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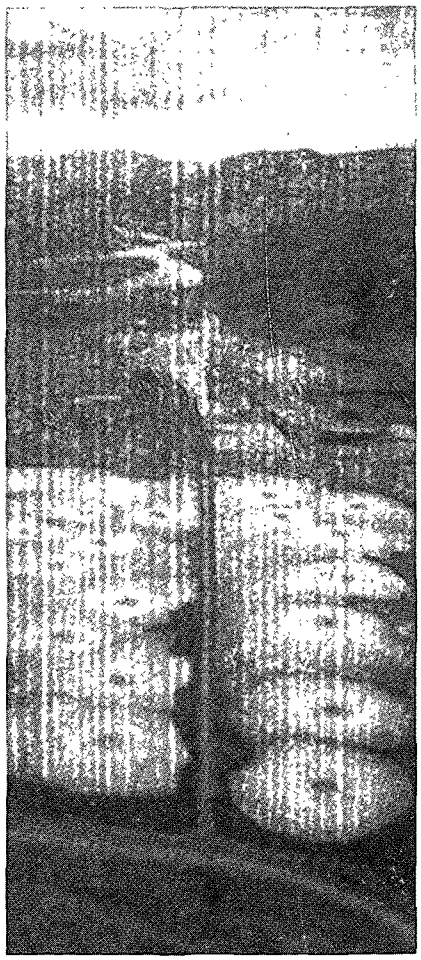

Reference Method for the Determination of Dibenzofuran and Dibenzo-*p*-dioxin in Defoamers

Reference Method EPS 1/RM/20
August 1991

Canada

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Reference Method for the Determination of Dibenzofuran and Dibenzo-*p*-dioxin in Defoamers

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The Weyerhaeuser Canada Ltd. bleached kraft pulp mill in Kamloops, British Columbia, with the Thompson River in the background and the effluent treatment lagoons in the foreground. (Photo by Mark Hewitt, University of Waterloo)

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Foreword

The use of defoamers contaminated with non-chlorinated dibenzofuran (DBF) and dibenzo-p-dioxin (DBD) in chlorine bleaching pulp mills has been shown to significantly increase the 2378-TCDF and 2378-TCDD levels of the final bleached pulp. To reduce amounts of these toxicants in pulp mill discharges, Environment Canada is developing regulations that will establish the maximum concentrations of DBF and DBD in defoamers for those applications.

This report is an analytical method for the determination of DBF and DBD in defoamers at low (ng/g) levels. It will be referenced in the regulations and has been developed jointly by the Pulp and Paper Research Institute of Canada (PAPRICAN) and Environment Canada.

In this method, defoamers are steam-extracted and the extract in iso-octane is cleaned up on a basic alumina column. Final analysis is performed by gas chromatography-mass spectrometry (GC-MS) in the selected ion-monitoring mode and the extraction recoveries of native DBD and DBF are monitored by using DBF-d_8 and DBD-d_8 as surrogates. Confirmation of DBD and DBF was done by comparing the ratio of peak areas for the quantitation and confirmation ions of each compound in the standard and the sample. Based on a 5.00 g sample and a final volume of 0.5 mL, the method detection limit is 1 ng/g for both DBF and DBD.

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General Information

1.1 Scope and Application

This method applies to the determination of non-chlorinated dibenzo-*p*-dioxin (DBD) and dibenzofuran (DBF) in defoamers at ng/g levels.

1.2 Principle and Theory

The defoamer is steam-extracted into iso-octane and the extract is cleaned up by column chromatography. The concentrated extract is analyzed by gas chromatography-mass spectrometry (GC-MS) in the selected ion-monitoring (SIM) mode.

1.3 Interferences

Other volatile and semi-volatile organics present in the sample and not removed by the column cleanup step may interfere. Combining a high resolution capillary column and a selective detector, such as a GC-MS operating in SIM mode, is usually sufficient to remove these interferences. Compound identity is confirmed by comparing the ratio of peak areas of the quantitation ion and the confirmation ion in the sample to an authentic standard.

1.4 Sample Storage

No stability data are available for DBD and DBF in defoamers. Defoamers are currently stored at room temperature until analysis. To avoid contamination, glass bottles with foil- or Teflon-lined caps should be used to store defoamers.

Section 2

Apparatus and Reagents

2.1 Apparatus

The following is a list of apparatus needed to carry out this procedure. Note that all glassware must be washed and dried, using the same procedure as that used for trace organic analysis.

a. Volumetric flasks - 10, 50 and 100 mL.

b. Steam distillation heads (see Figure 1 for construction and dimensions).

c. Round-bottom flasks - 500 and 250 mL.

d. Graduated centrifuge tubes - 15 mL with standard tapered glass stoppers or Teflon-lined screw caps.

e. Chromatographic columns - 400 × 10 mm (id) with Teflon stopcocks.

f. Three-stage Snyder columns - about 30 cm long.

g. Heating mantles with temperature controls.

h. Drying oven for glassware.

i. Oven for activating alumina at 130 °C.

j. A GC-MS with good sensitivity operating in selected ion-monitoring mode. As an example, a HP5880A GC interfaced to a HP5970B Mass Selective Detector and a data system were used. Other equally or more sensitive systems may be used.

k. Fused silica capillary column - 30 m × 0.25 mm (id) coated with 5% diphenyl, 94% dimethyl, and 1% vinyl polysiloxane phases, 0.25 μm film thickness.

l. Hamilton syringes - 10, 50, 100, 250 and 500 μL.

2.2 Reagents

The following reagents are used in this procedure. Note that all organic solvents must be of distilled-in-glass grade with blanks suitable for residue analysis.

a. Iso-octane.

b. Petroleum ether (P.E., b.p. 30 to 60°C).

c. Dichloromethane.

d. Alumina - basic, 100 to 200 mesh, Brockman Activity I, activated at 130°C overnight and kept in a tightly sealed bottle placed inside a desiccator until use. Reactivate adsorbent once every two weeks.

e. Anhydrous sodium sulphate previously heated at 600°C overnight.

f. Reagent water - defined as water in which an interferent is not observed at the method detection limit of the parameters of interest. For example, a sample was used that was prepared by passing distilled water through a 4-cartridge purification unit.

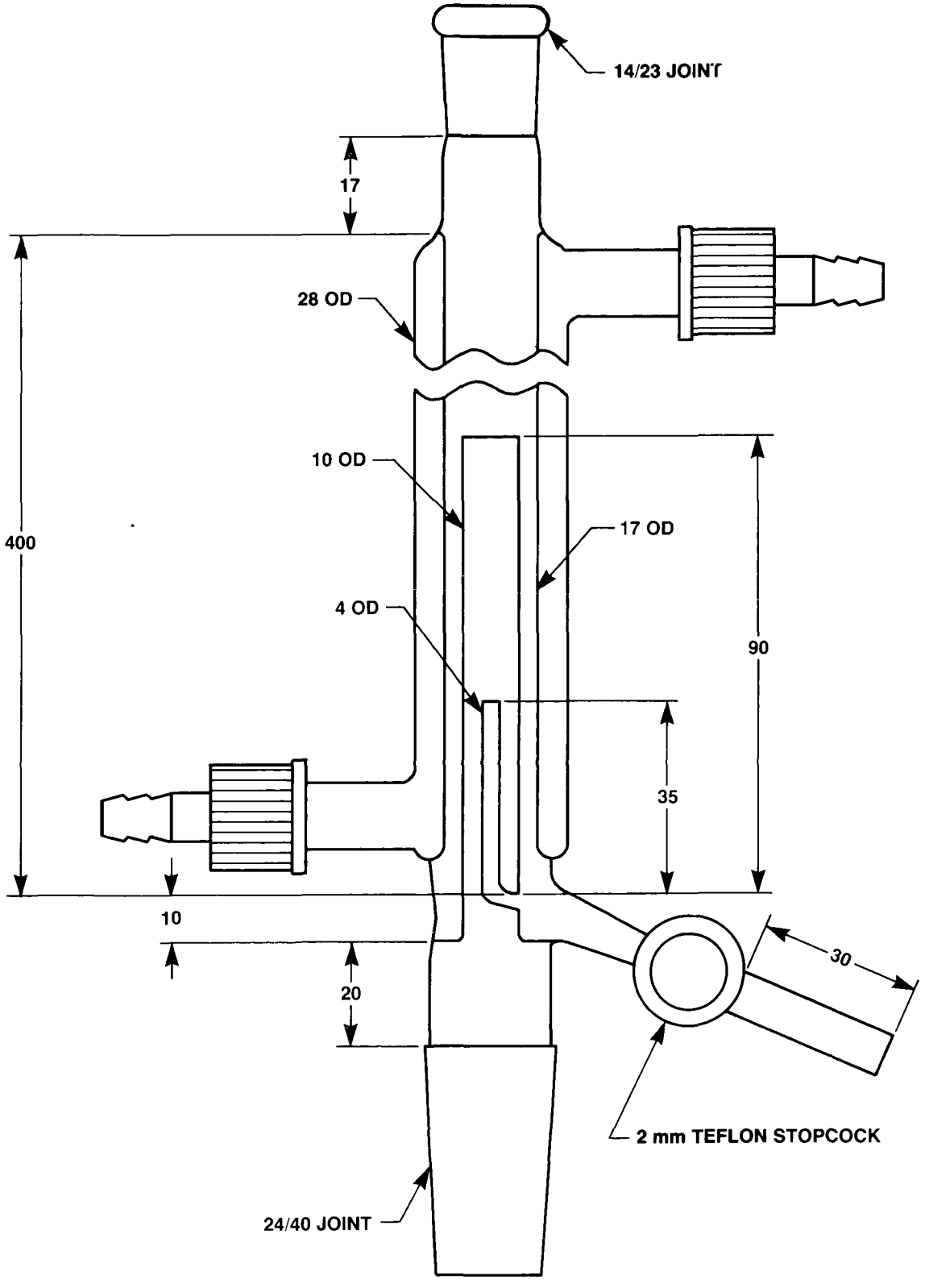

Figure 1 Steam Distillation Head

g. Dibenzofuran - 99+%.

h. Dibenzo-*p*-dioxin - 98+%.

i. Dibenzofuran-d_8 and dibenzo-*p*-dioxin-d_8 - 99.0 atom % D.*

j. Hexamethylbenzene - 99%.

k. Boiling chips - anti-bumping granules of fused alumina. Teflon boiling stones can also be used.

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* When available, ^{13}C-labelled DBF and DBD surrogates can be used instead of the deuterated surrogates.

Procedures

3.1 Extraction

The following are steps in the extraction procedure.

a. Shake sample well just before a subsample is taken for analysis.*

b. To 5.00 g defoamer sample in a 500 mL round-bottom flask, add 50 µL of a mixture of DBD-d_8 and DBF-d_8, internal standard surrogates of 5 ng/µL each in iso-octane, 200 mL of reagent water, and boiling chips.**

c. Place the flask into a heating mantle and attach a steam distillation condenser.

d. Add 3 mL of water and 2 mL of iso-octane inside the condenser.

e. Once a steady flow of cooling water is passing through the condenser, adjust the heater control of the mantle to bring the suspension to a vigorous boiling without bumping for 3 hours.

f. At the end of the extraction, let the condenser cool down to room temperature. Carefully drain off as much water as possible before draining the organic extract from the condenser into a 15 mL centrifuge tube.

g. Using a Pasteur pipet, transfer the organic extract into a second centrifuge tube containing a small amount of anhydrous sodium sulphate, while retaining the water in the first tube.

h. Rinse the condenser and the first tube twice with 2 mL aliquots of petroleum ether (P.E.) and transfer the rinsings to the second tube again.

i. Evaporate the combined extract down to 2 mL using a gentle stream of nitrogen and a water bath of 45°C.

3.2 Cleanup

The following are steps in the cleanup procedure.

a. Plug a 400 × 10 mm (id) glass column with a piece of glass wool. Add 1 cm of granular anhydrous sodium sulphate to the bottom.

b. Fill the column with 5.00 g of activated basic alumina and then add 1 cm of anhydrous sodium sulphate to the top.

c. Elute the column with 20 mL of P.E. and discard this fraction.

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* Since some defoamers are supplied in the form of a suspension, the sample should be homogenized by shaking to ensure a representative subsample is taken for analysis. A larger sample (i.e., 5 g instead of 1 g or less) also helps to minimize this potential inhomogeneity problem.

** In order to obtain quantitative recovery of DBD and DBF by steam distillation, about 100 boiling chips (0.6 to 0.7 g) were added to the water/defoamer sample to achieve vigorous boiling without bumping.

d. Quantitatively transfer the sample extract obtained in step i. (subsection 3.1) to the column, elute the column with 50 mL of P.E., and discard this fraction as well.

e. Continue the elution with 50 mL of 8% (v/v) dichloromethane in P.E. and collect this fraction in a 250 mL round-bottom flask as it contains all the native and deuterated DBD and DBF.

f. Evaporate the solvent down to about 5 mL with a three-stage Snyder column and a heating mantle.*

g. After cooling, transfer the extract to a 15 mL centrifuge tube and add 1 mL of iso-octane. Rinse the Snyder column and the flask with 2 × 2 mL of P.E. and combine the rinses in the above tube.

h. Using a gentle stream of nitrogen and a 45°C water bath, evaporate the solvent down to just below 0.5 mL.

i. After cooling, add 10 µL of a 25 ng/µL solution of hexamethylbenzene recovery standard in iso-octane, and adjust volume to 0.5 mL before GC-MS analysis.

3.3 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

a. The following is an example of the GC-MS operating conditions for analyzing DBD and DBF.

Instrument:	HP5880A GC, HP5970B MSD and data system
Column:	30 m x 0.25 mm, 0.25 µm film thickness
Carrier gas:	Helium with a head pressure of 69 kPa(10 psi), linear velocity 32 cm/s
Injection:	2 µL splitless (valve time 0.75 min)
Injector temperature:	250°C
Oven program:	70°C for 0.75 min then programmed to 140°C at 30°C/min, followed immediately by a 2°C/min temperature increase to 180°C. At the end of the run, bake the column at 280°C for 15 min.**
Ionization:	Electron impact (70 eV)
Source temperature:	200°C
Dwell time:	100 ms (milliseconds)
EM voltage:	200 V above autotune value
Ions monitored:	m/z 147[a] for hexamethylbenzene m/z 168[a] and 139[b] for DBF m/z 176[a] for DBF-d_8 m/z 184[a] and 155[b] for DBD m/z 192[a] for DBD-d_8
where:	[a] = quantitation ion [b] = confirmation ion

b. Prepare a series of standards in iso-octane that cover the expected concentration range of DBD and DBF in the sample extracts. Each solution must also contain DBD-d_8, DBF-d_8 and

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* Other techniques can be used for evaporating solutions containing DBD and DBF. The analyst must demonstrate, however, that losses of these compounds and their surrogates are negligible in the evaporative steps.

** To avoid interference by the high boiling co-extractives in the GC-MS analysis, the capillary column must be baked at 280°C for 15 minutes before injecting the next defoamer extract.

hexamethylbenzene at a concentration of 500 pg/μL.

c. To maximize sensitivity, divide the ions into three groups or retention time windows. Monitor m/z 147 (hexamethylbenzene) in group 1; m/z 139, 168 (DBF) and 176 (DBF-d_8) in group 2; and m/z 155, 184 (DBD), and 192 (DBD-d_8) in group 3.

d. Inject 2 μL of the standard. Analyze the standard by GC-MS in the selected ion-monitoring (SIM) mode using the masses given in step c. A typical chromatogram is depicted in Figure 2 and the order of elution is: hexamethylbenzene, DBF-d_8, DBF, DBD-d_8, and DBD.

e. Analyze the samples in the same way as the standards.*

3.4 Confirmation of Identity

a. Integrate the reconstructed ion chromatograms for the quantitation ions (m/z 168 for DBF and m/z 184 for DBD) and confirmation ions (m/z 139 for DBF and m/z 155 for DBD) in the sample. If the ratio of peak areas for the quantitation and confirmation ions at the expected retention time in the sample is within ± 20% of that of an authentic standard, then the presence of the parameter is confirmed.

b. To confirm DBD and DBF concentrations of ≤10 ng/g in samples, further evaporate the final extract to 100 μL or less.

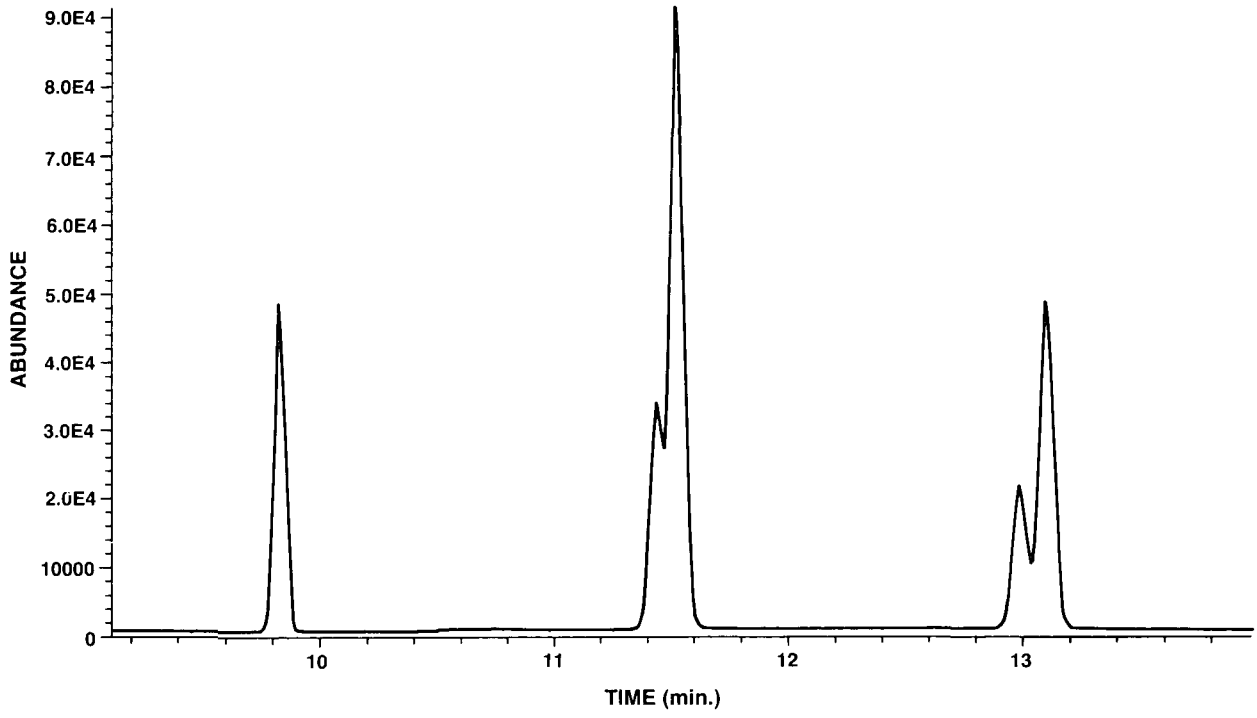

Figure 2 Typical Chromatogram

* If excessive interference is experienced in analyzing sample extracts, the use of a GC-MS system operating at a resolution of 5000 or higher is recommended. In this case, the ions monitored are: 147.1174 for HMB; 168.0575 and 139. 0548 for DBF; 176.1077 for DBF-d_8; 184.0524 and 155.0497 for DBD; and 192.1026 for DBD-d_8.

Section 4

Calculations

a. From the integrated ion chromatograms for the calibration runs, calculate the relative response factors for the native DBD and DBF relative to the corresponding perdeuterated DBD and DBF internal standards (=RRF_x) according to the following equation:

$$RRF_x = (A_{ix}/A_x)(C_x/C_{ix})$$

where:

A_{ix} = peak area of the quantitation ion for the appropriate labelled internal standard (m/z 176 for DBF-d_8 and m/z 192 for DBD-d_8)

A_x = peak area of the quantitation ion for the native analyte "x" (m/z 168 for DBF and m/z 184 for DBD)

C_x = concentration of native analyte "x", pg/μL

C_{ix} = concentration of appropriate internal standard "x", pg/μL

b. If the RRF for DBD and DBF are constant (relative standard deviation <10%) over the working range, it can be assumed that the RRF is invariant and the average RRF can be used. Alternatively, the results can be used to plot a calibration curve of response ratios, A_{ix}/A_x vs RRF.

c. Calculate the concentration of the native DBD and DBF in the sample, C_{sx}, as follows:

$$C_{sx} = (RRF_x)(A_x/A_{ix})(Q_{ix}/W)$$

where:

C_{sx} = concentration of native parameter "x" in the sample, ng/g

RRF_x=response factor of native parameter "x" relative to its perdeuterated internal standard

A_x = peak area of the quantitation ion for native parameter "x" in the sample (m/z 168 for DBF and m/z 184 for DBD)

A_{ix} = peak area of the quantitation ion for appropriate labelled internal standard "x" in the sample (m/z 176 for DBF-d_8 and m/z 192 for DBD-d_8)

Q_{ix} = amount in ng (i.e., 250 ng) of the appropriate labelled internal standard "x" added to the sample before extraction

W = weight of defoamer sample in grams

d. Calculate the percent recovery of the perdeuterated internal standards, % R_{ix}, measured in the sample extract using the formula:

$$\%\ R_{ix} = [(A_{ix}/A_r)_{sample}][(A_r/A_{ix})_{standard}](100)$$

where:

A_r = peak area of the quantitation ion (m/z 147) for

hexamethylbenzene recovery standard

A_{ix} = peak area of the quantitation ion for the appropriate labelled internal standard "x" (m/z 176 for DBF-d_8 and m/z 192 for DBD-d_8)

Quality Control and Method Performance

5.1 Quality Control

a. The acceptable range of surrogate recovery is from 50 to 120% for surrogate level of 50 ng/g. If the recovery of the surrogates is outside this range, the sample should be repeated and/or the entire analytical technique should be reviewed.

b. Method blanks should be run frequently to correct for background contamination.

5.2 Method Performance

a. Based on a 5.00 g sample and a final volume of 0.5 mL, the method detection limit (MDL) for both DBD and DBF is 1 ng/g. It was obtained by replicate analysis of spiked defoamer samples in a single laboratory. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and sample matrix effects.

b. The method has been tested for linearity of spike recovery from defoamers and has been demonstrated to be applicable over the concentration range from 1 to 100 ng/g.

c. In a single laboratory, six replicate determinations of DBF and DBD in a defoamer sample spiked at 10 ng/g level gave a mean recovery and a coefficient of variation of 103% and 8.9% respectively for DBF, and 106% and 5.9% respectively for DBD.

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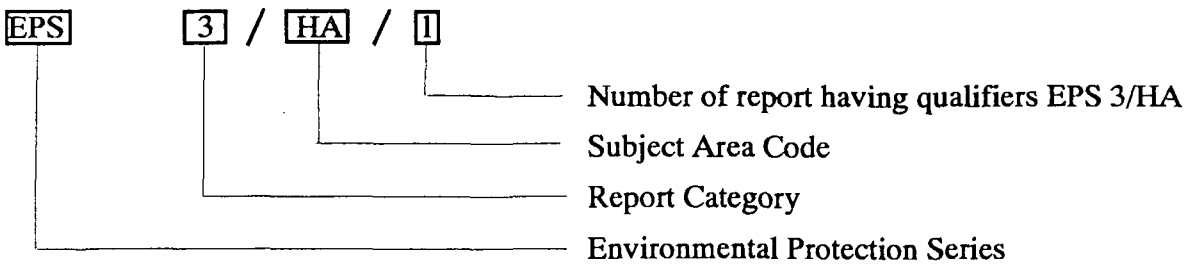

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