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Highlights

Using Py-GC/MS to detect and measure silicone defoamers in pulp fibres and mill deposits

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Bruce Sithole*, Chu Watanabe

►We describe the first know application for detection and determination of silicone defoamers in pulp and paper matrices. ►Silicone defoamer formulations from different suppliers can be differentiated by Py-GC/MS. ►Contrary to claims, silicone defoamers adsorb significantly to pulp fibres and significant amounts remain after washing of the pulp. ►Some silicone defoamer formulations contain penta and tetra cyclic silicone components that may be a health hazard. ►Silicone defoamers can cause pitch deposition in pulp and paper making operations.

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Using Py-GC/MS to detect and measure silicone defoamers in pulp fibres and mill deposits

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ABSTRACT

Defoamers are often used to control or reduce foam problems in a variety of pulp and papermaking processes. It has been recognised that non-judicious use of defoamers can lead to undesirable deposition problems. Amide-based defoamers have been largely supplanted by water-based or water-extended defoamers that are supposed to be non-depositing. However, mill experience and research has shown otherwise. Hence, there is a need for analytical procedures to determine silicone defoamer components in deposits. In this work, for the first time, Py-GC/MS has been used to analyse for silicone defoamers in pulp and paper matrices. This work demonstrates that the technique is ideal for analysis and characterisation of silicone defoamers on pulp fibres and in mill deposits. The technique is easier and much more rapid than using solvent extraction and solid phase extraction, previously developed for analysis of silicone oil defoamers in deposits. It is applicable to silicone defoamers irrespective of molecular weight and can be used to ascertain the source of a particular defoamer formulation. Application of the technique to a washed kraft pulp, previously treated with silicone defoamers, shows that silicone defoamer oil carryover on pulp fibres can be substantial, depending on the defoamer formulation used. In pitch deposits, the level of silicone oil can be over 25% (w/w). In addition, analysis of deposits from mills using the defoamers shows that silicone defoamers have the potential to cause pitch deposition contrary to claims that the defoamers do not cause such problems. Thus, the method can be used to assess the impact of defoamer carryover on pulp properties and the contribution of silicone defoamers to pitch deposition.

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1. Introduction

Silicone defoamers are now widely used in pulp and paper mills primarily for control or elimination of foam problems [1,2]. The silicone-based defoamers typically use in their formulation hydrophobic silica in place of ethylene bis-stearamide, which is one of the active ingredients in amide-based defoamers. In addition to providing excellent foam control, they are reported to have superior pulp drainage.

Similar to mineral oil-based defoamers, silicone defoamers are combined or formulated with other materials to produce cost-effective products. To develop efficient silicone foam control agents, specialty chemical formulators must consider a number of factors, including: the nature of the foaming media; process conditions in the application; the form of the defoamer; and perhaps most important, the characteristics of the base silicone antifoam compound technology.

The defoamer can be either an aqueous silicone emulsion or a non-aqueous silicone concentrate. The form of the product will

dictate which silicone technologies are likely to be the most effective for the application and also what other additives or materials will be required in the final product formulation.

Silicone concentrates are used globally, but aqueous silicone emulsions are the predominant choice of pulp mills for their foam control needs. The key active ingredient used in the production of aqueous silicone emulsions is typically a 100% active silicone antifoam compound. Silicone oil, that is, polydimethylsiloxane (PDMS), and silica particles are the two major ingredients of silicone defoamers. Silicone antifoam can be in the form of compound (100% active content), emulsion (variable active content) or powder formulations. In the simplest form, a silicone antifoam compound can be thought of as silica-filled silicone [1].

Formulated silicone defoamers combine the selected silicone antifoam compound with a number of other raw materials. These include water, surface-active agents, hydrophobic particulates and anti-microbial agents. In addition, various organic moieties can be incorporated into the PDMS backbone to make organo-modified siloxanes that are compatible with, or soluble in, aqueous and/or organic systems [2]. A schematic of the PDMS structure is shown in Fig. 1.

There are issues and problems associated with the use of silicone defoamers in the pulp and paper industry. They include: silicone

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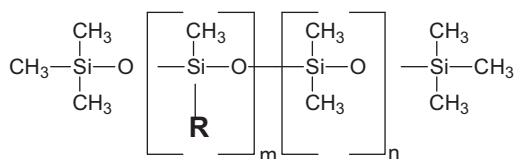


Fig. 1. Structure of organo-modified PDMS (R = organic moiety).

carryover on pulp fibres, contribution to deposition problems, and environmental/health concerns related to bioaccumulation and oestrogen activity of siloxanes, especially the cyclic ones.

1.1. Silicone carryover

When mills conduct trials with silicone defoamers, the evaluation criteria are usually limited to cost and efficacy of the defoamer. However, according to a technical data sheet from a defoamer supplier "PDMS has a very high ability to adsorb on sludge and therefore most of the injected PDMS (in an effluent treatment system) is attached to the sludge. Later, sludge is disposed to land and abiotic degradation of the PDMS occurs. Any remaining small amount of PDMS (analytical detection limit) tends to bind to solid particles suspended in the process water phase" [3]. From this it can be surmised that these defoamers could also adsorb strongly onto pulp and paper matrices and could have an impact on pulp properties such as their bonding ability and wettability. Before the potential impact can be assessed, the extent of defoamer carryover with pulp fibres must first be determined.

1.2. Defoamer deposition

According to a paper by Habermehl [1], the key benefits noted since the introduction of silicone defoamers in pulp and paper making processes include reductions in addition rates relative to mineral oil-based defoamers; reductions in pitch deposits associated with defoamer usage; dramatic reductions or complete elimination of chemical pitch control additives; and lower cost in use. However, silicone defoamer deposition issues have been reported [4] and observed [5], possibly due to overdosing.

1.2.1. Environmental/health concerns

Siloxanes have been detected in environmental matrices, especially in sewage sludge. In studies conducted by the Nordic countries, D5 was the dominant siloxane in all environmental matrices sampled except for air, where D4 dominated [6]; $D = (\text{CH}_3)_2\text{SiO}_2$. A cross comparison of the Environment Canada and US EPA lists of persistent, bioaccumulative and toxic compounds lists siloxanes as contributing 8% to the list of 610 compounds [7]. Dimethyl cyclic siloxanes with 4-6 siloxane groups appear to be particularly bioaccumulative and recent laboratory measurements confirm this [8].

As the first step in addressing these two issues, reliable techniques must be available for determining silicone defoamers in pulp fibres and in pitch deposits. In this report, we examine the relative merits of various analytical techniques for analysing silicone defoamers, and we show that pyrolysis-GC/MS (Py-GC/MS) is particularly well-suited for these analyses.

Several methods have been used to analyse for silicones in various matrices. They are summarised in the following paragraphs.

1.3. Solvent extraction and atomic absorption (AA) spectroscopy

Gooch [9] ascertained that residual silicones in fruit juices can be separated from the naturally occurring siliceous materials in fruit products and selectively recovered by solvent extraction, after suitable pre-treatment. The recovered silicone was measured by atomic

absorption spectroscopy. Silicone concentrations as low as about 1 ppm can be measured.

However, when the method was applied to tissue samples treated with silicone defoamers, it was found that the solvent extraction process was only 70-90% efficient [10]. Therefore, this methodology will not be suitable for assessing carryover of silicone defoamers with pulps.

1.4. Sample digestion and gas chromatography (GC)

With sample digestion and GC, the silicone defoamer is hydrolysed in strong acid to its monomer units that are derivatised with trimethylsilyl groups, extracted into

hexamethyldisiloxane and subsequently analysed by GC [11]. The turnaround time for this method is prohibitively high - approximately one week, with 18 h required to prepare each sample [11]. Unlike solvent extraction, the digestion process is virtually 100% efficient, and GC has the added benefit of being able to differentiate the functionality of the silicone. Thus any different groups present in the PDMS backbone can be determined. Unfortunately, information about the original starting compound is lost since the sample is digested into its monomer units.

1.5. Solvent extraction and solid phase extraction (SPE)

Sithole and Filion [5] described the determination of silicone defoamers in pitch deposits by SPE. The methods used entailed solvent extraction followed by separation by solid-phase extraction and identification of the separated components by FTIR. They are applicable to low molecular weight defoamers (up to 10,000 Da) and enable complete characterisation of deposits from mills that use such defoamers. The methods, however, are not applicable to pulp fibres as they are not sensitive enough and fail when applied to deposits that contain high molecular weight silicone oils.

1.6. Pyrolysis-gas chromatography (Py-GC)

Silicone vapours can be a problem in the electronics industry as they can affect electrical contacts. Aramata and Saitoh [12] developed a method for detecting silicone in the atmosphere that entailed adsorption of silicone vapours onto charcoal, desorption of the silicones with solvent, concentration by solvent evaporation, and analysis of the desorbed silicones by Py-GC. Atomic emission detection (AED) coupled to the Py-GC improved analytical precision and sensitivity by eliminating interferences from non-silicone compounds collected on the adsorption media. The AED monitors the Si atom in the silicones. The AED pyrograms showed several peaks corresponding to D3, D4, D5, D6 and D7, where $D = (\text{CH}_3)_2\text{SiO}_2$.

From the preceding information, it appears that Py-GC/MS should be a viable technique for the analysis and characterisation of silicone defoamers in fibres and deposits. We therefore proceeded to evaluate this technique on pulp and deposit samples.

2. Methods

2.1. Samples

Silicone defoamer samples were obtained from various supplier companies: they were obtained in formulations that are used in pulp and paper mills. The defoamers were homogenised well to assure sample homogeneity before analysis.

Pitch deposit samples were obtained from mills that used silicone defoamers in their processes. Typically the deposits occurred on wash process unit operations. The samples were freeze-dried and portions analysed by sequential solvent extraction with acetone and chloroform to yield three different fractions, namely,

acetone extracts, chloroform extracts and insoluble fractions. The extractions were conducted using a Soxtec extraction apparatus. The various fractions were dried to constant weight before weighing. Each fraction was then analysed for silicone oil content.

The samples were analysed by Py-GC/MS and the analytical conditions were as follows:

Pyrolyser:

PY-2020 (Frontier Laboratories, Japan) attached to a capillary column

Oven temperature: 300 °C

Pyrolysis temperature: 650 °C for 20 s

10–30 µg samples were loaded into stainless steel sample cups. 0.5 µL of tetramethyl ammonium hydroxide (25% in methanol; Sigma-Aldrich) methylating agent were added onto the samples to enable *in situ* methylation of the components

GC:

Varian 3900

Injection temperature: 300 °C

Injection method: 1:25 split

Column: DB5-HT: 30 m × 0.25 mm i.d. × 0.10 µm film thickness

Flow rate: 1.6 mL/min

Temperature programming: 50 °C for 2 min, 8 °C/min to 310 °C, hold for 0.5 min

MS:

Varian Saturn 2100 T ion trap

Interface temperature: 300 °C

Ion trap temperature: 250 °C

Electron ionisation

Scan range: m/z 50–650

Since siloxanes are ubiquitous, special care is required to avoid the risk of contamination of samples during sample collection, storage and analysis. Analyses of blank samples were run frequently to assure that there were no contaminations from the environment and from column bleed.

2.2. Silicone defoamer carryover

Silicone carryover on pulp fibres was determined by measuring the binding abilities of defoamers to a brownstock kraft pulp.

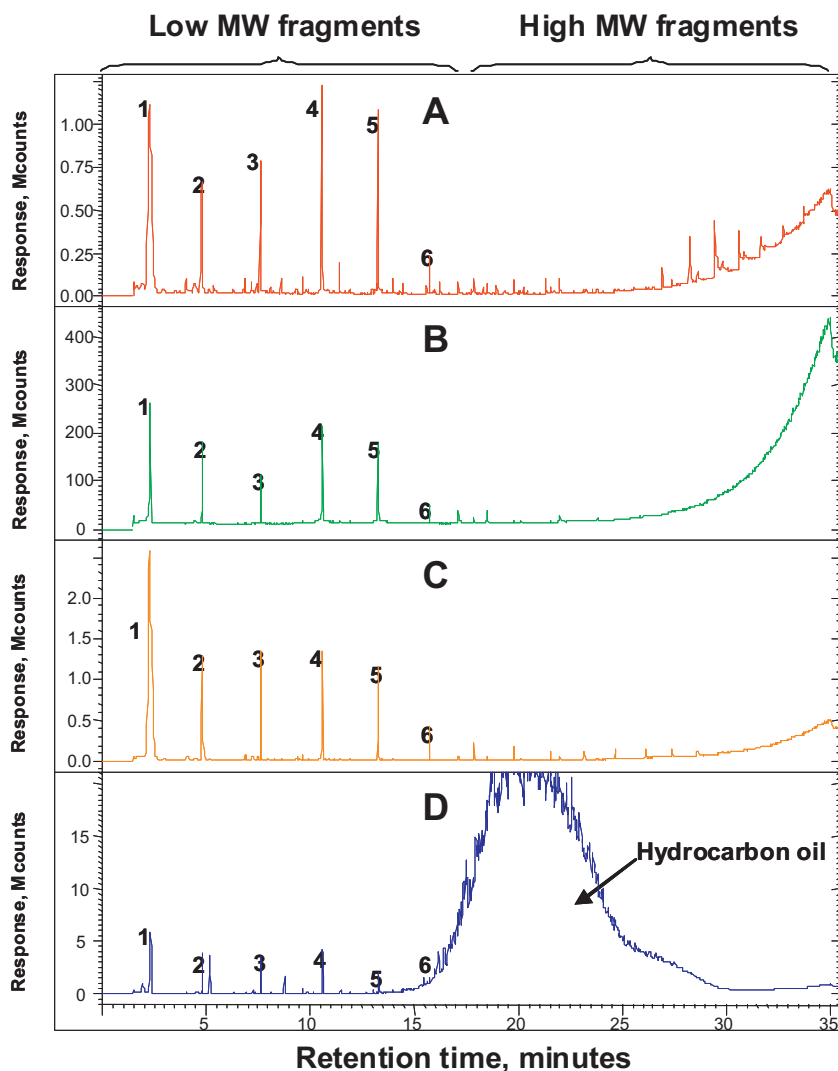


Fig. 2. (A) Pyrograms of different silicone defoamer formulations. (A and B) Refer to different defoamer formulations. Peaks labelled 1–6 are used for fingerprinting of the various silicone defoamer formulations. (B) Mass spectra and identities of the major pyrolysis products in defoamer formulations shown in A. Numbers 1–6 refer to peaks labelled in A.

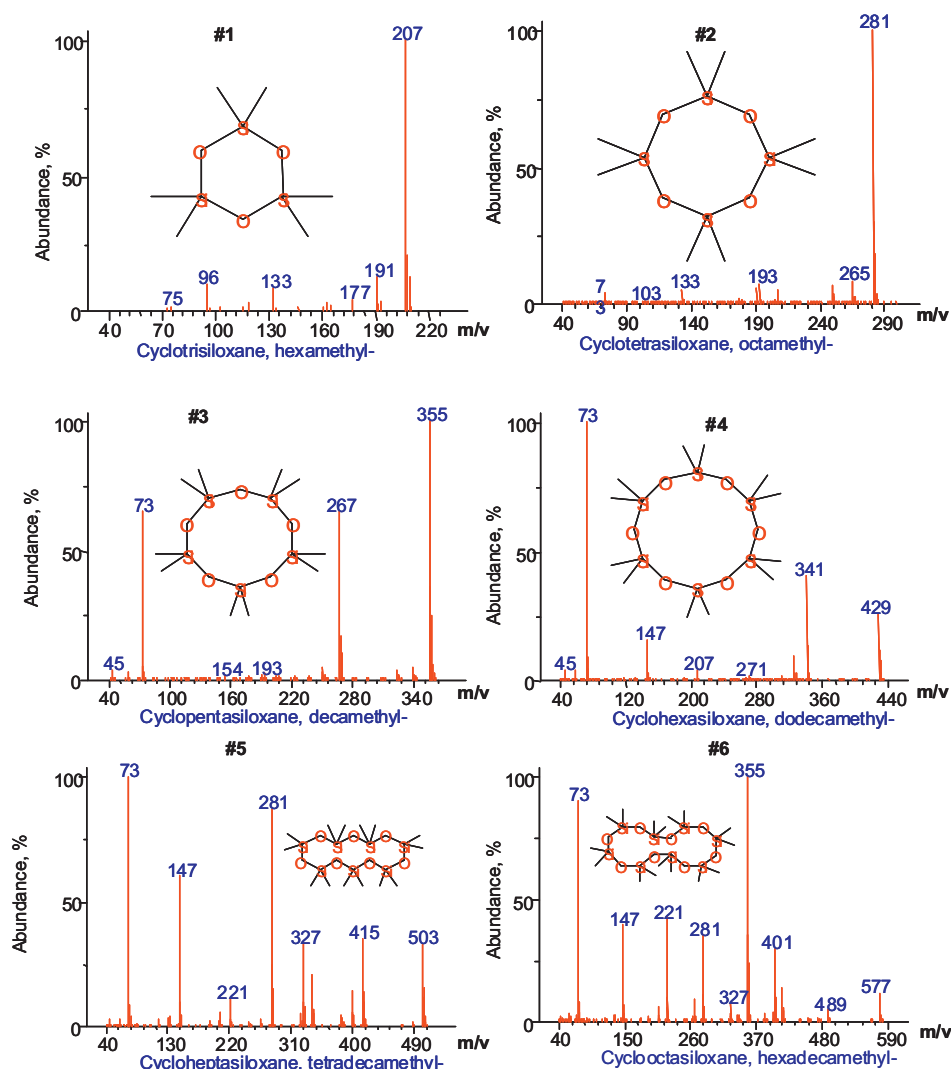


Fig. 2. (Continued)

Defoamers were obtained from 2 suppliers: Defoamer E (100% actives) and defoamer F (30% actives). The defoamers were mixed with a kraft brownstock pulp at 0.5 kg/ton. The amount of silicone oil carryover was determined by measuring the amount of silicone on the fibres after washing and vacuum filtration of the pulp with 3 volumes of water to simulate washing in an industrial process (procedure recommended by a defoamer supplier).

Initially, the silicone oil on the fibres was analysed directly by Py-GC/MS of small portions of the fibre but although the PDMS could be detected, the results were not reproducible due to sample non homogeneity. It was therefore decided to extract the defoamer from pulps with a solvent and analyse for the silicone defoamers in the extracts [5,6]. Hence, the pulp samples were Soxtec extracted with chloroform to recover the silicone defoamers. The extracts were dried under nitrogen, weighed and then reconstituted to a desired volume with chloroform. Known portions of the extracts (μL quantities) were analysed by Py-GC/MS. The reference defoamers were used as standards for quantification.

3. Results and discussions

The pyrograms in Fig. 2A show that Py-GC combined with mass spectrometric detection can differentiate silicone defoamers from

different suppliers. The pyrograms reveal a homologous series of peaks corresponding to PDMS monomer units. In addition, the pyrograms show that the defoamers contain mainly low molecular weight silicone defoamer groups (peaks eluting between 2 and 15 min) with smaller amounts of high molecular weight silicone oil fragments (peaks eluting at retention times >15 min). The mass spectra and identities of the major pyrolysis products are shown in Fig. 2B: it is evident that the major components in the formulation are comprised of cyclic moieties. An interesting observation is that Defoamer D contains a significant amount of hydrocarbon oil relative to the silicone oil as evidenced by the large hump eluting between 15 and 30 min. This hump profile is well known from previous analyses of hydrocarbon oils and is confirmed by mass spectral data on the eluted peaks [13,14]. Thus Py-GC/MS has the potential of not only determining the presence of silicone defoamer, but also can provide information about the type of defoamer formulation used.

3.1. Silicone defoamer carryover

Pyrograms and mass spectral data of the samples are shown in Figs. 3 and 4: it is evident that the pyrograms of the pulp extracts match very well with those of the starting defoamer compounds. The pyrograms display similar profiles and retention times. Further

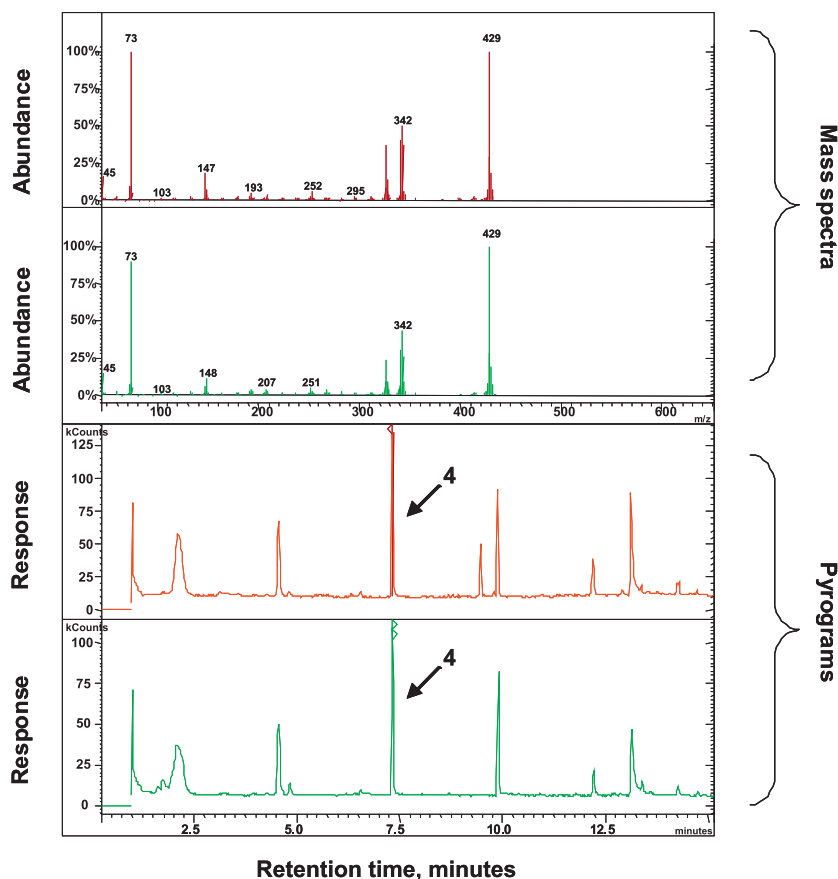


Fig. 3. Pyrograms of Defoamer E and extracts of pulp treated with Defoamer E. Quantification was done using peak # 4, corresponding to dodecamethyl cyclohexasiloxane.

confirmation of the presence of defoamer in the extracts is provided by mass spectral analysis of the peaks: as can be seen in the top part of Figs. 3 and 4, the mass spectra of peaks that are common in the pyrograms are identical.

The two major peaks in the pyrograms were used for quantification. The results (Table 1) show that pulp washing reduces defoamer content in the fibres by about 43%. Pulp samples treated with Defoamer E contain 10-fold lower amounts of defoamer than pulps treated with the Defoamer F. This is despite the fact that Defoamer E had 100% actives versus 30% actives in Defoamer F. This implies that one cannot predict which defoamer will result in lower silicone carryover based on their actives content. Thus it is clear that carryover of silicone defoamers with pulp will vary depending on the defoamer used. In addition, residual amounts of silicone defoamers on the fibres are quite appreciable and can potentially affect fibre properties.

3.2. Analysis of deposits

Pitch deposit samples from mills that were using silicone defoamers were analysed by SPE as previously described [5]. The results revealed that the SPE method failed since silicone defoamer

compounds were present in the methanol and chloroform fractions, and also in the non-extractable fraction of the deposit (confirmed by FTIR and Py-GC/MS). The deposits contained high molecular weight silicone oils some of which eluted in the chloroform fraction but significant amounts appeared to have remained on the SPE columns. For example, the total acetone extractives of one deposit were 77.65% but the total amount of material recovered from SPE separation was only 57.08%. Results from the analysis of several other deposits showed similar trends indicating that the SPE methodology fails when applied to samples that contain high molecular weight silicone defoamers. Consequently, the deposits were then analysed by Py-GC/MS as illustrated in the following examples.

3.3. Deposit 1

A deposit sample from a kraft mill was analysed in two ways: pyrolysis analysis of the whole deposit and pyrolysis analysis of deposit fractions obtained from sequential extraction with acetone and chloroform and of the residue after extraction. Previous work with low molecular weight defoamers has shown that sequential extraction is quantitative for silicone defoamer components [5].

Table 1

Determining silicone defoamer oil carryover on kraft pulps.

Sample description	Pulp treated with Defoamer E, washed	Pulp treated with Defoamer F, washed	Pulp treated with Defoamer E, unwashed	Pulp treated with Defoamer F, unwashed
Pulp sample weight (g)	1.785	2.046	1.576	2.046
Chloroform extracts (mg)	3.0	8.0	3.7	13.2
Silicone defoamer content of extracts (%)	14.92	64.77	17.71	68.68
Silicone defoamer content of pulp (%)	0.024	0.253	0.042	0.443

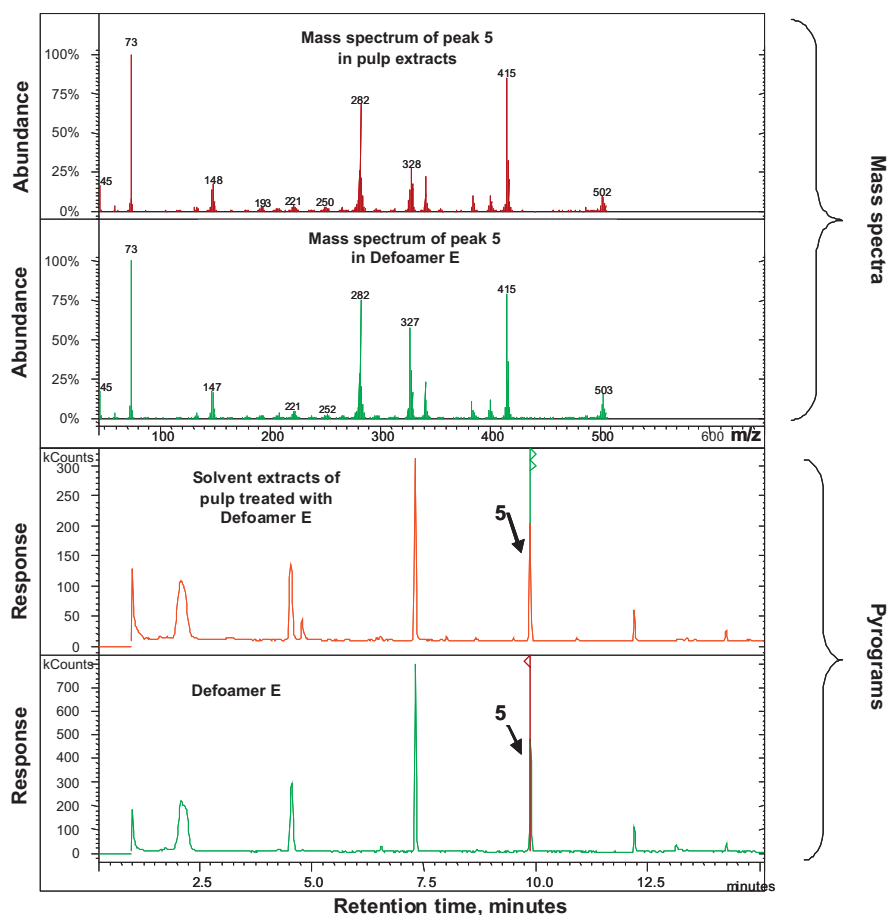


Fig. 4. Pyrograms of Defoamer E and extracts of pulp treated with Defoamer E. Quantification was done using peak # 5, corresponding to tetradecamethyl cycloheptasiloxane.

The defoamer used at the mill (Defoamer F) was used as a reference. The pyrograms indicate that the deposit contained silicone defoamer fragments that corresponded to those identified in Fig. 2B. Quantitative data shown in Tables 2 and 3, using Defoamer F as the standard, indicate that the deposit contained about 26% (w/w) silicone oil defoamer. The data on direct analysis of the deposit are encouraging considering that only small amounts of material are

Table 2
Analysis of silicone oil in the whole deposit sample.

Amount of deposit analysed (μg)	Silicone oil in the deposit (%)
10.5	32.27
100.9	31.63
133.2	25.79
150.9	22.13
153.5	25.96
93.6	23.08
88.6	20.32
47.1	27.62
Average	26.10
Std. deviation	4.30

Table 3
Analysis of silicone oil in a fractionated deposit sample.

Deposit fractions	Silicone oil content, % Trial 1	Silicone oil content, % Trial 2
Acetone fraction	7.24	8.37
Chloroform fraction	2.67	1.02
Non-extractable	15.28	17.14
Total	25.18	26.52
Average	25.85	

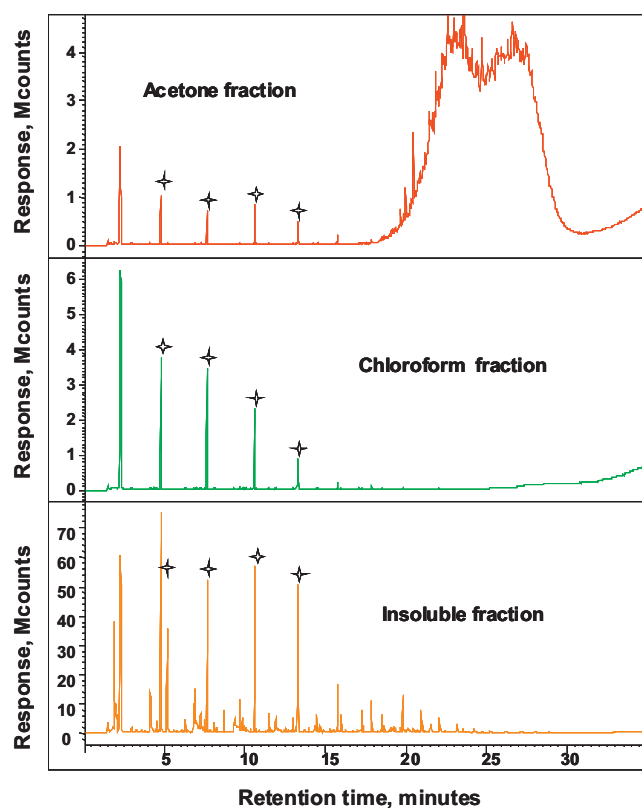


Fig. 5. Pyrograms illustrating the presence of silicone oil in a fractionated deposit sample. The asterisks refer to peaks that may be used for quantification.

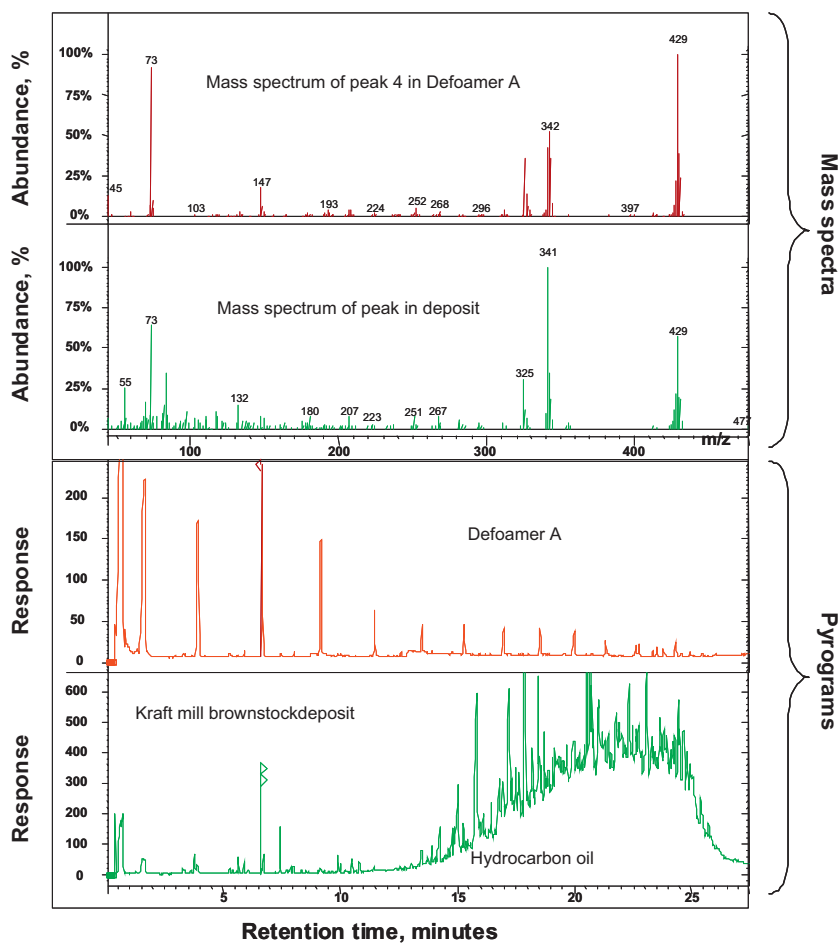


Fig. 6. Comparison of pyrograms of Defoamer A and a kraft mill brownstock deposit. Quantification was done using peak # 4, corresponding to dodecamethyl cyclohexasiloxane.

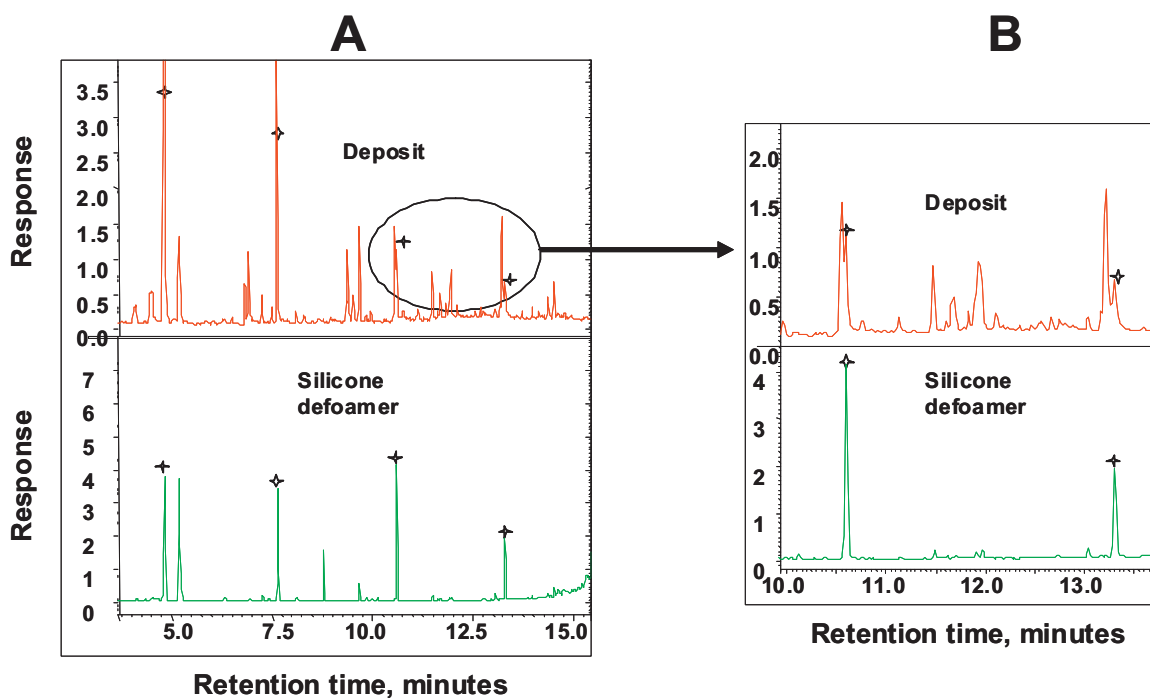


Fig. 7. Comparison of pyrograms of Defoamer D and a deposit sample. The asterisks show peaks that are common in both pyrograms (according to retention times and mass spectra).

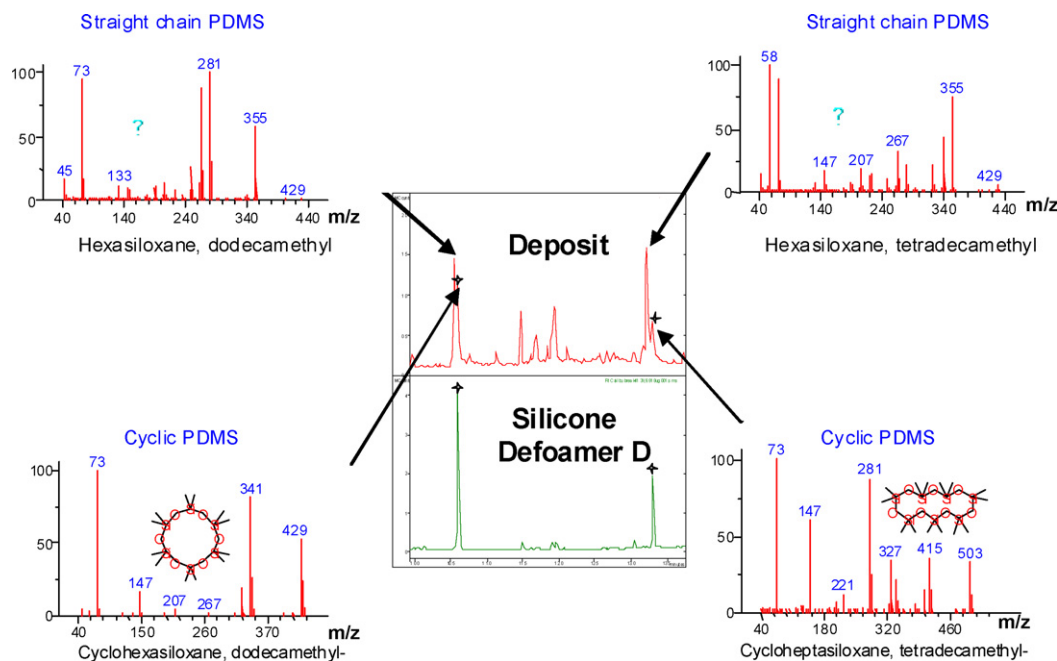


Fig. 8. Mass spectral identification of silicone oil fragments in a pitch deposit sample.

added to the pyrolyser. Consequently, direct analysis of deposits is preferable as this saves time and effort.

The presence of silicone oil defoamer in the different fractions of the deposit is illustrated in Fig. 5.

3.4. Deposit 2

The pyrogram of a kraft mill brownstock deposit sample (Fig. 6) shows that the deposit contains both silicone and hydrocarbon oils, but the silicone oil is present at lower concentration than the hydrocarbon oil. There is no evidence for the presence of high molecular weight silicone oils in the deposit. The average amount of silicone oil in the deposit (based on Defoamer A used at the mill) was 7.4% which is somewhat higher than the 5.4% value obtained with the SPE method.

3.5. Deposit 3

A deposit from a newsprint mill was pyrolysed to examine its silicone fragments. As shown in Fig. 7A, similar silicone components (marked in asterisks) are present in the deposit and in Defoamer D used as a reference in the absence of the defoamer used at the mill. However, as can be seen in the circled area, the deposit sample contains silicone oil components that are not present in the defoamer. An expanded view of this section is shown in Fig. 7B. The mass spectra of the compounds (Fig. 8) show that the defoamer standard contains two silicone components (marked with asterisks) that have a cyclic structure, namely, dodecamethyl cyclohexasiloxane and tetramethyl cycloheptasiloxane, whereas the deposit contains four silicone components, two that are cyclic (as in the defoamer) and two that are straight chains whose mass spectra closely matched with the mass spectra of hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl and heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl. These results further confirm the need to use silicone defoamers used at the mill as standards for quantification.

4. Conclusions

Py-GC/MS is a well-suited technique for analysis and characterization of silicone defoamers on pulp fibres and in mill deposits. The technique is easier and much more rapid than using solvent extraction and solid phase extraction, previously developed for analysis of silicone oil defoamers in deposits. It is applicable to silicone defoamers of all molecular weights and can be used to ascertain the source of a particular defoamer formulation. Application of the technique to a kraft pulp treated with silicone defoamers shows that silicone defoamer oil carryover on pulp fibres can be substantial, depending on the defoamer formulation used. In pitch deposits, the levels of silicone oil can be as high as 25% (w/w). In addition, analysis of deposits from mills using the defoamers shows that silicone defoamers have the potential to cause pitch deposition contrary to claims that the defoamers do not cause such problems.

For quantitative analysis, a defoamer formulation used in the process should be used as standard for quantification of defoamer carryover or defoamer in deposits. In its absence, the results can only be considered as qualitative.

The carry-over of silicone defoamers in pulp fibres may be a cause for concern, especially in environments where there is potential of inhaling pulp fibres in operations where such fibres are processed.

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References

- [1] J. Habermehl, Silicone processing benefits pulp brownstock washing operations, China Pulp Paper Technology, <http://www.dowcorning.com/content/publishedlit/30-1147-01.pdf>, 2005.
- [2] G. Mudaly, Bubreak siloxane technology: the key to profitable pulp-ling, TAPPSA Journal, http://www.tappsa.co.za/archive/Journal_papers/Bubreak_siloxane/bubreak_silo_xane.html, 2002.

- 361 [3] Anonymous, Flofoam defoamers, Technical pamphlet, SNF Floeiger SA, <http://www.snf-group.com/IMG/pdf/Antifoam-FLOFOAM.E.pdf>, 2003. 378
- 362 [4] S.-D. Clas, L.H. Allen, Comparison of the performances of water and oil-based 379
- 363 defoamers, *Pulp and Paper Canada* 95 (1) (1994) 33-36. 380
- 364 [5] B.B. Sithole, D. Filion, Determination of silicone defoamers in mill pitch 381
- 365 deposits, TAPPSA Journal, [http://www.tappsa.co.za/archive2/APPW_2004/](http://www.tappsa.co.za/archive2/APPW_2004/Title2004/Determination_of_silic_one_defo/determination_of_silicone_defo.html) 382
- 366 [Title2004/Determination_of_silic_one_defo/determination_of_silicone_defo.html](http://www.tappsa.co.za/archive2/APPW_2004/Title2004/Determination_of_silic_one_defo/determination_of_silicone_defo.html), 2004. 383
- 367 [6] Norden, Siloxanes in the Nordic Environment, TemaNord 2005:593, 384
- 368 Nordic Council of Ministers, Copenhagen, Available at <http://www.norden.org/pub/miljo/miljo/uk/TN2005593.pdf>, 2005. 385
- 369 [7] D. Muir, P.H. Howard, W. Meylan, Identification of new, possible PB&T sub- 386
- 370 stances important in the Great Lakes region by screening of chemicals in 387
- 371 commerce, <http://www.epa.gov/glnpo/p2/PBTRreport.pdf>, 2007. 388
- 372 [8] K.R. Drottar, R.L. Jezowski, D.A. McNett, J.M. Regan, J.Y. Domoradzki, K.P. Plotzke, 389
- 373 14C-Decamethylcyclopentasiloxane (14C-D5): dietary bioaccumulation in the 390
- 374 rainbow trout (*Oncorhynchus mykiss*) under flow-through test conditions, in: 391
- 375 Presented at SETAC Europe, Porto, Portugal, 2007. 392
- 376 [9] E.G. Gooch, Determination of traces of silicone defoamer in fruit juices by sol- 393
- 377 vent extraction/atomic absorption spectroscopy, *Journal of AOAC International* 394
- 76 (3) (1993) 581-583. 395
- [10] J.J. Kennan, L.L. Breen, T.H. Lane, R.B. Taylor, Methods for detecting silicones in biological matrices, *Analytical Chemistry* 71 (15) (1999) 3054-3060.
- [11] M. Costello, Just how do you determine the appropriate level of silicone addition for tissue substrates? *Tissue World* (April/May) (2006) 32-35.
- [12] M. Aramata, K. Saitoh, A new analytical method for silicone determination in the environment by pyrolysis/GC-AED, *American Laboratory* 29 (15) (1997) 19.
- [13] J.C. del Rio, R.P. Phil, J. Allen, Nature and geochemistry of high molecular weight hydrocarbons (above C40) in oils and solid bitumens, *Organic Geochemistry* 18 (4) (1992) 541-553.
- [14] C. Ovalles, P. Rengel-Unda, J. Bruzual, A. Salazar, Upgrading of extra heavy crude using hydrogen donor under steam injection conditions. Characterization by Pyrolysis GC-MS of the asphaltenes and effects of a radical initiator, *Fuel Chemistry Division Preprints* 48 (1) (2003) 60-61.