

GC ANALYSIS OF CHLORINATED CATECHOLS IN SOILS BY INTERNAL STANDARD METHOD

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An improved gas chromatography (GC) analysis method was developed with seven chlorinated catechol compounds in soils. Six solvent systems were tested by a shaking method of extraction. The method include extraction, mixing with internal standard 2,6-dimethoxyphenol, then derivatization with pentafluorobenzyl bromide, cleanup by water-toluene shaking and then injected to GC. The recovery yields varied largely from 67 to 90% within six solvent systems. Two solvent system: Diethylether-hexane-acetoneheptane (3:3:2:2) and hexane-heptane-chloroform (1:1:1) gave the highest yields in both soils. The standard deviations and t-test were applied to the results where some significant variations were also recorded.

Key words: Chlorinated catechols, Solvent system, Internal standard, Recovery yields, Soil analysis.

Introduction

Chlorinated catechols are environmental residues as the metabolites of herbicides or chlorination of lignin in pulp mills contained toxic phenolic compounds such as catechol [1-4] and its chloro derivatives [5] 4,5-dichlorocatechol and tetrachlorocatechol were reported to be toxic fish since 1968 [6]. Recently chlorinated phenolic compounds were studied from pulp bleach liquors and environmental samples, Lindstrom and Nordin [7]. They produced their first interests on the subject in Europe by detecting several chlorinated phenols, guaiacols and some other related compounds, both trichloro and tetrachloro-catechol isomers including one unknown dichloro-catechol isomer.

Gaunt and Evans [8] concluded that 4-chloro-o-cresol and 5-chloro-3-methyl-catechol were the early intermediates in the degradation of MCPA by Pseudomonas, and this MCPA is the widely using herbicides in many countries of the world. 4-chloro-o-cresol has been identified to be the metabolite of MCPA [9] and some other phenoxyacetic acid herbicides [10]. The technical product of MCPA in Finland usually contains 4% of 4-chloro-o-cresol [11]. MCPA of Kemira Co. In Finland contains several chlorinated cresols as impurities which is confirmed by GC, IR, mass and NMR spectrometry [12]. Generally, the catechol compounds are known as the metabolites of chlorinated phenols [13-15]. Some of the chlorinated phenols are also known as the metabolites of chlorophenoxyacetic herbicides [16-18].

Paasivirta [19] detected the tetrachlorocatechol from the snow samples at different places of Jyvaskyla, and the residues are widely varied from one to another locations. Model compounds of chlorinated catechols were separated with a gas chromatography (GC) and a mass spectrometry [5]. The catechol compounds were also studied by ¹H and ¹³NMR

(nuclear magnetic resonance) spectrometry [20].

Sattar [21] widely studied the TLC of chlorinated catechols in various layer materials with different solvent systems. A gas chromatography was also studied with 5-chloro-3-methyl catechol as metabolite of MCPA [22-24]. In the present study a GC method is developed with different chlorinated catechols in soils by the internal standard method.

Materials and Methods

Compounds tested. The following catechol compounds were applied in the experiment and the structures are presented in Fig. 1. (1) Catechol, (2), 3, 4-dichlorocatechol, (3) 3, 5-dichlorocatechol, (4) 4, 5-dichlorocatechol, (5) 3, 4, 5-trichlorocatechol, (6) 5-chloro-3-methylcatechol, (7) Tetrachlorocatechol.

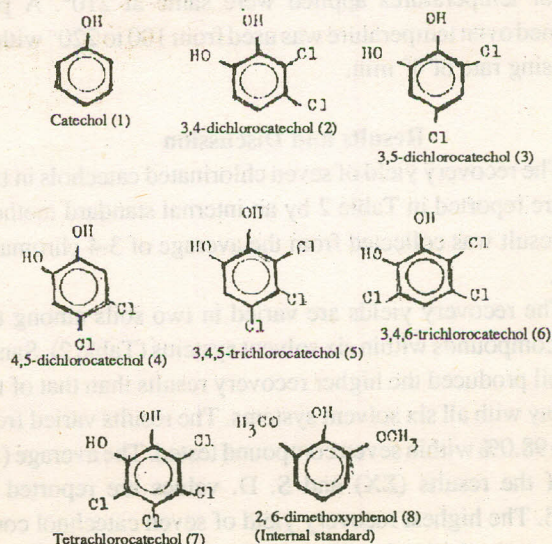


Fig. 1. Structures of the chlorinated catechols (1-7) and the internal standard 2,6-dimethoxy phenol (8).

Soil samples. A sandy clay and a silty clay (Table 1) soils were treated in the experiment. The soils were collected at 0-15 cm depth, dried at laboratory room temp, ground to pass through a 10-mesh sieve and stored in glass containers. The soils properties are shown in Table 1.

Solvent systems. Six different solvent system were tested to measure the recovery yield of the compounds, and they are as follows: (i) Diethylether-hexane-acetone-heptane (3:3:2:2; v/v), (ii) Hexane-heptane-chloroform (1:1:1), (iii) Diethylether-acetone-chloroform (1:1:1), (iv) Diethylether-hexane-heptane (1:1:1), (v) Chloroform-hexane-acetone (1:1:1), (vi) Dichloromethane-diethylether-acetone (1:1:1)

Analytical methods. Ten g soil was treated with 500-800 μ l of 1-7 chlorinated catechols (0.1% solution in diethylether) in a beaker, mixed well with a glass rod, then added 1-2ml of distilled water, and again mixed uniformly. The samples were first extracted with 50 ml of solvent mixture by a shaking method for 45 mins by adding 2 g of anhydrous sodium sulphate, and filtered over 1-2 g of sodium sulphate, and repeated the extraction procedure with another 50 ml of solvent. The combined filtrate was evaporated and transferred to a 10 ml volumetric flask with ether. An aliquot of the extract was treated for the pentafluorobenzyl bromide derivatization by adding the internal standard, 2, 6-dimethoxy-phenol (compound No.8, Fig. 1), and then the cleanup was done by water-toluene (3:1) (v/v). After necessary dilutions, toluene solution was injected to the GC.

GC determination. A varian Model 2400 gas chromatograph with ^3H ECD was used. One or two μ l of the toluene solution was injected to a 25 meter long glass capillary column, external diameter 0.3mm coated with SE-30 silicone phase. Nitrogen was used as carrier gas 1ml/min. Injector and detector temperatures applied were same at 210°. A programmed oven temperature was used from 100 to 220° with an increasing rate of 4° min.

Results and Discussion

The recovery yield of seven chlorinated catechols in two soils are reported in Table 2 by an internal standard method. Each result was collected from the average of 3-4 chromatograms.

The recovery yields are varied in two soils among the seven compounds within six solvent systems (Table 2). Sandy clay soil produced the higher recovery results than that of the silty clay with all six solvent systems. The results varied from 65.8 to 98.0% within seven compound tested. The average (\bar{x}), sum of the results (ΣX) and S. D. values are reported in Table 3. The highest recovery yield of seven catechnol compounds was obtained with a solvent (No.I) Diethylether-acetone-hexane-heptane (3:3:2:2:) in both sandy clay and silty

TABLE 1. SOIL CHARACTERISTICS.

	Sandy clay	Silty clay
Moisture %	3.3	3.5
Sand %	50.2	12.8
Silt %	32.5	50.2
Clay %	18.1	36.8
pH	5.2	5.0
Organic matter %	3.8	3.5

TABLE 2. AVERAGE PER CENT RECOVERY YIELDS OF SEVEN CHLORINATED CATECHOL COMPOUNDS (1-7) IN TWO SOILS WITH SIX (1-VI) SOLVENT SYSTEMS.

Solvent system	Compounds						
	1	2	3	4	5	6	7
SANDY CLAY SOIL							
I	95.5	93.8	95.8	89.3	90.7	64.8	97.8
II	94.0	92.0	90.7	83.5	85.7	95.0	98.0
III	85.0	80.3	89.4	74.7	81.6	83.6	90.6
IV	80.4	80.0	81.2	70.8	72.3	81.4	73.3
V	97.0	92.5	89.8	67.7	74.7	82.5	95.5
VI	81.4	80.0	75.0	70.5	76.9	76.0	79.0
SILTY CLAY SOIL							
I	93.8	93.4	90.3	88.8	89.4	92.4	96.5
II	93.5	91.2	90.0	80.6	86.5	95.1	95.8
III	84.4	80.0	88.2	73.5	80.5	83.2	90.1
IV	75.8	73.0	80.0	70.0	65.8	80.2	73.2
V	95.7	90.5	90.0	65.8	74.0	80.5	73.0
VI	80.0	79.5	74.0	68.8	75.0	74.8	76.9

TABLE 3. AVERAGE PER CENT (\bar{X}), SUM (ΣX) OF THE RECOVERY YIELD AND STANDARD DEVIATION (S.D.) OF CATECHOL COMPOUNDS IN TWO SOILS.

Solvent system	\bar{X}	ΣX	S.D.
SANDY CLAY SOIL			
I	93.6	657.7	2.988
II	91.27	638.9	5.146
III	83.60	585.2	5.457
IV	77.06	539.4	4.686
V	85.67	599.7	11.120
VI	76.97	538.8	3.640
SILTY CLAY SOIL			
I	92.09	644.6	2.752
II	90.39	632.7	5.368
III	82.84	579.9	5.549
IV	74.00	518.0	5.205
V	81.40	569.5	11.030
VI	77.8	544.7	4.002

TABLE 4. A PAIRED T-TEST COMPARISON OF I-IV SOLVENT SYSTEMS FOR THE RECOVERY YIELD OF SEVEN CATECHOL COMPOUNDS (DEGREES OF FREEDOM = 6).

Solvent system	II	III	IV	V	VI
SANDY CLAY SOIL					
I	1.196	4.405	8.023	1.905	9.539
II		2.705	5.386	1.209	6.000
III			2.390	0.442	2.674
IV				1.878	0.040
V					1.968
SILTY CLAY SOIL					
I	0.763	3.092	8.130	2.487	7.783
II		2.587	5.799	1.938	4.976
III			3.074	0.345	1.868
IV				1.605	1.532
V					0.812

clay soils. A good recovery yield was also obtained with hexane-heptane-chloroform (1:1:1) (Solvent II). A low yield was recorded with solvent IV or VI. For separate analysis of catechol compounds, most of the solvents might be applied where the collected recovery yield was above 80%. The overall average recovery results were 93.96, 91.27, 83.60, 77.06, 85.67 and 76.97% with solvents I, II, III, IV, V, VI and VII respectively, in sandy clay soil, and that of silty clay soil was 92.09, 90.39, 82.84, 74.00, 81.40 and 77.8%, for I, II, III, IV, V and VI respectively (Table 3).

Standary deviations produced the group variations of different catechol compounds (Table 3). The highest variation was recorded with solvent V in sandy clay and silty clay soils (S.D.=11.120, in sandy clay; 11.030, in silty clay), and the lowest with solvent I (S.D.=2.988, in sand clay; 2.752, in silty clay). The variation of recovery yields of seven compounds was nearly similar with solvents II, IV and VI.

The results of Table 2 have been applied to a paired t-test (t) comparison with I to VI solvent systems (Table 4). The t-values were varied in two soils. The highest variations were observed when comparison were done between solvents I and VI (t=9.539; 7.783), and between I and IV (t=0.040; 1.532) or III and V (t=0.442; 0.345). The recovery yields differed significantly within different solvent systems ($P < 0.001-0.1$; degrees of freedom 6).

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