abscissa. The standard curve concentration of each organochlorine pesticide is 0.005 mg/L, 0.01 mg/L, 0.05 mg/L, 0.1 mg/L, 0.5 mg/L, which conforms to the "Determination of Soil and Sediment Organochlorine Pesticides by Gas Chromatography" (HJ 921-2017) (correlation coefficient should be greater than or equal to 0.995) requirements. The linear range of specific detection indicators and the correlation results of linear equations are as follows:

Table 1. Summary table of standard curve

No.	Detection index	Linear range	Linear equation	Correlation (r)
1	α -BCC	0-0.5mg/L	y= 415577.0x-2043.8	0.99974
2	Hexachlorobenzene	0-0.5mg/L	y=368106.5x-1117.6	0.99990
3	β -BHC	0-0.5mg/L	y=127298.6x-638.5	0.99963
4	γ -BHC	0-0.5mg/L	y=366177.7x-1914.1	0.99968
5	δ-BHC	0-0.5mg/L	y=279191.1x-1808.8	0.99947
6	Aldrin	0-0.5mg/L	y=419281.1x-1652.1	0.99985
7	Epoxy heptachlor	0-0.5mg/L	y=326951.7x-1266.8	0.99981
8	External epoxy heptachlor	0-0.5mg/L	y=286059.1x-1867.3	0.99973
9	γ -Chlordane	0-0.5mg/L	y=354856.7x-1720.9	0.99974
10	o,p' -DDE	0-0.5mg/L	y=183094.7x-1100.0	0.99949
11	Endosulfan I	0-0.5mg/L	y=242736.6x-960.4	0.99980
12	α -Chlordane	0-0.5mg/L	y=343767.7x-1104.2	0.99990
13	trans-Nachloro	0-0.5mg/L	y=264440.8x-778.4	0.99987
14	p,p' -DDE	0-0.5mg/L	y=193033.7x-1511.0	0.99891
15	Dieldrin	0-0.5mg/L	y=277445.0x-1211.7	0.99971
16	o,p' -DDD	0-0.5mg/L	y=88953.5x-400.8	0.99928
17	Endrin	0-0.5mg/L	y=151708.0x-787.1	0.99964
18	Endosulfan II	0-0.5mg/L	y=217440.8x-1474.8	0.99934
19	p,p' -DDD	0-0.5mg/L	y=63585.1x-605.9	0.99850
20	o,p' -DDT/cis-Nachloro	0-0.5mg/L	y=445940.4x-2772.5	0.99951
21	p,p' -DDT	0-0.5mg/L	y=107037.5x-1285.3	0.99758
22	Mirex	0-0.5mg/L	y=166566.1x-821.0	0.99962

3.2. The Detection Limit of the Method and the Lower Limit of Determination

According to the relevant regulations of HJ 168-2010 "Technical Guidelines for the Development and Revision of Environmental Monitoring and Analytical Methods", the method for determining the detection limit of organochlorine pesticides in soil is: for the target substance detected in the blank test, follow all the steps of sample analysis , Repeat the blank

test for n ($n \geq 7$) times, convert each measurement result to the content in the sample, calculate the standard deviation of n parallel determinations, and calculate the detection limit according to the formula. The calculation results of the detection limit and quantification limit of the method are shown in Table 2.

$$MDL = t(n-1, 0.99) \times S \text{ (Formula 1)}$$

Where: MDL—method detection limit;

n —the number of parallel determinations of the sample;

t — t distribution (one-sided) with a degree of freedom of $n-1$ and a confidence of 99%;

S —The standard deviation of n parallel determinations.

Among them, when the degree of freedom is 6, the t value with a confidence of 99% is 3.143.

Table 2. Method detection limit, measurement lower limit test data table Unit: $\mu\text{g/kg}$

No	Component	1	2	3	4	5	6	7	Standard deviation	Detection limit	Quantitative limit
1	α -BCC	1.56	1.56	1.57	1.56	1.57	1.57	1.57	0.00	0.01	0.05
2	Hexachlorobenzene	1.34	1.36	1.38	1.36	1.37	1.39	1.38	0.02	0.05	0.20
3	β -BHC	1.65	1.68	1.69	1.69	1.70	1.70	1.70	0.02	0.05	0.19
4	γ -BHC	1.64	1.64	1.64	1.63	1.64	1.64	1.63	0.00	0.01	0.05
5	δ -BHC	1.82	1.83	1.88	1.84	1.84	1.85	1.85	0.02	0.06	0.23
6	Aldrin	1.40	1.39	1.39	1.40	1.40	1.40	1.40	0.00	0.01	0.06
7	Epoxy heptachlor	1.47	1.46	1.46	1.46	1.46	1.46	1.46	0.00	0.01	0.06
8	External epoxy heptachlor	1.61	1.60	1.60	1.61	1.61	1.62	1.61	0.01	0.02	0.06
9	γ -Chlordane	1.59	1.58	1.59	1.58	1.59	1.59	1.59	0.00	0.01	0.04
10	o,p' -DDE	1.83	1.83	1.85	1.85	1.85	1.87	1.86	0.02	0.05	0.19
11	Endosulfan I	1.51	1.50	1.50	1.49	1.50	1.49	1.48	0.01	0.03	0.14
12	α -Chlordane	1.26	1.26	1.28	1.27	1.27	1.29	1.29	0.01	0.04	0.16
13	trans-Nachloro	1.28	1.28	1.28	1.28	1.28	1.28	1.28	0.00	0.01	0.03
14	p,p' -DDE	2.08	2.09	2.11	2.10	2.08	2.12	2.09	0.01	0.05	0.18
15	Dieldrin	1.76	1.78	1.76	1.79	1.78	1.80	1.77	0.01	0.04	0.16
16	o,p' -DDD	1.88	1.86	1.86	1.87	1.86	1.88	1.84	0.01	0.04	0.16
17	Endrin	1.75	1.73	1.75	1.73	1.73	1.73	1.72	0.01	0.03	0.13
18	Endosulfan II	1.98	1.97	1.99	1.98	1.98	1.99	1.98	0.01	0.02	0.08
19	p,p' -DDD	2.41	2.44	2.44	2.45	2.44	2.44	2.44	0.01	0.04	0.16
20	o,p' -DDT/cis-Nachloro	1.80	1.81	1.79	1.80	1.80	1.81	1.78	0.01	0.04	0.15
21	p,p' -DDT	2.83	2.82	2.79	2.77	2.80	2.79	2.82	0.02	0.06	0.23
22	Mirex	1.74	1.75	1.77	1.76	1.75	1.76	1.76	0.01	0.04	0.14

Conclusion: The detection limit of organochlorine pesticides in 23 kinds of soil is $0.01 \sim 0.06 \mu\text{g/kg}$, and the limit of quantification is $0.05 \sim 0.23 \mu\text{g/kg}$. The detection limit and quantification limit of organochlorine pesticides in soil are in line with the Determination of Organochlorine Pesticides in Sediments Gas Chromatography (HJ 921-2017) requirements.

3.3. Verification of Method Precision

The laboratory analyzed and determined organochlorine pesticides in the same soil. The determination was carried out in accordance with all the steps of sample analysis. Each sample was tested in parallel 6 times. The data summary table is shown in Table 3. Calculate the average value, standard deviation, relative deviation and other parameters of different samples.

Table 3. Precision test data Unit: ug/kg

No.	Component name	1	2	3	4	5	6	Average Standard	Deviation Relative	Deviation%
1	α -BCC	18.81	18.75	18.85	18.96	18.81	19.03	18.87	0.11	0.04-0.42
2	Hexachlorobenzene	19.35	19.31	19.46	19.60	19.46	19.73	19.48	0.16	0.06-0.63
3	β -BHC	18.31	18.24	18.41	18.52	18.37	18.61	18.41	0.14	0.01-0.54
4	γ -BHC	18.57	18.50	18.61	18.73	18.57	18.77	18.62	0.10	0.03-0.39
5	δ -BHC	18.09	17.99	18.16	18.29	18.13	18.38	18.17	0.14	0.03-0.57
6	Aldrin	19.23	19.19	19.19	19.38	19.22	19.47	19.28	0.12	0.14-0.49
7	Epoxy heptachlor	19.03	19.00	19.10	19.12	18.96	19.28	19.08	0.11	0.06-0.51
8	External epoxy heptachlor	18.81	18.80	18.92	19.03	18.89	19.13	18.93	0.13	0.03-0.52
9	γ -Chlordane	18.84	18.82	18.93	19.07	18.89	19.15	18.95	0.13	0.05-0.51
10	<i>o,p'</i> -DDE	18.14	18.11	18.35	18.46	18.38	18.69	18.36	0.21	0.02-0.90
11	Endosulfan I	18.71	18.73	18.62	18.40	18.60	18.67	18.62	0.12	0.00-0.59
12	α -Chlordane	19.02	18.85	19.16	19.48	19.02	19.41	19.16	0.24	0.02-0.83
13	trans-Nachloro	18.80	18.72	18.84	18.93	18.74	19.02	18.84	0.12	0.01-0.47
14	<i>p,p'</i> -DDE	16.65	16.63	16.98	17.51	17.09	17.83	17.11	0.48	0.06-2.05
15	Dieldrin	19.00	19.02	19.02	20.02	18.84	20.11	19.34	0.57	0.81-1.96
16	<i>o,p'</i> -DDD	17.08	17.10	17.27	21.48	17.19	21.85	18.66	2.33	3.88-7.88
17	Endrin	18.50	18.56	18.68	18.74	18.57	18.99	18.67	0.18	0.02-0.85
18	Endosulfan II	17.85	17.82	17.94	18.04	17.84	18.12	17.94	0.12	0.01-0.51
19	<i>p,p'</i> -DDD	16.51	16.54	16.84	17.05	16.75	17.16	16.81	0.26	0.08-1.03
20	<i>o,p'</i> -DDT /cis-Nachloro	18.24	18.28	18.45	18.57	18.43	18.75	18.45	0.19	0.00-0.79
21	<i>p,p'</i> -DDT	15.34	15.06	15.38	15.73	15.84	16.18	15.59	0.41	0.69-1.86
22	Mirex	18.39	18.15	18.39	18.64	18.36	18.68	18.43	0.20	0.11-0.78

Conclusion: For the same soil sample measured 6 times, the relative deviation of 23 kinds of organochlorine pesticides is 0.00%-7.88%, which meets the requirements of "Determination of Soil and Sediment Organochlorine Pesticides by Gas Chromatography" (HJ 921-2017) (the results are relative The deviation should be within 30%) in the precision requirements.

3.4. Method Accuracy Verification

Table 4. Test data of standard addition recovery test (ug/kg)

No	Component Name	1	2	3	4	5	6	Average Standard	Deviation Standard	Addition	Recovery %
1	α -BCC	18.81	18.75	18.85	18.96	18.81	19.03	18.87	0.11	20	94.0
2	Hexachlorobenzene	19.35	19.31	19.46	19.60	19.46	19.73	19.48	0.16	20	96.8
3	β -BHC	18.31	18.24	18.41	18.52	18.37	18.61	18.41	0.14	20	91.6
4	γ -BHC	18.57	18.50	18.61	18.73	18.57	18.77	18.62	0.10	20	92.9
5	δ -BHC	18.09	17.99	18.16	18.29	18.13	18.38	18.17	0.14	20	90.4
6	Aldrin	19.23	19.19	19.19	19.38	19.22	19.47	19.28	0.12	20	96.1
7	Epoxy heptachlor	19.03	19.00	19.10	19.12	18.96	19.28	19.08	0.11	20	95.1
8	External epoxy heptachlor	18.81	18.80	18.92	19.03	18.89	19.13	18.93	0.13	20	94.1
9	γ -Chlordane	18.84	18.82	18.93	19.07	18.89	19.15	18.95	0.13	20	94.2
10	<i>o,p'</i> -DDE	18.14	18.11	18.35	18.46	18.38	18.69	18.36	0.21	20	90.7
11	Endosulfan I	18.71	18.73	18.62	18.40	18.60	18.67	18.62	0.12	20	93.5
12	α -Chlordane	19.02	18.85	19.16	19.48	19.02	19.41	19.16	0.24	20	95.1
13	trans-Nachloro	18.80	18.72	18.84	18.93	18.74	19.02	18.84	0.12	20	94.0
14	<i>p,p'</i> -DDE	16.65	16.63	16.98	17.51	17.09	17.83	17.11	0.48	20	83.2
15	Dieldrin	19.00	19.02	19.02	20.02	18.84	20.11	19.34	0.57	20	95.0
16	<i>o,p'</i> -DDD	17.08	17.10	17.27	21.48	17.19	21.85	18.66	2.33	20	85.4
17	Endrin	18.50	18.56	18.68	18.74	18.57	18.99	18.67	0.18	20	92.5
18	Endosulfan II	17.85	17.82	17.94	18.04	17.84	18.12	17.94	0.12	20	89.2
19	<i>p,p'</i> -DDD	16.51	16.54	16.84	17.05	16.75	17.16	16.81	0.26	20	82.5
20	<i>o,p'</i> -DDT /cis-Nachloro	18.24	18.28	18.45	18.57	18.43	18.75	18.45	0.19	20	91.2
21	<i>p,p'</i> -DDT	15.34	15.06	15.38	15.73	15.84	16.18	15.59	0.41	20	76.7
22	Mirex	18.39	18.15	18.39	18.64	18.36	18.68	18.43	0.20	20	92.0

The laboratory verifies the accuracy of the method through a standard addition test for organochlorine pesticides. The same sample was spiked and measured according to all the steps of sample analysis. Each sample was measured in parallel 6 times. The data summary

table is shown in Table 4. Calculate the average value, relative deviation/scaling amount, spiked recovery rate and other parameters of different concentrations of certified reference material samples.

Conclusion: For the same sample, the recovery rate of 23 kinds of organochlorine pesticides is 76.7%~96.8%, and the relative error meets the requirements of "Determination of Soil and Sediment Organochlorine Pesticides by Gas Chromatography" (HJ 921-2017) (the actual sample is added The standard recovery rate should be between 60% and 120%, and the relative deviation of the measurement results of the spiked parallel samples should be within 30%).

4. Conclusion

4.1. Linear Range

The correlation coefficients of 23 kinds of organochlorine pesticides are 0.99758~0.99990, which meets the requirements of Gas Chromatography Method for Determination of Organochlorine Pesticides in Soils and Sediments (HJ 921-2017) (the correlation coefficient should be greater than or equal to 0.995).

4.2. Detection Limit

The detection limit of 23 organochlorine pesticides in soil determined by gas chromatography is 0.01~0.06 µg/kg, and the limit of quantification is 0.05~0.23 µg/kg. Chromatography (HJ 921-2017) requires the detection limit and quantification limit of organochlorine pesticides in soil.

4.3. Precision

For the same soil sample tested 6 times, the relative deviation of 23 kinds of organochlorine pesticides is 0.00%-7.88%, which meets the requirements of "Determination of Soil and Sediment Organochlorine Pesticides by Gas Chromatography" (HJ 921-2017) (the relative deviation of the measurement results should be Within 30%) of the precision requirements.

4.4. Accuracy

For the same sample spiked, the recovery rate of 23 kinds of organochlorine pesticides is 76.7%~96.8%, and the relative error meets the requirements of "Determination of Soil and Sediment Organochlorine Pesticides by Gas Chromatography" (HJ 921-2017) (the actual sample is spiked) The recovery rate should be between 60% and 120%, and the relative deviation of the measurement results of the spiked parallel samples should be within 30%).

The method of applying gas chromatography to detect organochlorine pesticides in soil has high sensitivity, good repeatability, accurate results and strong operability, and is suitable for laboratory testing.

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