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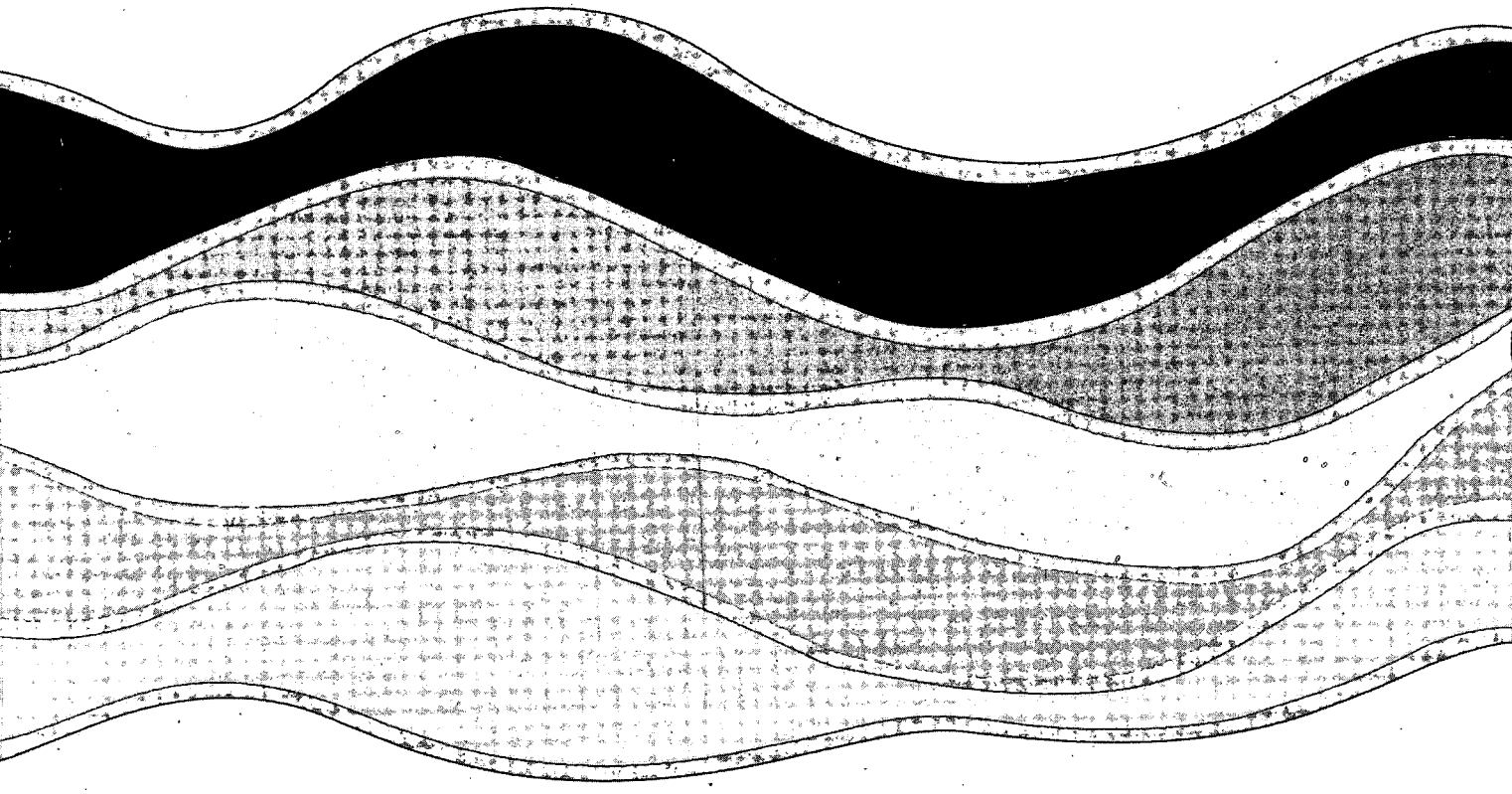

A PROPOSED REFERENCE METHOD FOR THE DETERMINATION OF DIBENZOFURAN AND DIBENZO-P-DIOXIN IN DEFOAMERS

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A PROPOSED REFERENCE METHOD FOR THE DETERMINATION OF DIBENZOFURAN AND DIBENZO-P-DIOXIN IN DEFOAMERS

by

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Management Perspective

The use of defoamers contaminated with non-chlorinated dibenzofuran (DBF) and dibenzo-p-dioxin (DBD) in chlorine bleaching pulp mills was shown to cause a significant increase in the 2378-TCDF and 2378-TCDD levels of the final bleached pulp. In order to reduce the amount of these toxicants in pulp mill discharges, Environment Canada is developing regulations that would set the maximum concentrations of DBF and DBD in defoamers for those applications. An analytical method for the determination of DBF and DBD in defoamers to be referenced in the regulations has been jointly developed by the Pulp and Paper Research Institute of Canada (PAPRICAN) and Environment Canada.

Dr. J. Lawrence
Director
Research and Applications Branch

Perspective administrative

On a montré que l'utilisation d'antimousses contaminés par du dibenzofurane (DBF) et de la dibenzo-p-dioxine (DBD) non chlorés, dans les papeteries produisant de la pâte blanchie au chlore, entraînait une augmentation marquée des concentrations de 2,3,7,8-TCDF et de 2,3,7,8-TCDD dans la pâte ainsi blanchie. Afin de réduire la quantité de ces produits dans les effluents de papeterie, Environnement Canada prépare une réglementation qui fixera la concentration maximale du DBF et de la DBD dans les antimousses utilisés. La méthode de dosage du DBF et de la DBD qui sera mentionnée dans le règlement a été préparée conjointement par l'Institut canadien de recherches sur les pâtes et papiers (PAPRICAN) et Environnement Canada.

J. Lawrence
Directeur
Direction de la recherche et des applications

Abstract

Based on a method developed by the Pulp and Paper Research Institute of Canada, a procedure optimized for the determination of dibenzofuran (DBF) and dibenzo-p-dioxin (DBD) in defoamers at low ng/g levels is presented. The defoamer is steam extracted and the extract in iso-octane is cleaned up on a basic alumina column. Final analysis is performed by 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 g sample and a final volume of 0.5 mL, the method detection limit is 1 ng/g for both DBF and DBD.

NOTE: Mention of trade names or commercial products does not constitute endorsement for use by Environment Canada.

Résumé

On présente une procédure optimisée, basée sur une méthode mise au point par l'Institut canadien de recherches sur les pâtes et papiers, pour doser le dibenzofurane (DBF) et la dibenzo-p-dioxine (DBD) présents dans les antimousses à des concentrations de l'ordre du ng/g. L'antimousse est extrait à la vapeur, puis l'extrait dans l'iso-octane est purifié sur une colonne d'alumine basique. L'analyse finale est effectuée par CG-SM en mode de détection d'ions spécifiques. La récupération de la DBD et du DBF naturels est mesurée en utilisant la DBD-d_8 et le DBF-d_8 comme analogues. La confirmation de la DBD et du DBF est faite en comparant le rapport des aires sous les pics pour les ions de mesure et les ions de confirmation de chaque composé dans l'étalon et l'échantillon. Avec un échantillon de 5 g et un volume final de 0,5 mL, la limite de détection de la méthode est de 1 ng/g pour le DBF et la DBD.

REMARQUE: Le fait que l'on mentionne une marque de commerce ou un produit du commerce ne signifie pas qu'Environnement Canada le recommande.

1. Scope and Application

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

2. Principle and Theory

2.1. 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.

3. Interferences

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

4. Sample Storage

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

5. Apparatus

5.1. All glassware must be washed and dried by the same procedure used for trace

organic analysis.

5.2. Volumetric flasks, 10, 50 and 100 mL.

5.3. Steam distillation heads (see Figure 1 for construction and dimension, these may be purchased from Verrerie de Précision, Montreal, Quebec, tel: (514) 398-6217).

5.4. Round bottom flasks, 500 and 250 mL.

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

5.6. Chromatographic columns, 400 mm x 10 mm id with Teflon stopcocks.

5.7. Three-stage Snyder columns, ca. 30 cm in length.

5.8. Heating mantles with temperature controls.

5.9. Drying oven for glassware.

5.10. Oven for the activation of alumina at 130 ± 1 °C.

5.11. 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 (both available from Hewlett-Packard) and a data system were used. Other systems of equal or better sensitivity may be used.

5.12. Fused silica capillary column, 30 m x 0.25 mm id coated with 5% diphenyl, 94% dimethyl, and 1% vinyl polysiloxane phases, 0.25 μm film thickness, such as DB-5, SPB-5 and SE-54 from various suppliers.

5.13. Hamilton syringes, 10, 50, 100, 250 and 500 μL.

6. Reagents

6.1. All organic solvents must be of distilled-in-glass grade with blanks suitable for residue analysis.

6.2. Iso-octane.

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

6.4. Dichloromethane.

6.5. Alumina, basic, 100 - 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.

6.6. Anhydrous sodium sulfate previously heated at 600°C overnight.

6.7. 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 prepared by passing distilled water through a 4-cartridge Milli-Q purification unit was used.

6.8. Dibenzofuran, 99+%, Aldrich Chemicals.

6.9. Dibenzo-p-dioxin, 98+%, Ultra Scientific.

6.10. Dibenzofuran-d_8 and dibenzo-p-dioxin-d_8, 99.0 atom % D, MSD Isotopes (Division of Merck Frosst Canada Inc.). (See note 14.1)

6.11. Hexamethylbenzene, 99%, Aldrich Chemicals.

6.12. Boiling chips, anti-bumping granules of fused alumina from BDH Inc. Teflon boiling stones can also be used.

7. Extraction Procedure

7.1. Shake sample well just before a subsample is taken for analysis (See note 14.2).

7.2. 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 (See note 14.3).

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

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

7.5. After 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 hr.

7.6. 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.

7.7. Using a Pasteur pipet, transfer the organic extract into a second centrifuge tube containing a small amount of anhydrous sodium sulfate while leaving the water behind in the first tube.

7.8. 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.

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

8. Cleanup Procedure

8.1. Plug a 400 mm x 10 mm id glass column with a piece of glasswool. Add 1 cm of granular anhydrous sodium sulfate to the bottom.

8.2. Fill the column with 5.00 g of activated basic alumina and then with 1 cm of anhydrous sodium sulfate at the top.

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

8.4. Quantitatively transfer the sample extract in step 7.9 to the column, elute the column with 50 mL of P.E. and also discard this fraction.

8.5. Continue the elution with 50 mL of 5 % (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.

8.6. Evaporate the solvent down to ca. 5 mL with a three-stage Snyder column and a heating mantle (See note 14.4).

8.7. 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 x 2 mL of

P.E. and combine the rinses in the above tube.

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

8.9. 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.

9. GC-MS Analysis

9.1. An example of the GC-MS operating conditions for the analysis of DBD and DBF is given below.

Instrument:	HP5880A GC, HP5970B MSD and data system
Column:	30 m x 0.25 mm x 0.25 μm SPB-5 (Supelco)
Carrier gas:	Helium with a head pressure of 10 psi, linear velocity 32 cm/sec
Injection:	2 μL splitless (valve time 0.75 min)
Injector temp.:	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. (See note 14.5).
Ionization:	Electron impact (70 eV)
Source temp.:	200°C
Dwell time:	100 msec
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

9.2. 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 hexamethylbenzene at a concentration of 500 pg/μL.

9.3. 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.

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

9.5. Analyze the samples in the same way as the standards (See note 14.6).

10. Calculations

10.1. 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

10.2. If the RRF for DBD and DBF are constant (<10% RSD) over the working range, then the RRF can be assumed to be 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.

10.3. 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

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

$$\% R_{ix} = (A_{ix}/A_r)Spl * (A_r/A_{ix})Std * 100$$

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)
Spl = measurement made for sample
Std = measurement made for calibration standard

11. Confirmation of Identity

11.1. 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.

11.2. For the confirmation of DBD and DBF in samples of ≤ 10 ng/g, further evaporation of the final extract to 100 μL or less may be necessary.

12. Quality Control

12.1. 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..

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

13. Method Performance

13.1. Based on a 5 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.

13.2. 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.

13.3. In a single laboratory, six replicate determinations of DBD and DBF 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.

14. Notes

14.1. ^{13}C-labelled DBF and DBD surrogates, when available, can be used in place of the deuterated surrogates.

14.2. 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.

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

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

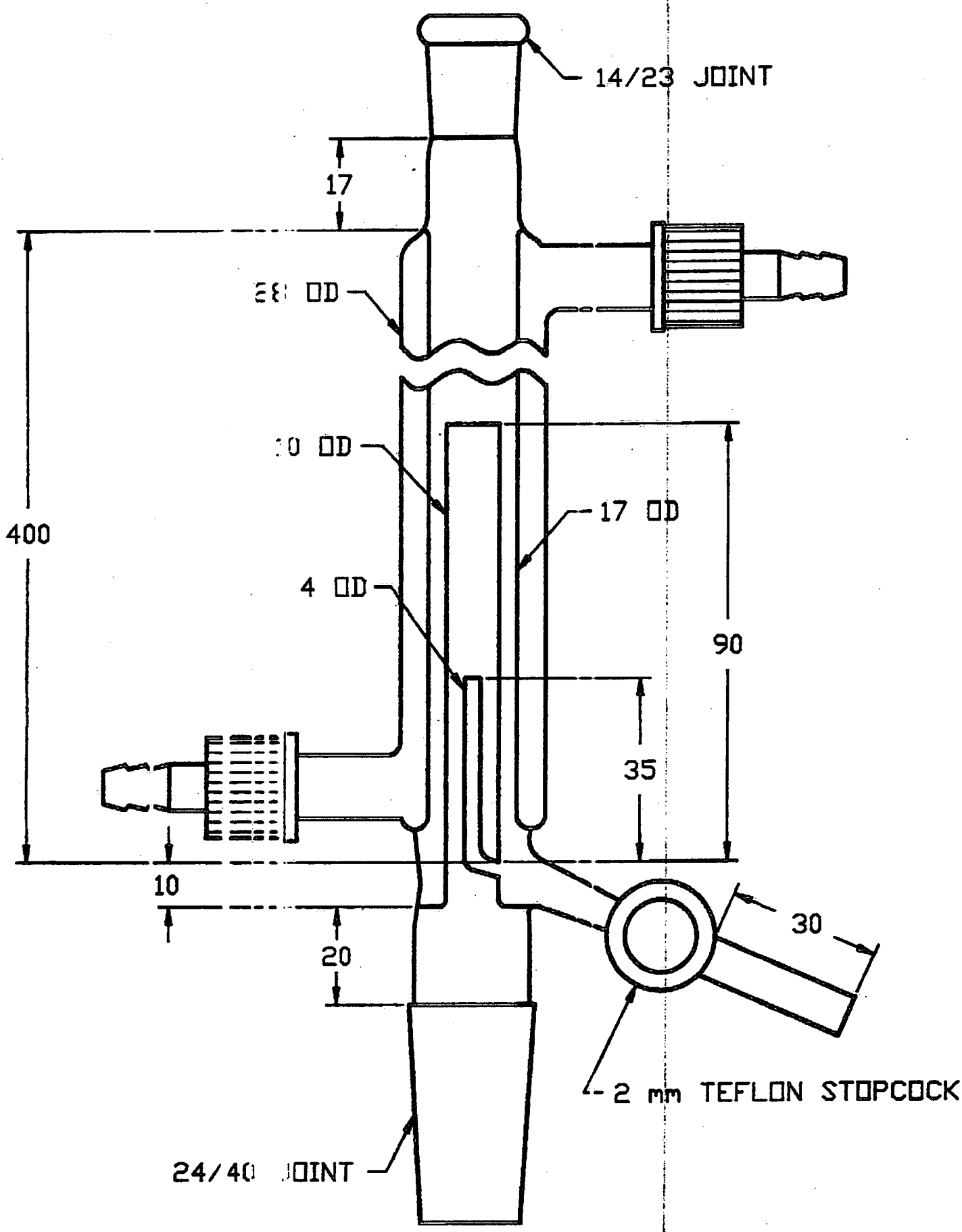
14.5. To avoid interference by the high boiling co-extractives in the GC-MS analysis, it is necessary to bake the capillary column at 280°C for 15 min before the next defoamer extract is injected.

14.6. If excessive interference is experienced in the analysis of 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.

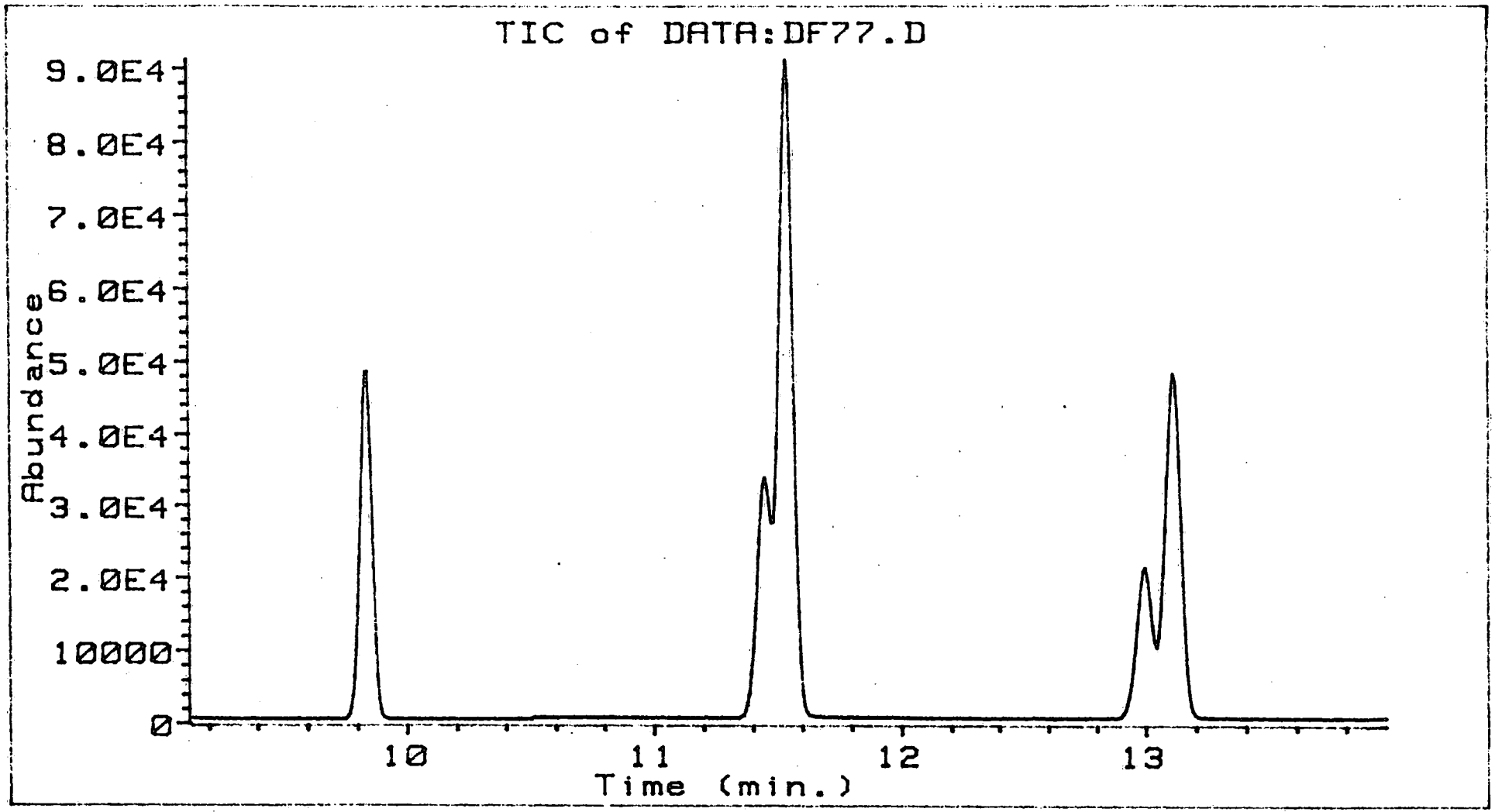
15. References

15.1. R.H. Voss, C.E. Luthe, B.I. Fleming, R.M. Berry and L.H. Allen, 1988, "Some New Insights into the Origins of Dioxins Formed During Chemical Pulp Bleaching", Pulp Pap. Can. 89(12):151-162 (1988).

15.2. D.W. Kuehl and R.C. Dougherty, Environ. Sci. Technol., 14(4), 447-449 (1980).



NOTE: ALL DIMENSIONS ARE IN MILLIMETERS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11
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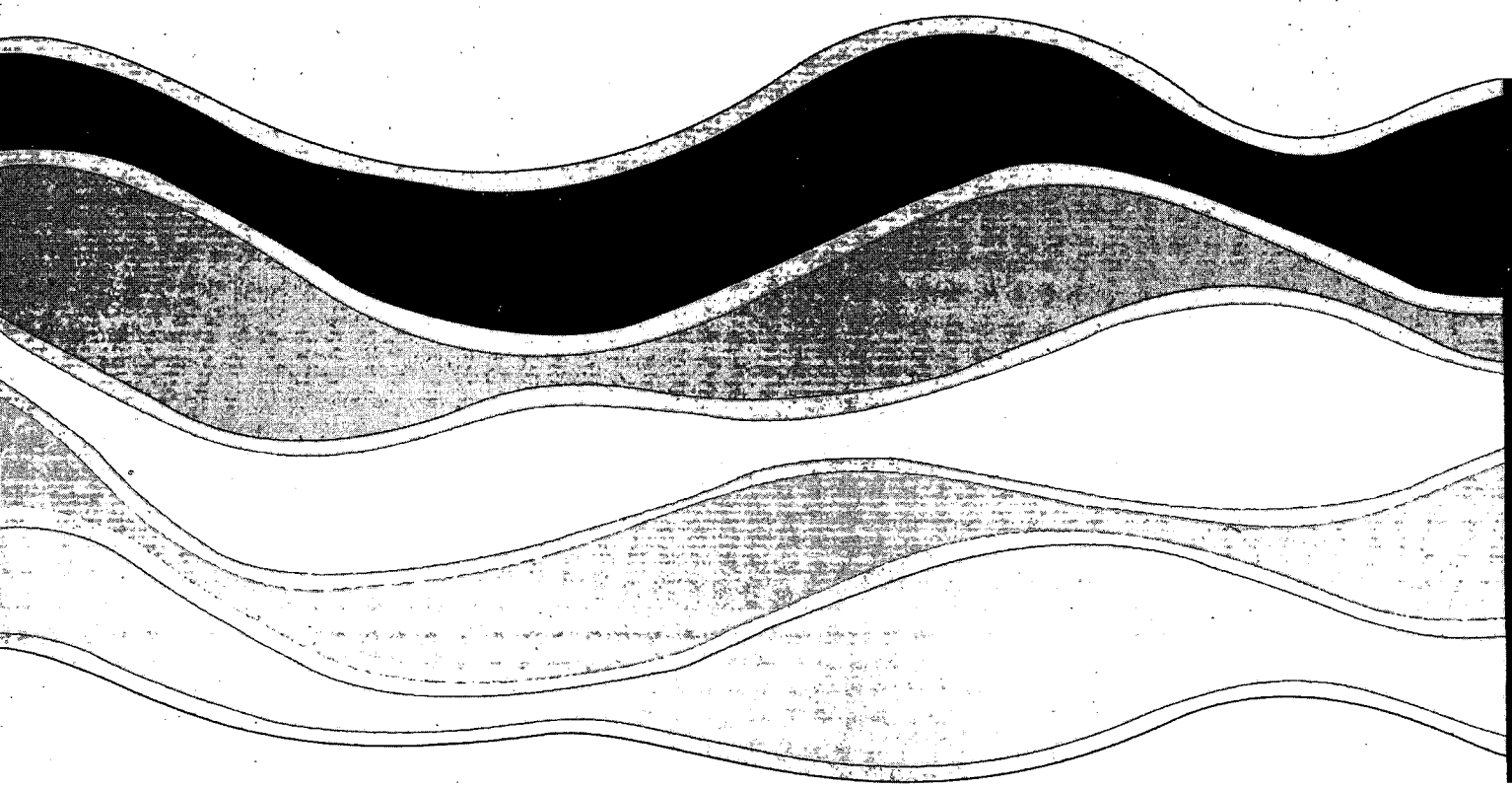
Time (min.)

FIGURE 2



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