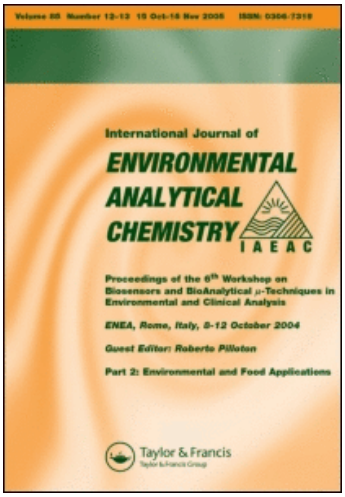

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FAST GAS CHROMATOGRAPHIC ASSESSMENT OF POLYCHLOROBIPHENYL LEVELS IN WALL PLASTER COATS

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Sampling ("scrape test") and analytical procedures were defined to determine PCBs in sorbing solid surfaces such as wall plaster. After sampling, samples were extracted by means of a mechanical device. Following steps included clean-up on a multilayer chromatographic column and assessment with macrobore capillary gas chromatography equipped with an electron capture detector. Mean recovery yields were $\geq 75\%$ for PCB levels from 2.00 to 7000 $\mu g/m^2$ (0.550–1940 $\mu g/kg$). Intralaboratory tests performed by two independent operators yielded: (a) maximum deviation from expected value, 25%; (b) maximum deviation between operators, 17%; and (c) maximum variation coefficient, 20%. Background PCB levels in wall surface layer samples were $\geq 2.9\ \mu g/m^2$ ($\geq 0.81\ \mu g/kg$). The analytical procedure tested with agricultural topsoil samples provided mean recovery yields $>65\%$ for PCB levels $\geq 500\ \mu g/kg$ ($\geq 50\ mg/m^2$).

KEY WORDS: PCBs, dielectric fluids, electric apparatus.

INTRODUCTION

Formation of the highly toxic polychlorinated dibenzodioxins (PCCDs) and dibenzofurans (PCDFs) has been associated with trace chemistries of fire.[1–4] In particular, PCCDs and PCDFs were observed in fires and explosions involving electric apparatus and equipment where PCB-based dielectric fluids were used.[5–8] Due to the widespread diffusion of such materials and the relatively high frequency of fire-type accidents, these events present a great interest for public and occupational health protection.[7,8]

PCBs themselves were involved in numerous accidental releases into the environment,[9,10] and thus have become a threat to man's health and the environment owing to their persistence and toxic potency associated with some specific cogeners.[11–13] PCDDs and PCDFs are also normally present in commercial PCBs as trace-level contaminants.[14]

In the light of the above, a project has been undertaken aimed at (a) defining

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sampling criteria and procedures, and (b) setting up screening analytical procedures for fast assessment of contamination due to PCBs, PCDDs, and PCDFs in various environmental and occupational sorbing matrices. An additional outcome of the project would be the assessment of PCB conversion rate to PCDDs and PCDFs with time in stressed dielectric fluids. In this progress report, the procedures to sample and analyze wall surfaces are described with specific reference to Apirolio 1488-T, a commercial mixture of Aroclor 1260-like PCBs and trichlorobenzenes (6:4, w/w) utilized as a dielectric fluid in domestic railroads electric equipment.

EXPERIMENTAL

Chemicals and Glassware

Various Fenclors—PCB mixtures similar to Aroclors—were obtained from Caffaro (Genoa, Italy). Apirolio 1488-T was also provided by Caffaro.

Analytical-grade anhydrous sodium bicarbonate and (dehydrated) sodium chloride, and spectral-grade acetone, dichloromethane, hexane, iso-octane and pentane were supplied by Carlo Erba (Milan, Italy) and Fluka (Buchs, Switzerland). Celite 545 and anhydrous sodium sulfate were purchased from BDH Italia (Milan, Italy). Silica gel (70–230 mesh) and concentrated sulfuric acid were from E. Merck (Darmstadt, FRG). Prior to use, pentane was distilled in a glass apparatus; other solvents, reagents, and reference compounds were used without further purification.

Pyrex glassware was used throughout: after cleaning, it was heated to 250 °C overnight before use. Cleaned-up extracts were kept in 8-ml cone-shaped bottom vials equipped with PTFE-lined screw caps.

Instrumentation

Extraction A mechanical extractor (Figure 1) was used to carry out extraction of organic compounds from ground wall matrices. The extractor consisted of an electric motor driving a two-blade shaft. Blades were immersed in the sample-solvent system and their rotation speed set according to requirements. A 800-ml beaker was used to accommodate sample and solvent.

Gas chromatography A Hewlett-Packard model 5710 gas chromatographic unit was used throughout. The unit was equipped with an electron capture detector (GC/ECD) and an HP-5 30-m long 0.53-mm i.d. fused silica macrobore capillary column. Argon-10% methane was employed as a carrier at a flow rate of 2 ml/min. GC conditions were: (a) injection block, 250 °C; (b) oven, temperature-programmed from 160 to 280 °C; (d) temperature rate, 2 °C/min; (e) 30 min final isotherm: (f) detector, 300 °C.

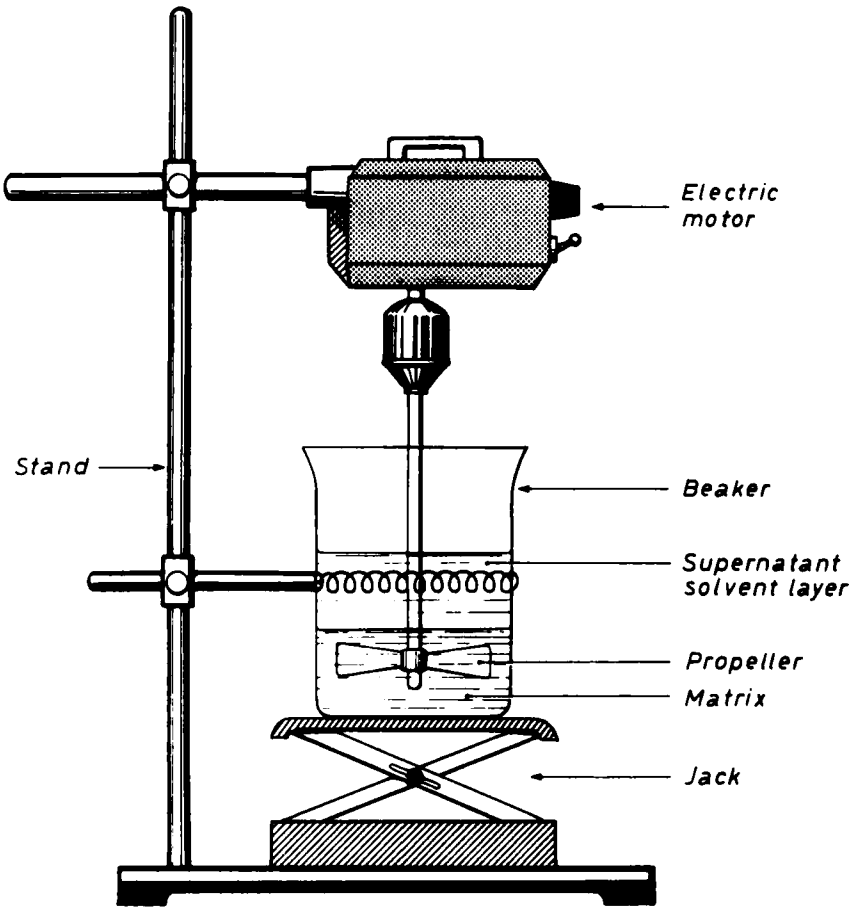

Figure 1 Extractor scheme. Blade rotation speed was chosen to have the entire mixture in fast motion and thoroughly mixed. Details in text.

Analytical Procedure

Sampling A wall surface of $25 \times 25\,cm^2$ size was evenly scraped off with the aid of a robust flat-edged spatula so as to reach a depth of approximately 0.3 cm.[15,16] Alternatively, an entire portion of plaster layer was removed from the wall, broken into small pieces, and mechanically ground. Powdered wall matrices were allowed to dry naturally until constant weight (variations over 24 h, $<1\%$), sifted through a 10-mesh size sieve, carefully homogenized, and made into 200–250 g samples.

Extraction Each sample was transferred to an 800-ml beaker and soaked with hexane–acetone 1:1 (v/v) (approximately, 150 ml). An equal amount of solvent was added prior to initiating extraction.[17] Then, the sample-solvent system was subjected to vigorous stirring with the mechanical extractor for 3 min. Bulk

stirring was characterized by a whirl and complete mixing of ground matrix and solvent. Phase separate took 15 min. The upper layer was decanted on paper filter for quantitative analysis and collected in a 1000-ml round flask for a rotavapor (Büchi Laboratoriums, Flawil, Switzerland). The extract was gently concentrated to a small volume under reduced pressure and mild heating (water bath, $<40\,^{\circ}C$).

Each sample was extracted six times as described above. Each filtered extract was added to the previous concentrated fraction and, in its turn, evaporated as said. The final extract was a <5-ml six-ectraction pool.

To avoid interfering reactions with the sulfuric acid layer (cf. *Clean-up*), acetone was removed by adding sequentially five 10-ml portions of pentane, each time evaporating the mixture carefully until near-dryness. For prolonged storage, the extract was taken up with 5 ml pentane and kept at $4\,^{\circ}C$.

Clean-up The extract was taken up with 5 ml pentane and purified by a freshly-made 20-cm long 10-mm i.d. multilayer chromatographic column (Figure 2).[15] Packing was as follows (from bottom to top): glasswool; 1 cm sodium sulfate; 2 cm silica gel; 2 cm 4:1 (w/w) sodium sulfate–sodium bicarbonate; 1 cm Celite; 4 cm 1:1 (w/w) sulfuric acid–Celite mixture (obtained by careful mixing in mortar); and 3 cm 3:1 (w/w) sodium sulfate–sodium chloride.

The column was pre-eluted with 30 ml dichloromethane followed by an equal volume of pentane. Before the column ran dry, the extract was transferred quantitatively from the evaporating flask to the column and percolated by gravity. Ten additional 5-ml fractions of pentane were added sequentially to complete elution. Each fraction had previously been used to wash the evaporating flask inner walls. The whole eluate (<60 ml) was collected in a beaker and gently evaporated until near-dryness. The purified extract was transferred carefully with pentane to a cone-shaped bottom vial, again evaporated until almost dry, and taken up in 1 ml iso-octane.

Quantitation PCBs were determined by GC/ECD using the external standard technique. Sample patterns (Figure 3a) were compared with standard PCB gas chromatograms (Figure 3b); the standard exhibiting the analytical pattern most similar to that of the sample(s) was selected as a reference for quantitative assessment. For this work, Apirolio or Fenclor 60 proved to be, in general, adequate.

The PCB amount of a sample was calculated by singling out in the sample gas chromatogram from two to four reference peaks which, from previous trials, were known to have little or no interference from other components eventually present in that specific matrix or, more in general, from the background (detection threshold set at $2.0\,\mu g/m^2$, or $0.55\,\mu g/kg$). Reference peaks were selected so that their retention times differed remarkably; in addition, their relative intensities proved to be adequately stable (variations $<25\%$ of the base peak intensity). When possible—i.e. in the absence of interferences—determination statistics were improved by employing the maximum number (four) of reference peaks; however, two peaks were successfully used for quantitation in a number of cases.

As each reference peak remained substantially constant in the PCB mixture, it

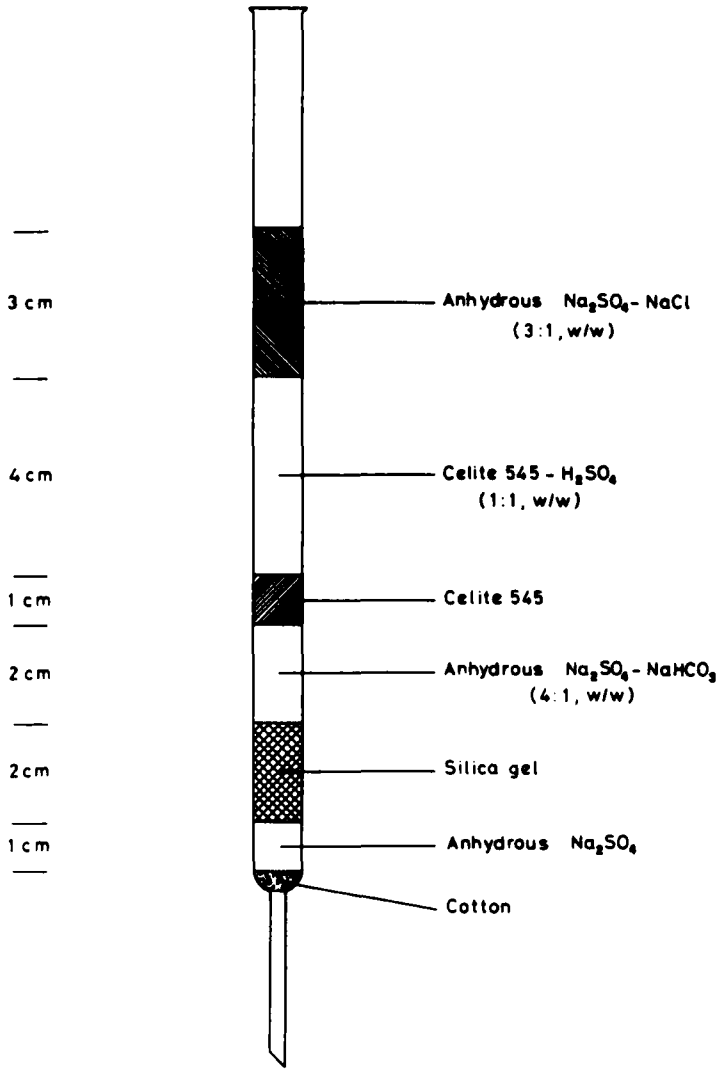

Figure 2 Multilayer chromatographic column.

was thought to be representative for the PCB amount injected. Thus, the area of each reference peak in the sample was used for an independent quantitative assessment against the corresponding peak in the external standard chromatogram. Alternatively, heights were used reliably when retention times did not change significantly ($<5\%$). Then, the different assessment figures associated with the different peaks utilized were averaged to yield a final mean PCB amount in the sample.

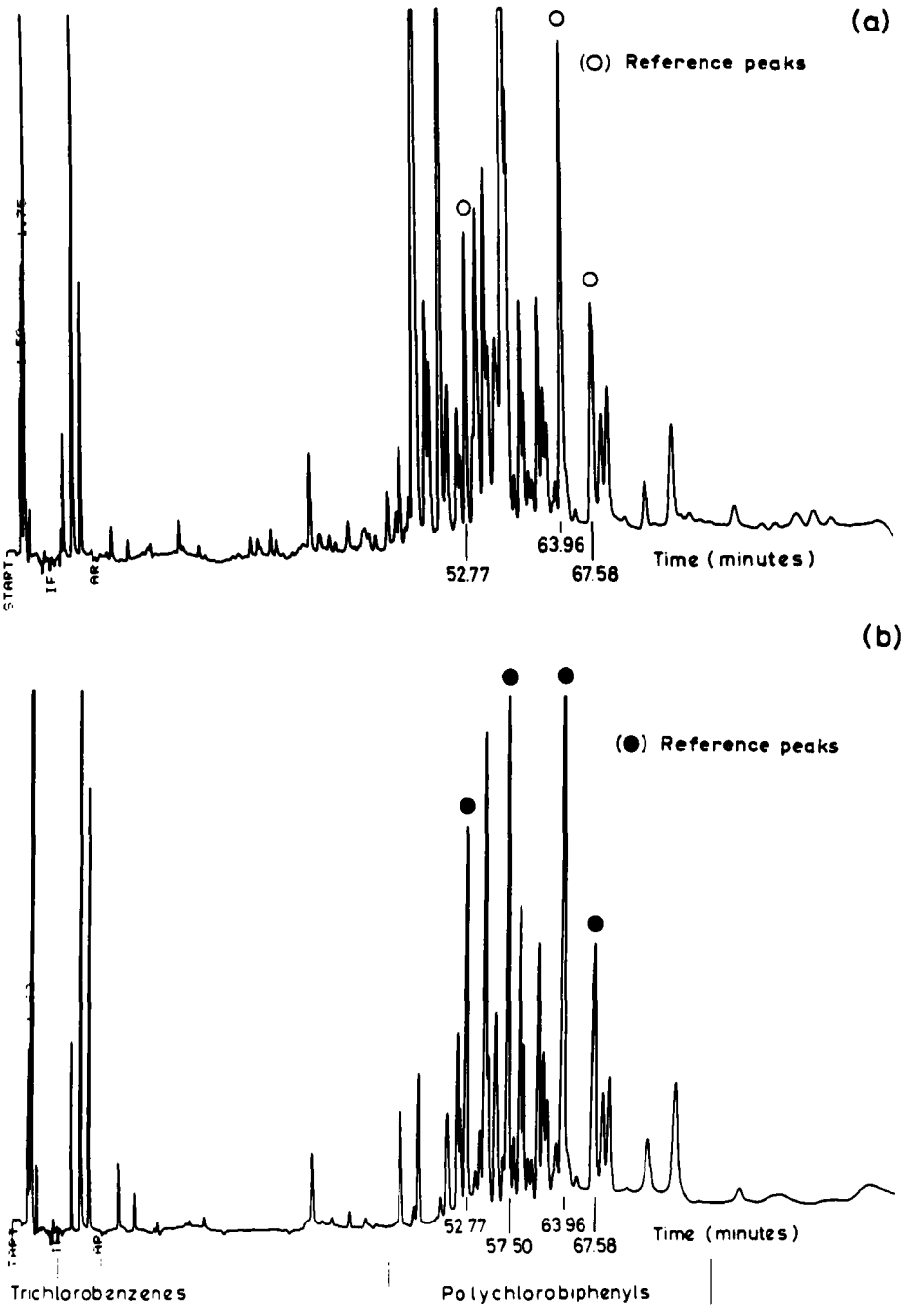

Figure 3 Macrobore capillary gas chromatograms of (a) an electric cabin wall plaster sample, and (b) a 0.40-ng Apirolio standard mixture. In (a), open circles indicate the three reference peaks used for quantitation of PCBs in that specific sample; in (b), solid circles identify the four reference peaks more frequently used for quantitation. For practical purposes, instrumental detection threshold for PCBs was set at approx. 0.1 ng injected amount.

Table 1 PCBs recovered in multilayer chromatographic column recovery tests

Substrate	*PCB amount (ng)*	*No. of samples*	*Recovery (%)*	*Variation coefficient (%)*
Fenclor	$1.00 \cdot 10^2$	3	76	16
Apirolio	$1.25 \cdot 10^2$	2	83	11
Fenclor	$1.70 \cdot 10^2$	3	83	9.0
Apirolio	$2.50 \cdot 10^2$	3	91	10
Fenclor	$8.75 \cdot 10^2$	2	88	7.4
Fenclor	$1.70 \cdot 10^3$	3	90	4.3
Apirolio	$1.25 \cdot 10^4$	2	98	1.1
Fenclor	$2.50 \cdot 10^4$	3	91	7.3
Apirolio	$1.19 \cdot 10^5$	2	85	11
Fenclor	$4.37 \cdot 10^5$	3	97	3.9

RESULTS AND DISCUSSION

Mean recovery yields for the multilayer column are summarized in Table 1. For this test, 0.100 to 437 μg amounts of Fenclor 60 or Apirolio (as PCBs) were used. Yields, obtained from duplicate or triplicate independent trials and assessed as reported under *Quantitation*, were always $>75\%$ with variation coefficients $\leqq 16\%$.

The recovery and two-operator intralaboratory reproducibility of the entire procedure were tested on fresh uncontaminated (PCB level, $\ll 2.0\ \mu g/m^2$) plaster. The wall plaster coat was scraped, sifted, allowed to dry, and made into individual samples (*Sampling*). From each sample, a 30% aliquot was removed and stored for later usage. Then, different amounts (2.00–7000 $\mu g/m^2$) of PCBs were added in <1-ml iso-octane. To achieve a reasonable dispersion of contaminant, several small droplets of PCB solution were scattered over the exposed surface of sample, which was later covered with the portion previously removed. Contaminated samples were allowed to dry and age at room temperature for at least 48 h before the assay; each sample was thoroughly mixed with a spatula immediately prior to extraction. Each contamination level was analyzed with at least triplicate samples.

Results of recovery yield tests are reported in Table 2; the mean yields were always $\geqq 75\%$, with variation coefficients $\leqq 20\%$. Here and on other occasions, column chromatography was repeated as described, if a single clean-up proved insufficient.

Mean results of the intralaboratory reproducibility test are shown in Table 3; the maximum deviation from the expected value was 25%; the maximum deviation between operators was 17%, and variation coefficients were always $\leqq 20\%$.

Background PCB levels in virtually unexposed walls were obtained as a by-product while searching for a "non-detectable PCB level" matrix. The search was carried out by sampling plaster scrapings and layers from different places in Rome. Sampling was performed randomly and without specific strategy. Findings are summarized in Table 4; mean background PCB levels were found to be between 2.9 and 3.3 $\mu g/m^2$.

Table 2 PCBs recovered from laboratory-contaminated wall plaster matrices

Substrate	*PCB amount* ($\mu g/m^2$)	*No. of samples*	*Recovery* (%)	*Variation coefficient* (%)
Apirolio	2.00	3	84	12
Apirolio	3.60	3	87	3.4
Apirolio	6.50	6	102	3.7
Fenclor	14.0	3	119	3.9
Apirolio	19.6	6	92	20
Apirolio	65.1	4	75	7.0
Fenclor	100	3	85	6.5
Apirolio	131	4	89	11
Apirolio	200	3	110	2.0
Apirolio	800	3	100	6.2
Apirolio	1900	3	107	4.0
Fenclor	7000	3	115	10

Table 3 Results of a two-operator intralaboratory reproducibility test

PCB added ($\mu g/m^2$)	*No. of samples*	*Operator 1*			*Operator 2*			*Deviation between operators* (%)
		Recovery (%)	*Variation coefficient* (%)	*Deviation* (%)[a]	*Recovery* (%)	*Variation coefficient* (%)	*Deviation* (%)[a]	
6.52	3	104	5.9	+3.6	101	3.6	+1.2	2.9
19.6	3	85	2.7	−15	100	20	0.0	16
65.1	2	75	6.9	−25	76	4.5	−24	1.3
131	2	81	4.3	−19	96	11	−3.9	17
270[b]	3	–	11	−0.2[c]	–	3.6	+0.2[c]	0.4

[a]From expected value.

[b]Sample of wall plaster containing unknown quantity of PCBs. PCB estimate as obtained from analytical assessments of Operators 1 and 2 (mean value).

[c]Deviation of each operator's estimate from mean value.

Table 4 PCB background levels assessed in random samples

Source of samples	*No. of samples*	*PCB found*		
		($\mu g/m^2$)	*Standard deviation* ($\mu g/m^2$)	*Variation coefficient* (%)
Private household	4	2.9	0.82	28
Institute, animal house	6	3.3	0.40	12
Institute, first floor office	10	3.0	0.53	18

An example of a PCB-exposed wall surface assessment is shown in Figure 3a and at the bottom row of Table 3, and reported in the table as part of the intralaboratory reproducibility test. Tested wall surfaces had been exposed to PCB vapours from PCB-filled electric equipment having run for several years. In this case, PCB levels were found to reach a mean 270 $\mu g/m^2$.

Finally, preliminary findings of an environmental monitoring program in progress seem to indicate the analytical procedure described to be suitable for detecting PCBs in agricultural topsoil (7-cm thick layer) at least at a detection threshold of 500 $\mu g/kg$ (50 mg/m^2). From triplicate trials, mean recovery yields $>65\%$ and variation coefficients $\leqq 12\%$ were obtained for PCB levels of 500, 1000, and 2000 $\mu g/kg$. Soil sampling and sample pretreatment were derived from previous works.[15,18] A full appraisal of the analytical procedure applicability to PCB determination in soil matrices will be provided on completion of the monitoring program.

CONCLUSIONS

As previously stated, the analytical procedure dealt with was developed to assess PCB levels mainly in sorbing matrices of internal environments characterized by a high risk of becoming contaminated, either because of slow and prolonged volatilization from electric equipment in use, or following an accident accompanied by spillage and possible thermal destruction and/or transformation of a fraction of PCBs. The latter event is known to produce highly hazardous amounts of the much more toxic tetra- to octachlorosubstituted PCDDs and PCDFs.

In general, if the wall surfaces become highly contaminated, detoxification is called for to permit man's use of the facility without heavy protective gear. The effectiveness of the detoxification operation needs to be checked carefully and frequently—also in order to avoid overdoing which will entail unnecessary expense. The analytical procedure described seems to be reliable enough to be applicable as a fast screening tool for the above purpose.

From research in progress, there is some preliminary evidence that PCDD and PCDF formation does not exceed a given conversion rate, approximately

$$\frac{[\text{PCDDs} + \text{PCDFs}]}{[\text{PCBs}]} = 10^{-3} - 10^{-4}$$

even in highly stressed thermal accidents. In such case, PCDD and PCDF levels—either in wall plaster or in soil—could be estimated indirectly from the PCB assessment, thereby avoiding the requirement for highly specialized analyses which would be time-consuming and expensive. However, although encouraging, the experimental evidence is still insufficient to prove unquestionably the feasibility of a reliable indirect assessment of PCDDs and PCDFs.

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