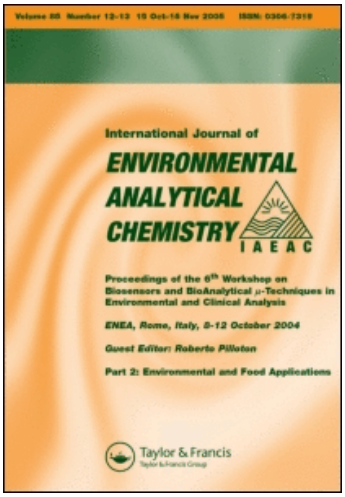

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Determination of chlordecone in soils by GC/MS

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The objective of this study was to develop and characterize an extraction method for chlordecone determination in soils. An accelerated solvent extractor was found to be suitable for extracting chlordecone from soils, but a clean-up step was necessary to recover chlordecone from the hexane solution. Analysis was performed by GC/MS using a PTV injector with a large-volume injection. Validation of the method showed that calibration was linear from 0.23 to 5.3 mg L^{-1} (0.023–0.53 mg kg^{-1}), and the method was repeatable and reproducible. The mean recovery was 79%. The specificity was acceptable from 1 to 25 mg kg^{-1}. A limit of quantification of 1 mg kg^{-1} was attained.

Keywords: Chlordecone; Volcanic soil; Method validation; ASE

1. Introduction

Chlordecone is a chlorinated pesticide ($C_{10}Cl_{10}O$) applied to soils to combat weevil. Chlordecone has been mainly used in banana and sweet-potato cultivation in Martinique and Guadeloupe (France), and various parts of South America, Africa, and Asia.

For chlordecone and other pesticides in general, there are concerns over the transfer of soil residues to rotating crops as well to surface and groundwater systems. Chlordecone is considered to have a long persistence in soils.

Our laboratory was required to quantify chlordecone in soils, mainly surface water and banana trees, to evaluate potential contamination in Martinique. Soils are supposed to contain β-HCH and mainly chlordecone. They are young volcanic soils containing amorphous clay (allophan), which has particular exchange characteristics and complexes the organic matter.

Chlordecone was in use for many years; nevertheless, dedicated methods for its analysis are rare in international literature. The analytical methods reported so far include two GC methods [1, 2].

The present study presents the method development for chlordecone in soils. The strategy for the chlordecone determination was to start with the accelerated solvent

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extractor (ASE) method used for β-HCH determination in soils in our laboratory [3] with GC/MS analysis, and then to validate the method to ensure the reliability and quality of the data produced. The required performance characteristics are defined in international and national legislations such as the Directive 91/414/EEC [4] in the case of the European Union or the AFNOR XP T 90-210 French norm [5] in the case of France. The present validation was a 'single laboratory' validation [6], following the requirements of AFNOR XP T 90-210 [5]. As β-HCH extraction and analysis are well known, β-HCH was added in all experiments as a tracer, to help understand the behaviour of chlordecone.

2. Experimental

2.1. *Chemicals*

Chlordecone (chlordecone hydrate) [143-50-0] solid compound (98.5% purity) and a solution of 10 mg L^{-1} in isooctane, and β-HCH [319-85-7] solid compound (98.0% purity) and 2,2′,5,6′-tetrachlorobiphenyl (CB53) [41464-41-9] and a solution of 10 ng μL^{-1} in iso-octane were purchased from CIL Cluzeau. Acetone and diethyl ether were supplied by SDS. Hexane and cyclohexane were purchased from Carlo Erba.

Independent stock solutions of standards were prepared by weighing 1 mg of β-HCH into 100 mL of cyclohexane and 20 mg of chlordecone into 100 mL of isooctane. A second solution of 10 mg L^{-1} of chlordecone was prepared by mixing 0.5 mL of stock solution and 9.5 mL of isooctane. CB53 was used as an internal standard, and the stock solution was used as received.

For GC calibration, standard solutions were prepared by adding volumes of each 10 mg L^{-1} solution and bringing the volume to 1 mL with isooctane, to yield concentrations of 0.2–5 mg L^{-1} for GC/MS. Fifty microlitres of CB53 solution was added in each standard solution by weighing.

2.2. *Preparation of soil samples*

Soils were dried at 40°C, crushed, sieved through a 2 mm mesh screen, and mixed thoroughly. A Dionex ASE (ASE 200) was used for soil extraction, with 11 mL stainless steel extraction cells and 40 mL vials for collection of extracts. Aliquots of soils (10 g) were weighed into extraction cells between two sand beds. Extraction was performed using a mixture of hexane : acetone (1 : 1, v/v), with the following ASE conditions: oven temperature 100°C; pressure 14 MPa (2000 psi); oven heat-up time 5 min; static time 5 min; flush volume 5 min; nitrogen purge 1 MPa (150 psi) for 60 s.

2.3. *Clean-up*

Extracts (30 mL) were evaporated by vacuum rotary evaporation at 40°C to ca. 3 mL. Florisil cartridges (Sep Pack Plus Florisil cartridges WATERS WA020525) were conditioned with ca. 6 mL of hexane/diethyl ether (80 : 20, v : v) and ca. 6 mL of diethyl ether. Glass vials (10 mL) were placed into vacuum flasks. Extracts were eluted through cartridges slowly by using a slight vacuum. Cartridges were rinsed with 6 mL of diethyl ether. This volume was reduced to 1 mL under a gentle stream of nitrogen. After weighing, 50 μL of internal standard solution was added by weighing. This extract was analysed by GC/MS to determine both β-HCH and chlordecone.

2.4. *Instrumentation and chromatographic conditions*

The gas chromatograph system consisted of a Varian 3800 model equiped with a SATURN 2000 mass detector, 1079 temperature-programmable vaporizing injector and 8200 autosampler.

The column CP-Sil 8 CB for pesticides fused-silica WCOT was purchased from Supelco. The optimized instrumental parameters for the chromatographic analysis of Chlordecone and β-HCH are described in section 3.

3. Results and discussion

3.1. *GC/MS analysis*

PTV injector was tested with GC/MS. A first test with the temperature injection at 40°C allowed chlordecone detection. Then, the appropriate temperature programme for the injector was determined with an injection volume of 20 µL: 55°C (1.5 min) to 300°C at 200°C min^{-1}. The retention times were 35.4, 38.5, and 46.1 min for β-HCH, CB53, and chlordecone, respectively, with the following oven temperatures: 55°C (3 min) to 300°C at 5°C min^{-1} (holding for 5 min). Identification was attained using specific masses, as shown in figure 1.

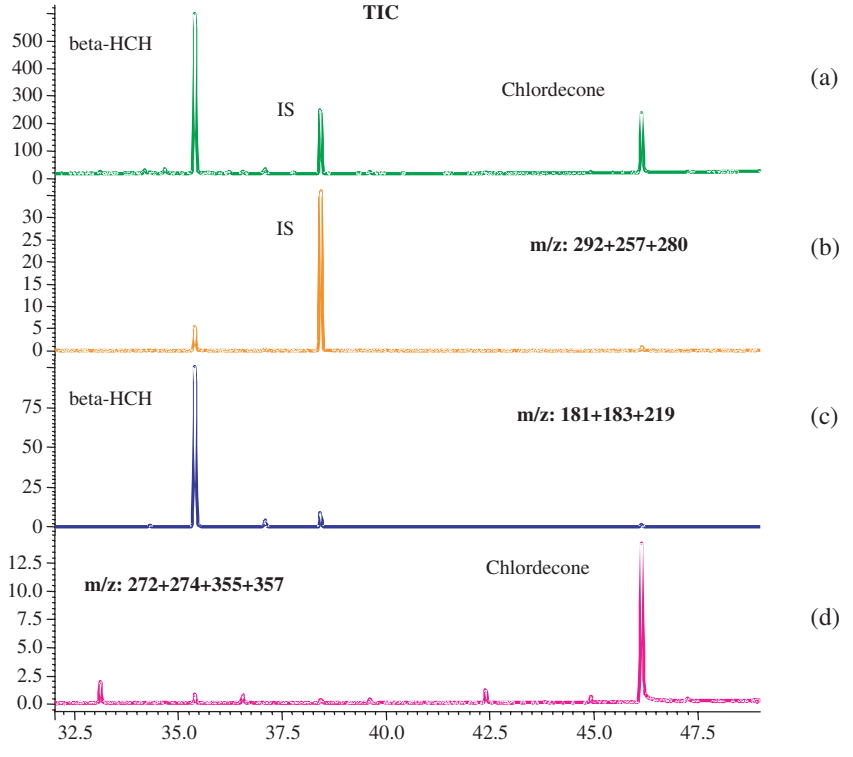

Figure 1. Chromatograms of a standard solution of chlordecone and β-HCH with CB 53 as internal standard (IS) by GC/MS with a PTV injector (20 µL injected). (a) Total ion current (TIC) chromatogram. (b) Mass selection for IS identification. (c) Mass selection for β-HCH identification. (d) Mass selection for chlordecone identification.

Table 1. Recoveries (R, %), means (x) and standard deviations (σ) obtained for spiked sand (chlordecone (CD) and β-HCH, 100 and 200 $\mu g\,kg^{-1}$ both) extracted with ASE using three temperatures (ambient, 50, and 100°C).

	20°C				50°C				100°C			
	β-HCH		CD		β-HCH		CD		β-HCH		CD	
Spike	100	200	100	200	100	200	100	200	100	200	100	200
R%	110	88	91	81	97	93	98	96	97	93	112	108
	119	95	85	72	109	92	115	96	81	88	97	113
	79	109	84	62	99	97	97	99	89	93	104	149
x	103	98	86	72	102	94	103	97	89	92	104	124
σ	21	11	4	10	6	3	10	2	9	3	8	23

3.2. *ASE conditions*

ASE conditions were determined by testing three oven temperatures, ambient (20°C), 50°C, and 100°C, with spiked sand samples. Two spiking concentrations, 100 and 200 $\mu g\,kg^{-1}$, for β-HCH and chlordecone were tested in triplicate.

The results of β-HCH and chlordecone recovery are listed in table 1. These showed that a temperature of 50 or 100°C did not result in degradation of chlordecone. A temperature of 100°C was therefore selected to ensure the best extraction efficiency.

3.3. *Clean-up conditions*

ASE method was applied to one soil sample (A1). The extract was diretly injected (without clean-up); no chlordecone and β-HCH were detected. The soil was then spiked (0.23 $mg\,kg^{-1}$ chlordecone and β-HCH) before extraction; β-HCH was recovered, but no trace of chlordecone was detectable.

The problem was supposed to be due to two factors: (1) the matrix that could not be extracted with ASE or (2) the extract composition would contain small particles able to adsorb chlordecone. As small solid particles were present in the extracts, clean-up on florisil cartridges was decided.

Tests with florisil cartridges were performed with standard solutions. Elution was first performed with hexane and hexane/diethyl ether (80 : 20, v/v). This composition did not allow chlordecone recovery; only β-HCH was recovered (70–80%). Composition of the eluent was increased with diethyl ether, and 100% diethyl ether only allowed chlordecone recovery from the cartridge (98%).

Florisil clean-up with single elution with diethyl ether was applied to the spiked soil sample; chlordecone recovery was 81% and β-HCH recovery 80%.

3.4. *ASE recovery*

Five consecutive extractions were performed with soil sample A2 (spiked at a concentration of 3.2 $mg\,kg^{-1}$). The first extraction was sufficient to recover chlordecone, while subsequent extractions showed no trace of chlordecone.

3.5. *Performance of the method*

A validation procedure was conducted to determine the response linearity, repeatability, reproducibility, specificity, and LOQ of the method according to the AFNOR XP T 90-210 French norm [5].

3.5.1. Linearity. Calibration of the GC/MS was performed using independent standard solutions. Five series of five standard solutions (0.2–1.1–2.6–3.9–5.3 mg L^{-1} for chlordecone) were injected consecutively. The equation for the calibration was $y = 0.1014x - 0.03$ with $R^2 = 0.9921$. Grubbs' test was first applied to detect aberrant values; it showed no outlier. Then, Cochran's test was applied to determine whether variances obtained for each standard concentration were homogeneous; it indicated that variances were acceptable. Therefore, a least-squares method could be applied to calculate a simple regression, and a statistical test was applied to determine its adequacy to the linear model (table 2). Tests showed that the model was linear, with a negligible model error (table 2).

3.5.2. Repeatability. Nine different soil samples containing 0.2–10 mg kg^{-1} of chlordecone were extracted in duplicate on the same day by the same operator. Determinations were performed with the same calibration line. Results showed that the repeatability of the method was constant for the whole working range (0.673 compared with $C_{\text{cohran}} = 0.754$, 99% confidence with 9 and 2 df); the variance was 0.318.

3.5.3. Reproducibility. Two aliquots of sample A3 per day were extracted by two operators over nine different days. Analyses were performed over 20 days with five calibration lines.

The statistical test showed a variance of within-laboratory reproducibility of 0.527. The standard deviation was therefore 0.35 mg kg^{-1} for a 3.26 mg kg^{-1} chlordecone concentration. The relative standard deviation (or coefficient of variation) was 22%.

3.5.4. Specificity. The specificity was performed to verify the matrix effect according to [5]. Twelve different soil samples containing 0.15–10 mg kg^{-1} of chlordecone were extracted. In the same period of time, they were fortified with the appropriate chlordecone solutions and extracted. All samples were analysed in the same period; dilution of the extracts was necessary for concentrations higher than 0.5 mg kg^{-1}. The results are listed in table 3.

Statistical tests showed that the slope of the line (recovered concentration vs. spiking concentration) was not equivalent to 1 (table 3). Examination of the recoveries shows that low recoveries were obtained for chlordecone concentrations lower than 1 mg kg^{-1}. For higher concentrations, recoveries ranged from 51 to 115%.

Concerning low concentrations, the hypotheses were: (1) there was a dilution effect, as only those samples were injected without dilution; (2) the method is not appropriate for low contaminated samples (<1 mg kg^{-1}).

A test of dilution was performed, comparing values of a soil extract and a standard solution (both at the same concentration) measured after several dilutions from 1/2 to 1/30, according to the calibration working range. Concentrations were recovered with 15% variation in both samples. The hypothesis that the dilution effect involved incomplete determination had to be rejected.

The method was therefore not appropriate to accurately determine concentrations lower than 1 mg kg^{-1}. The average of recoveries, for concentrations higher than 0.9 mg kg^{-1}, gave a 79% mean recovery with a 21% standard deviation. In conclusion, the method was considered to be specific for concentrations from 1 to 50 mg kg^{-1}.

Table 2. Test of linear model for chlordecone calibration.

Test of linear model					
$y = b_0 + b_1 \cdot u$	b_1	0.1014	−0.0300	b_0	
Number of injections					
$N = 25$	s_{b1}	0.0019	0.0133	s_{b0}	
	r^2	0.9921	0.0393	s_{ey}	
	F	2876.4943	23	df	
	SCE $I(Y)$	4.4364	0.0355	SCE res	
Source of variation	Sum of the squared deviations	Degrees of freedom	Variance	F calculated	Critical value with 99% confidence
Regression	SCE $I(Y) = 4.4364$	1	$s^2I(Y) = \text{SCE } I(\text{Y})$	$FI = s^2I(Y)/s^2e(sY) = 4163.07$	VCI $= F(1, np-p, 1-\alpha) = 8.10$
Model error	SCE $nI(\text{Y}) = \text{SCE } I(\text{Y})$ SCE $e(Y) = 0.0142$	$p-2$	$s^2nI(Y) = \text{SCE } nI(\text{Y})/(p-2)$	$FnI = s^2nI(Y)/s^2e(Y) = 4.43$	VCI $nI = F(p-2, np-p, 1-\alpha) = 4.94$
Experimental error	SCE $e(Y) = 0.0213$	$np-p$		$s^2e(Y) = \text{SCE } e(Y)/[p(n-1)+1]$	
Sum	SCE $(Y) = \text{SCE } I(Y) + \text{SCE } e(Y) +$ SCE $nI(Y) = 4.4718$	$np-1$			

I: Acceptability of regression model, FI > VCI Linear model is acceptable, FI ≤ VCnI Calibration is not linear.
I: Acceptability of calibration model, FnI ≤ VCnI Calibration range is validated; model error is negliligble, FnI > VCnI Model error is significant; curvature of line.

Table 3. Specificity test[a].

Sample	Initial concentration (1) ($mg\,kg^{-1}$)	Spiking (2) ($mg\,kg^{-1}$)	Concentration after spiking (3) ($mg\,kg^{-1}$)	Recovered concentration (4) ($mg\,kg^{-1}$)	Recovery (5) (%)
A64	0.158	0.080	0.135	−0.023	−29
A67	0.589	0.181	0.595	0.006	3
A69	0.592	0.334	0.563	−0.029	−9
A71	0.241	0.655	0.951	0.710	108
A6	0.595	1.061	1.814	1.219	115
A40	1.865	2.621	3.214	1.349	51
B76	1.884	4.520	4.489	2.605	58
B9	6.754	7.613	11.792	5.038	66
B56	7.820	10.959	16.395	8.575	78
B30	7.984	10.791	16.515	8.531	79
B45	8.504	7.277	14.160	5.656	78
B23	6.337	25.154	26.558	20.221	80
Student's t for 99% confidence, 10 degrees of freedom					$t = 3.169$
Confidence interval for the slope				0.74254	0.86608
Confidence interval for the intercept				−0.85373	0.27922
Slope				c_1	0.80431
Standard deviation for the slope				sc_1	0.01949
Intercept				c_0	−0.28725
Standard deviation for the intercept				$s(c_0)$	0.17887
Correlation coefficient				r	0.99416
Is the slope equivalent to 1?					No
Is the intercept equivalent to 0?					Yes
Is the specificity acceptable?					No

[a]*Initial concentration* (1) is the sample native concentration; *spiking* (2) is the chlordecone concentration added to the native sample; *concentration after spiking* (3) is the concentration measured in the spiked sample; and *recovered concentration* (4) is obtained by (3)–(1). *Recovery* (5) is obtained by (4)/(2); negative recoveries have no physical meaning.

3.5.5. LOQ. An LOQ of $1\,mg\,kg^{-1}$ was tested. Uncontaminated soil was spiked at $0.9919\,mg\,kg^{-1}$ with chlordecone. Ten replicates were extracted and analysed. Comparison of the mean with the reference value revealed that the LOQ of $1\,mg\,kg^{-1}$ was acceptable (table 4). The limit of detection was calculated as LOQ/3, i.e. $0.33\,mg\,kg^{-1}$.

3.6. *Uncertainty*

To fulfil the requirements of ISO 17025 [7], the uncertainty associated with the method was estimated as part of the method development. The uncertainty was estimated according to the recommendation of the International Organization for Standardization's Guide to expression of uncertainty in analytical measurements (GUM) [8] and the EURACHEM/CITEC Guide to Quantifying the Uncertainty in Analytical Measurements [9].

A four-step procedure was used in the quantification of uncertainty: specify the measurand, identify uncertainty sources, quantify uncertainty components, and calculate the combined uncertainty.

The measurand is the chlordecone concentration in soil (C_{kp}) given by:

$$C_{kp} = \frac{C \times v_{fe}}{m},$$

Table 4. Limit of quantification (LOQ) test.

Replicate	u_i	LOQ to validate = 0.9919
1	0.656	
2	1.04	
3	1.023	
4	1.332	
5	1.323	
6	1.105	
7	0.923	
8	1.212	
9	0.868	
10	1.070	
p	10	
Mean u_m	1.085	
S_{LOQ}	0.174	

		Values		
		Calculated	Critical	Conclusion
Accuracy criteria	abs[(LOQ − u_m)/(s_{LOQ}/rac(p))]	0.96	10	LOQ true if $V_{calc} < 10$
Confident criteria	CV = s(LOQ)/LOQ%	19.7	20	If CV < 20%, LOQ > 0

where C = chlordecone concentration in the extract (mg L^{-1}); v_{fe} = volume of the extract (L) calculated from weighing; m = mass of the soil sample.

The uncertainty sources are identified as:

1. The soil sample weighing;
2. The homogeneity (recovery) and clean-up step;
3. The extract weighing;
4. The preparation of the calibration standards;
5. The calibration curve;
6. The peak integration (operator effect).

As the mass of soil sample and mass of final extract volume are involved in the chlordecone concentration calculation, the weighing contribution ($s(m)$) must be included in the investigation. It is calculated with several potential uncertainty sources (balance calibration uncertainty, linearity, daily drift, and run to run variation) as

$$s(m) = 5.77^{E-05} + 1.80^{E-06} \times m,$$

where m = weighing mass (g).

For weighing 10 g of soil, $s(m_{10}) = 7.58^{E-05}$ and $u(m_{10}) = 7.58^{E-04\%}$. For a 0.806 g final extract obtained by weighing 0.756 g of extract and 0.050 g of internal standard solution, $s(m_{0.806}) = 1.16^{E-04}$ and $u(m_{0.806}) = 1.45^{E-02\%}$.

The issue of whether to include the recovery contribution in the uncertainty estimation is currently being discussed by experts. Recovery and clean-up step uncertainties were both determined using the specificity test results. The average recovery was $79 \pm 21\%$ from nine experiments. The recovery contribution was determined as: $u(R) = 21/\sqrt{9} = 7\%$.

The uncertainty of calibration standard preparation ($u(S)$) was determined from the sum of the five standard uncertainties ($u(C_s)$). For each concentration

standard, the uncertainty (%) was obtained from:

$$u(C_s) = \sqrt{\left[\frac{U_{CM}^2}{C_M^2} + \frac{U_{mM}^2}{\rho_M^2} \cdot \frac{V_M^2 U_{ms}^2}{\rho_s^2} \cdot \frac{(V_M + V_s)^2 + U_{mM}^2}{\rho_M^2 \cdot (V_M + V_s)^2}\right]},$$

where: C_s = concentration of the standard solution; U_{CM} = uncertainty of the concentration of the 100 mg L^{-1} stock solution; C_M = concentration of the 100 mg L^{-1} stock solution; U_{mM} = uncertainty of the mass of the 100 mg L^{-1} stock solution used to prepare the standard; ρ_M = volumic mass of the 100 mg L^{-1} stock solution; V_M = volume of the 100 mg L^{-1} stock solution used to prepare the standard; U_{ms} = uncertainty of the mass of the solvent used to prepare the standard; ρ_s = volumic mass of the solvent; V_s = volume of the solvent used to prepare the standard.

The uncertainty for the whole calibration standards preparation was $u(S) = 0.71\%$. The contribution of the calibration curve was determined by calculating the uncertainty for each value of concentration measured with the linear regression from:

$$s(U_i) = \sqrt{\left[\left(\frac{s_{ey}^2}{b_1}\right) + \frac{1}{N} + \frac{(y_i - x(y))^2}{b_1^2} \times \mathrm{SCE}(u)\right]}.$$

Details for the formula are given in table 2. For example, with $y = 0.25$ and $U = 2.76$, $s(U_{2.76}) = 0.40$ and $u(U_{2.76}) = 14.5\%$. For other concentrations of the calibration working range, see table 5.

The uncertainty due to the peak integration by the technician is estimated from reproducibility experimentation on a soil sample. The mean A/A_{IS} measurement was 0.7669 ± 0.0475 for five integration replicates. Grubbs' test showed no outlier. The peak integration contribution was determined from: $u(P) = 0.0475/\sqrt{5} = 2.1\%$.

The total uncertainty was based on estimated uncertainties expressed as variances from calibrations standards, linear model, specificity, reproducibility, and weighing precision, and given by the law of propagation:

$$u(C_{Kp}) = \sqrt{[u^2(m) + u^2(R) + u^2(S) + u^2(U_i) + u^2(P)]}$$

Table 5. Values of uncertainty due to calibration ($u(U_i)$%) for each standard ($u_i = C_{Kp}/C_{is}$) and values of combined uncertainty (%) for chlordecone concentrations (C_{Kp}, mg kg^{-1}) and contribution of each source.

u_i	1.04	2.76	5.23	10.65
$S(U_i)$	0.40	0.40	0.40	0.41
$u(U_i)$ (%)	38.5	14.5	7.6	3.8
C_{Kp} mg kg^{-1}	0.053	0.14	0.27	0.55
Total uncertainty u(C_{Kp}) (%)	39.2	16.2	10.6	8.3
Combined uncertainty $2 \times u(C_{Kp})$ (%)	78	32	21	17
Standards preparation contribution (%)	0.03	0.19	0.45	0.74
Calibration contribution (%)	96.5	79.6	52.0	21.6
Extract volume contribution (%)	0.00	0.00	0.00	0.00
Peak integration contribution (%)	0.29	0.00	0.00	0.00
Mass sample contribution (%)	0.00	0.00	0.00	0.00
Recovery contribution (%)	3.2	18.6	43.6	71.3

The combined uncertainty is given as the total uncertainty multiplied by a coverage factor of 2, which correspond to a confidence level of 95%.

Table 5 presents the combined uncertainties vs. chlordecone concentrations of the working-range calibration. They varied from 78 to 17%. For chlordecone concentrations higher than $1\,mg\,kg^{-1}$, extracts have to be diluted. With appropriate dilutions being in the $1–4\,mg\,L^{-1}$ range, the combined uncertainty was in the 17–32% range. The main uncertainty contributions were the calibration curve and the recovery.

4. Conclusions

A method for chlordecone determination was developed by GC/MS with a PTV injector. Kepone calibration was found to be linear from 0.23 to $5.3\,mg\,L^{-1}$ ($0.023–0.53\,mg\,kg^{-1}$). Soil extraction was performed with ASE, but a clean-up step was necessary to recover chlordecone from the hexanic solution. An LOQ of $1\,mg\,kg^{-1}$ was found; if a lower LOQ is needed, further work would be necessary with this type of soil. The method was repeatable and reproducible, and was specific from 1 to $25\,mg\,kg^{-1}$. The method uncertainty could be lower than 30% with the appropriate dilution of the extract.

Young volcanic soils were validated. A whole validation has to be carried out again if another type of soil is studied, due to the chemical structure of chlordecone, which can interact with organic matter with its C=O bond.

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