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SUMMARY FICP REPORT
Interlaboratory Study on the Analysis of Chlorophenols in Natural Waters

by

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MANAGEMENT PERSPECTIVE

This is a summary report for the 1987 FICP Interlaboratory Study on the analysis of chlorophenols in natural waters. Fifty-six laboratories in the FICP Water and Soils sub-programs were contacted concerning the above study, twenty-three of them agreed to participate, but only ten laboratories provided results.

This study illustrates well the wide variety of methods currently being used for the analysis of chlorophenols in water. Despite the extensive range in the submitted results, the interlaboratory medians for the higher chlorophenols were, with few exceptions, in good agreement with their design values. However, the erratic results submitted for phenol and the two monochlorophenols confirm our previous experience that one should interpret the data for these compounds with caution.

Dr. J. Lawrence
Director
Research and Applications Branch

PERSPECTIVES DE GESTION

Voici un rapport sommaire concernant l'étude interlaboratoires de 1987 du CFIP portant sur l'analyse des chlorophénols dans les eaux naturelles. Au sujet de cette étude, on a communiqué avec cinquante-six laboratoires dans le cadre des sous-programmes du CFIP pour l'eau et les sols; vingt-trois ont accepté d'y participer, mais seulement dix ont fourni des résultats.

Cette étude illustre bien la grande variété de méthodes actuellement utilisées pour l'analyse des chlorophénols dans l'eau. En dépit de la grande variabilité des résultats présentés, les médianes interlaboratoires pour les chlorophénols supérieurs étaient, à de rares exceptions près, en bonne corrélation avec leurs valeurs nominales. Cependant, les résultats aberrants obtenus pour le phénol et les deux monochorophénols confirment nos constatations antérieures, à savoir qu'il faut interpréter avec grande prudence les données relatives à ces composés.

J. Lawrence, Ph.D.
Directeur
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ABSTRACT

An interlaboratory study for the analysis of chlorophenols in natural waters was conducted for the Federal Interdepartmental Committee on Pesticides (FICP) Check Sample Program. Participants were requested to analyze for phenol and eight chlorinated phenols in five test samples. The results of the study indicated that most laboratories have the capability of performing sensitive and isomer-specific analysis for chlorophenols in water. Comparable and satisfactory results were generated for pentachlorophenol and the higher chlorinated phenols. In the analysis of phenol and the two monochlorophenols, however, the data for the "standard" solutions were considerably better than those for the water samples. Thus, it was believed that the extraction procedures and not the derivatization and analysis were most likely to be the major sources of error for these compounds in this study. The intralaboratory precision (or in-house reproducibility) for the majority of participating laboratories was very good. However, the interlaboratory precision (or between-lab repeatability) for the same compound was extremely poor. This would suggest that there could be a need for more accurate analytical standard solutions as well as external reference solutions to which they can be compared in order to monitor their accuracy over time. Lastly, this study also indicated that at least one laboratory could benefit from more stringent in-house quality control.

RÉSUMÉ

Une étude interlaboratoires portant sur l'analyse des chlorophénols dans les eaux naturelles a été effectuée dans le cadre du Programme d'échantillons de contrôle du CFIP (Comité fédéral interministériel sur les pesticides). On a demandé aux participants d'analyser cinq échantillons pour le phénol et huit phénols chlorés. Les résultats de l'étude ont montré que la plupart des laboratoires étaient capables d'effectuer des analyses sensibles et spécifiques pour les isomères, des chlorophénols dans l'eau. Des résultats comparables tout à fait satisfaisants ont été obtenus pour le pentachlorophénol et les phénols chlorés supérieurs. Par contre, dans l'analyse du phénol et des deux monochlorophénols, les résultats pour les solutions "titrées" étaient nettement meilleurs que ceux correspondant aux échantillons d'eau. On pense donc que ce sont les méthodes d'extraction, et non la dérivatisation ou l'analyse, qui constituaient probablement les principales sources d'erreur lors de l'étude. La précision intra-laboratoire (ou reproductibilité maison) était très bonne pour la majeure partie des laboratoires participants. Mais, la précision interlaboratoires (ou répétabilité d'un laboratoire à l'autre) pour le même composé se révélait très médiocre. Il est donc possible qu'il faille utiliser des solutions analytiques titrées plus précises ainsi que des solutions externes de référence auxquelles elles pourraient être comparées, si on veut connaître la précision en fonction du temps. Enfin, l'étude a montré qu'un laboratoire au moins aurait intérêt à mettre en oeuvre un contrôle de qualité maison plus strict.

SUMMARY FICP REPORT

Interlaboratory Study on the Analysis of Chlorophenols in Natural Waters

by

Yvonne D. Stokker and A.S.Y. Chau

Introduction

The following is a summary of the above study which is now closed.

In April, 1987, 54 participants in the Water and Soils subprograms of the FICP Check Sample Program were invited to participate in a round robin study on the analysis of chlorophenols in water. In early June, 21 sets of samples were sent to those who had indicated an interest in participating. A few months later two additional laboratories were sent samples in response to their telephone requests to join both this study and the FICP Water subprogram. For the 23 sets of samples sent out, only ten sets of results were provided. A list of the participating laboratories is given in Table 1.

Study Design

The participants in this study were requested to analyze for phenol and eight chlorinated phenols in five test samples. More specifically, the nine parameters of interest were: phenol, 2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,4,5- and 2,4,6-trichlorophenol, 2,3,4,5- and 2,3,5,6-tetrachlorophenol, and pentachlorophenol. These particular compounds were selected because they have been found and are of concern in real test samples. Furthermore, the results of surveys conducted in 1986 and 1987 revealed that these are the chlorophenols most commonly analyzed by the FICP laboratories.

The sample set was comprised of three 1.0 L Lake Ontario water samples and five sealed glass ampules, each containing different mixtures of the nine phenols in toluene. 1.00 mL aliquots of Ampules 1,2 and 3 were to be spiked respectively into the three water samples provided. These samples had previously been shown to be clean of the phenols under study. The resultant chlorophenol concentrations in the water samples are listed as the "Design Values" on the data summaries in Tables 3 to 5. Following fortification, each sample was to be extracted using the laboratory's own routine method of analysis. Ampules 4 and 5 were to be treated as "standards", either as injection-ready samples or derivatized as needed before subsequent analysis. The participants were requested to determine the concentrations of the phenols using their own in-house standards and calibration procedures. All five samples were designed so as to contain the same level of 2,4,6-trichlorophenol in order to monitor each participant's intralaboratory precision of analysis.

Methodologies

The analytical procedures used by the participants in this study are presented in Table 2. A wide variety of techniques were used for the extraction of the phenols as well as in their analytical measurement.

The most commonly used method of extraction was by means of dichloromethane after acidification of the water samples. Two laboratories pre-washed the samples with solvent under alkaline conditions prior to the dichloromethane extraction and one participant used ethyl ether as the extracting solvent. Only one laboratory acetylated the phenols *in situ* before extracting the resultant acetate derivatives with dichloromethane.

Five of the ten participants in this study derivatized the phenols with diazomethane to yield the corresponding chloroanisoles. Two of these laboratories cleaned the extract by means of a Florisil

column, one used concentrated sulfuric acid and mercury to remove interferences, and the two remaining laboratories analyzed the methylated extract directly without further cleanup. Each of these five participants used GC-ECD for quantitation and one used, in addition, GC-FID for analysis of the parent phenols in an underivatized portion of the extract.

Two laboratories derivatized the phenols with acetic anhydride, then analzyed the resultant phenol acetates by GC-MSD. Lab F40a used an *in situ* acetylation procedure with no sample cleanup while Lab F33 had a much lengthier method involving extraction of the parent phenols into dichloromethane, back-extraction into 2% potassium carbonate, acetylation while simultaneously extracting into petroleum ether, followed by a Silica Gel column cleanup step.

The final three participants in this study extracted the phenols from the acidified water samples, and without any derivatization or cleanup, analyzed for them by GC/MS or GC-MSD.

Results and Discussion

All sample results reported by the participants are listed in Tables 3 to 7. No laboratory provided individual results for all nine phenols although most analyzed for at least five of the parameters of interest. Possible reasons for the missing results could be that the compounds were not analyzed routinely or that the standards were not available. Outliers were not rejected when calculating the interlaboratory medians because for some of the chlorophenols, only two or three results were provided.

The data for 2,4-dichlorophenol, the two tetrachlorophenols and for pentachlorophenol were quite satisfactory as illustrated by the general agreement of the interlaboratory medians for these parameters with their corresponding design values. Moreover, the comparability of the laboratories with their different methodologies

was also good, as the lowest and highest results reported, rarely exceeded a factor of two from the design values.

Participants were generally much less accurate in their analyses for phenol and the two monochlorophenols than for the more chlorinated phenols. Many of these results were considerably lower than their design values and the ranges for these parameters were quite broad. Losses of these phenols due to improper sample preservation or to suspect storage conditions were avoided by providing the participants with blank water samples and the spiking solutions with which to fortify them. Since the data for the "standard" solutions in Ampules 4 and 5 were considerably better than for the three water samples, it was believed that the extraction procedures and not the derivatization and analysis were most likely to be the major sources of error. Furthermore, some laboratories reported low % recovery results for known levels of these phenols in spiked samples extracted and analyzed alongside the FICP water samples. The data provided by at least three of the participants had not been corrected for low extraction recoveries. However, it is not known whether the remaining participants used a correction factor or even if they had assessed their % recovery of any of the phenols from the water samples.

On a more positive note, the in-house precision for the analysis of 2,4,6-trichlorophenol, which had been fortified to the same concentration level in each of the water samples, was very good. As seen in Table 8, the intralaboratory precision of analysis for each participant was better than ±15% (except for Lab F58 who produced very erratic results for this compound). It should be noted, however, that the interlaboratory precision for this same compound in each of the three water samples and in Ampules 4 and 5 was more than ±50%. The individual results reported for 2,4,6-trichlorophenol had a range larger than a factor of 15 in each of the three water samples. It seems apparent then, that while sample results were reproducible within most laboratories, the between-lab repeatability was poor. A possible reason for this problem could be the use of old analytical

standards. A good correction measure would be better in-house quality control and verification of extraction recoveries with external reference standards and spike solutions.

Conclusion

In conclusion, the results of this study indicate that most laboratories, while using widely differing analytical methodologies, have the capability of performing sensitive and isomer-specific analysis for chlorophenols in water. They generated comparable and satisfactory results for pentachlorophenol and the selected higher chlorinated phenols, but were more erratic in their analyses of phenol and the two monochlorophenols under study. The reproducible results for the analysis of identical levels of 2,4,6-trichlorophenol in each of the water samples indicates that the in-house precision of most laboratories was excellent. However, the wide range of results and very poor interlaboratory precision of analysis for this phenol in these samples suggests a need for more accurate analytical standard solutions as well as external reference solutions to which they can be compared in order to monitor their accuracy over time. Lastly, this study also indicated that at least one laboratory could benefit from more stringent in-house quality control.

FICP INTERLABORATORY QC STUDY

ON

THE ANALYSIS OF CHLOROPHENOLS IN WATER

Table 1. List of Participating Laboratories

1. Environment Canada
   National Water Quality Laboratory
   Burlington, Ontario

2. Environment Canada
   C&P (EPS) Laboratory Services
   West Vancouver, BC

3. Alberta Agriculture
   Food Lab. Services Branch
   Edmonton, Alberta

4. Alberta Environmental Centre
   Pesticide Analysis and Research Section
   Vegreville, Alberta

5. Manitoba Environment and Workplace Safety and Health
   Technical Service Laboratory
   Winnipeg, Manitoba

6. Ontario Ministry of the Environment
   Drinking Water Organics Section
   Rexdale, Ontario

7. Ontario Ministry of the Environment
   Pesticide Laboratory
   Rexdale, Ontario

8. Enviro-test Laboratories
   Edmonton, Alberta

9. Novalab Ltée
   Lachine, P.Q.

Table 2. Summary of Analytical Methodologies for Chlorophenol Samples

Lab. No.	Extraction	Derivatization/Cleanup	Analysis	Comments
F33	-acidify to pH 2 -extract with 3 x 60 mL dichloromethane -back-extract into 4 x 40 mL 2% K_2CO_3	-derivatization with 3 x 3 mL acetic anhydride while extracting into petroleum ether -dry through Na_2SO_4 -concentrate to 2 mL iso-octane -5% deact. Silica Gel mini-column	GC-MSD	
F35	-pH > 11; extract with dichloromethane -pH < 2; extract with dichloromethane -concentrate to 100 uL		GC/MS	-(EPA Method 625) -in-house QC monitored with internal standards, relative response factors, EPA reference standards and QC of surrogate standards
F36	-acidify -extract with dichloromethane -dry through Na_2SO_4 -K.D. evaporation	-diazomethane methylation	GC-ECD	-usual Florisil cleanup omitted
F40a		-in situ acetylation -extract with dichloromethane	GC-MSD	-standards not analyzed
F40b	-extract with dichloromethane	-diazomethane methylation -Florisil column; elute with (1+3) CH_2Cl_2/hexane	dual GC-ECD	-standards not analyzed
F43	-acidify with (1+1)H_2SO_4 -extract with 3 x 60 mL dichloromethane -dry with Na_2SO_4 -rotary evaporate to 0.5 mL methanol	-dilute with methanol as needed	GC-MSD	-(EPA Method 625) -calibration curve from EPA-QAR standards -no corrections made for % recovery

(Table 2 continues next page)

Table 2 (continued)

Lab. No.	Extraction	Derivatization/Cleanup	Analysis	Comments
F58	-pH > 12 with 5N KOH -100 mL CH_2Cl_2 wash (discard) -pH < 2 with H_2SO_4 -extract with 3 x 100 mL dichloromethane -dry through Na_2SO_4 -rotary evaporate to 5 mL iso-octane	-split extract; one portion methylated with diazomethane generator -second portion: no derivatization, no cleanup	GC-ECD (packed 3% OV-17) GC-FID (megabore DB-5)	-(EPA 604 / EPA 625 methods) -phenol recovery 55% -all other recoveries 85-100%
F61	-acidify to pH 2 with 6N H_2SO_4 -extract with 3 x 100 mL dichloromethane -dry through acid-rinsed Na_2SO_4 -rotary evaporation, N_2 concentration		GC/MS	-35% phenol recovery, 53% 2-chlorophenol recovery on EPA QC spiked sample -no corrections made for % recovery
F83	-acidify to pH 2 with 2N H_2SO_4 -extract with ethyl ether -concentrate	-methylation with ethereal diazomethane -cleanup with conc. H_2SO_4 and Hg	GC-ECD	
F85	-reduce sample volume to 800 mL -acidify with H_3PO_4 -extract with (80+40+40)mL dichloromethane -dry with Na_2SO_4 -evaporate to 0.5 mL iso-octane	-diazomethane methylation -evaporate to 0.5 mL iso-octane -Florisil column; elute with 30 mL (1+5) CH_2Cl_2/hexane -evaporate to 10 mL -Hg cleanup	dual GC-ECD (SPB-1, DB-1701)	-standards not analyzed

FICP Interlaboratory QC Study

The Analysis of Chlorophenols in Water

Table 3. Sample 1 (water) ug/L

Lab. No.	Phenol	2-chloro-	4-chloro-3-methyl-	2,4-DCP	2,4,5-TCP	2,4,6-TCP	2,3,4,5--TeCP	2,3,5,6--TeCP	PCP
F33	nd	22.5	29.5	9.3	6.9	71.9	7.5	7.4	5.2
F35	32	22	36	8	—— (53)*——		nd	nd	12
F36	nd	nd	nd	nd	nd	nd	7.0	8.1	8.6
F40a	150.0	41	65	11	nd	120	145	16	12
F40b	nd	nd	nd	nd	11.0	7.7	10.6	11.5	10.9
F43	44	25	55	nd	nd	96	nd	nd	28
F58	101	33	40	1000	(23)**	16.3	12.4	(**)	11
F61	29	14	42	6.5	nd	59	nd	nd	10
F83	nd	nd	nd	nd	nd	29	7.3	10	7.0
F85	nd	nd	nd	nd	9.3	18.3	12.9	9.2	11.7
Interlab Median	44	23.8	41	9.3	9.3	44	10.6	9.6	11
Design Value	104.4	28.5	52.7	12.2	9.8	93.8	10.3	11.1	10.3

nd = not determined

* Total of (2,4,5-TCP + 2,4,6-TCP)

** Total of (2,4,5-TCP + 2,3,5,6-TeCP)

FICP Interlaboratory QC Study

The Analysis of Chlorophenols in Water

Table 4. Sample 2 (water) ug/L

Lab. No.	Phenol	2-chloro-	4-chloro-3-methyl-	2,4-DCP	2,4,5-TCP	2,4,6-TCP	2,3,4,5--TeCP	2,3,5,6--TeCP	PCP
F33	nd	279.5	575.2	40.1	16.5	63.6	3.5	6.3	1.7
F35	210	320	460	37	—— (66)*——		nd	nd	6
F36	nd	nd	nd	nd	nd	nd	3.8	8.1	5.0
F40a	267	137	126	72	nd	115	71	16	6
F40b	nd	nd	nd	nd	28.0	6.4	4.7	10.0	4.8
F43	640	830	1000	66	nd	102	nd	nd	18
F58	1000	830	797	1000	(24)**	48	6.6	(**)	6
F61	260	380	430	27	28	61	nd	nd	5.0
F83	nd	nd	nd	nd	nd	23	4.0	10	3.8
F85	nd	nd	nd	nd	10.1	17.5	1.6	3	1.6
Interlab Median	267	350	517.6	53.1	22.3	54.5	4.0	9.1	5.0
Design Value	1566.5	853.8	1053.2	60.9	29.4	93.8	5.1	11.1	5.2

nd = not determined

* Total of (2,4,5-TCP + 2,4,6-TCP)

** Total of (2,4,5-TCP + 2,3,5,6-TeCP)

FICP Interlaboratory QC Study

The Analysis of Chlorophenols in Water

Table 5. Sample 3 (water) ug/L

Lab. No.	Phenol	2-chloro-	4-chloro-3-methyl-	2,4-DCP	2,4,5-TCP	2,4,6-TCP	2,3,4,5--TeCP	2,3,5,6--TeCP	PCP
F33	nd	552.0	601.0	60.1	27.4	61.0	19.2	8.5	4.7
F35	180	230	560	58	—— (74)*——		nd	nd	10
F36	nd	nd	nd	nd	nd	nd	53	16	15
F40a	456	197	350	106	nd	127	63	33	13
F40b	nd	nd	nd	nd	45.0	6.1	3.6	19.0	9.6
F43	460	480	1020	110	nd	105	nd	nd	nd
F58	1000	635	135	1000	(58)**	84	57	(**)	14
F61	140	150	380	49	34	55	nd	nd	9.3
F83	nd	nd	nd	nd	nd	28	25	19	6.9
F85	nd	nd	nd	nd	45.5	18	26.5	10.8	11.3
Interlab Median	456	355	470	83.1	39.5	58	26.5	17.5	10
Design Value	1305.5	569.2	1316.5	97.4	49.0	93.8	41.1	22.1	10.3

nd = not determined

* Total of (2,4,5-TCP + 2,4,6-TCP)

** Total of (2,4,5-TCP + 2,3,5,6-TeCP)

FICP Interlaboratory QC Study

The Analysis of Chlorophenols in Water

Table 6. Sample A4 (ampule) ng/L

Lab. No.	Phenol	2-chloro-	4-chloro-3-methyl-	2,4-DCP	2,4,5-TCP	2,4,6-TCP	2,3,4,5--TeCP	2,3,5,6--TeCP	PCP
F33	nd	686	532	126	44	68	8	10	20
F35	850	910	600	140	—— (130)*——		nd	nd	48
F36	nd	nd	nd	nd	nd	nd	9.0	11	55
F40a	nd	nd	nd	nd	nd	nd	nd	nd	nd
F40b	nd	nd	nd	nd	nd	nd	nd	nd	nd
F43	850	960	800	190	nd	130	nd	nd	97
F58	810	865	700	1000	(16)**	138	16	(**)	73
F61	220	300	250	49	58	61	nd	nd	17
F83	nd	nd	nd	nd	nd	24	6.7	8.9	27
F85	nd	nd	nd	nd	nd	nd	nd	nd	nd
Interlab Median	830	865	600	140	51	68	8.5	10	48
Design Value	783.3	853.8	789.9	182.6	78.4	93.8	10.3	11.1	51.5

nd = not determined

* Total of (2,4,5-TCP + 2,4,6-TCP)

** Total of (2,4,5-TCP + 2,3,5,6-TeCP)

FICP Interlaboratory QC Study

The Analysis of Chlorophenols in Water

Table 7. Sample A5 (ampule) ng/L

Lab. No.	Phenol	2-chloro-	4-chloro-3-methyl-	2,4-DCP	2,4,5-TCP	2,4,6-TCP	2,3,4,5--TeCP	2,3,5,6--TeCP	PCP
F33	nd	192	964	60	20	62	13	25	7
F35	920	290	760	82	—— (110)*——		nd	nd	21
F36	nd	nd	nd	nd	nd	nd	20	28	9.7
F40a	nd	nd	nd	nd	nd	nd	nd	nd	nd
F40b	nd	nd	nd	nd	nd	nd	nd	nd	nd
F43	1670	380	1500	110	nd	95	nd	nd	37
F58	1000	265	37.5	1000	(43)**	70	73	(**)	14
F61	390	110	510	28	32	63	nd	nd	2.3
F83	nd	nd	nd	nd	nd	12	22	29	7.6
F85	nd	nd	nd	nd	nd	nd	nd	nd	nd
Interlab Median	960	265	760	82	26	63	21	28	9.7
Design Value	1566.5	284.6	1579.7	97.4	39.2	93.8	30.8	44.3	10.3

nd = not determined

* Total of (2,4,5-TCP + 2,4,6-TCP)

** Total of (2,4,5-TCP + 2,3,5,6-TeCP)

FICP Interlaboratory QC Study

The Analysis of Chlorophenols in Water

Table 8. Intralaboratory Precision on the Analysis of 2,4,6-Trichlorophenol

Sample No.	Laboratory								Design Value	Interlab. Median	Interlab. Mean	SD	%RSD
	F33	F40a	F40b	F43	F58	F61	F83	F85					
Water Samples:													
#1 (ug/L)	71.9	120	7.7	96	16.3	59	29	18.3	93.8	44	52.3	41.2	78.9
#2 (ug/L)	63.6	115	6.4	102	48	61	23	17.5	93.8	54.5	54.6	39.2	71.9
#3 (ug/L)	61.0	127	6.1	105	84	55	28	18	93.8	58	60.5	42.8	70.7
Ampules:													
A4 (ng/uL)	68	-	-	130	138	61	24	-	93.8	68	84.2	48.5	57.6
A5 (ng/uL)	62	-	-	95	70	63	12	-	93.8	63	60.4	30.2	50.0
Water Samples only:													
Intralab. Mean	65.5	120.7	6.7	101.0	49.4	58.3	26.7	17.9					
SD	5.7	6.0	0.9	4.6	33.9	3.1	3.2	0.4					
%RSD	8.7	5.0	12.6	4.5	68.5	5.2	12.1	2.3					
Samples and Ampules:													
Intralab. Mean	65.3	-	-	105.6	71.3	59.8	23.2	-					
SD	4.6	-	-	14.3	45.2	3.0	6.8	-					
%RSD	7.0	-	-	13.5	63.5	5.1	29.1	-					