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# Thermal decomposition of frothing agents adsorbed onto activated carbon

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## Abstract

The thermal decomposition of four frothing agents used in the flotation of gold bearing sulfide minerals was investigated, both alone and when adsorbed on activated carbon. Thermal desorption-pyrolysis-gas chromatography-mass spectrometry (TD-py-GC-MS) was used to determine the gases evolved from the thermal decomposition. Thermogravimetry (TG), coupled to either a mass spectrometer (MS) or a Fourier transform infrared (FTIR) spectroscope, was used to determine the temperature range of decomposition as well as confirm the gaseous products. Three of the frothing agents, polypropylene glycol (PPG), the closely related polypropylene glycol methyl ether (PPGME), and methyl *iso*-butyl carbinol (MiBC), boiled off unchanged when heated. α-terpineol decomposed by about 20%, of which the major compound was the dehydration product, limonene. When adsorbed on activated carbon and heated, PPG, PPGME and α-terpineol all produced a complex range of gases, which included propanal, 2-ethyl-4-methyl-1,3-dixolane, 3,3-oxybis-2-butanol and dioxanes. MiBC again just boiled off the carbon without appreciable alteration. Since the frothing agents all decomposed below 400°C, the usual process temperature of 650°C for the regeneration of activated carbon should be sufficient to remove any adsorbed frothing agent, although for PPG and PPGME there was evidence that not all the decomposition products were volatile. In addition, the evolved gas profile was very characteristic of the adsorbed frothing agents, and should permit identification of any contamination present on unknown plant samples.

*Keywords:* Activated carbon; Evolved gas analysis; Frothing agents; Fouling

## 1. Introduction

Activated carbon is widely used for the adsorption of aqueous gold cyanide complexes during the recovery of gold from concentrates. One of the disadvantages of activated carbon is its lack of selectivity. The carbon will adsorb, with various degrees of efficiency, most of the dissolved inorganic or organic compounds present in the leach solution. Thus, some of the active sites are occupied by unwanted compounds, and the quantity of gold that can be adsorbed is diminished. Even when the gold has been dissolved from the carbon by alkaline cyanide solution, the other adsorbents remain on the carbon, and its activity towards gold is diminished. Such carbons are said to be fouled. Recycling of the activated carbon is required due to its high cost. There are two stages to the regeneration step: acid washing to remove inorganic contaminants,

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and thermal reactivation at around 650°C to remove volatile or unstable organic impurities.

It is the organic fouling agents that are of a greater concern in plant circuits, since these cause the largest decrease in activity of the carbon. Organic compounds (oils, greases, process chemicals) are present in most carbon in pulp or carbon in leach (CIP/CIL) circuits as a result of their addition or spillage during mining, milling, flotation, and equipment maintenance operations. The effect of frothing agents, amongst other fouling agents, on the activity of carbon has been previously reported [1–3]. The frothing agents studied were of the polyoxyethylene/propylene glycol ether type (Teric frothing agents) and methyl *iso*-butyl carbinol (MiBC). The polyoxyethylene/propylene glycol ether frothing agent had a serious effect on carbon activity, and reduced the activity by a factor of 5, relative to a control sample. On the other hand, MiBC reduced the activity by a factor of 2.5, and hence is not such a serious fouling agent.

In the current study, the thermal properties of four common frothing agents, namely, polypropylene glycol (PPG) (Fig. 1a); the closely related polypropylene glycol methyl ether (PPGME) (Fig. 1b); pine oil, of which the important component is α-terpineol (Fig. 1c); and MiBC (Fig. 1d), were investigated. The results of the thermal decomposition of the four frothing agents alone and adsorbed on activated carbon are described. Studies were performed using three techniques: thermal desorption-pyrolysis-gas chromatography-mass spectrometry (TD-py-GC-MS); thermogravimetry-mass spectrometry (TG-MS); and thermogravimetry-Fourier transform infrared (FTIR) spectroscopy.

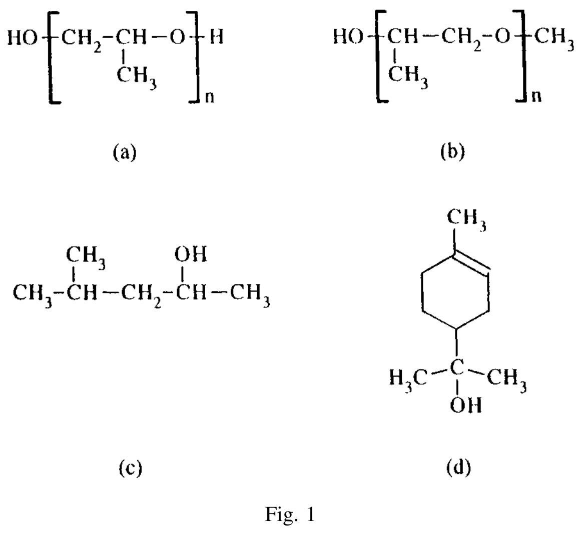

Fig. 1

## 2. Experimental

A commercial activated carbon derived from coconut fibre, trade name Haycarb, was obtained from the Chemistry Centre of Western Australia. The Haycarb was conditioned before use, using the method described by Ruane et al. [4]. Briefly, this consisted of soaking 100 g of activated carbon in HCl (200 ml, 5%) for 30 min in a wide mouth plastic bottle, bottle rolling for 24 h, decanting any fine carbon, and washing twice with deionised (DI) water. The carbon was then soaked twice for 1 h each in DI water (200 ml). Finally, the carbon was filtered and dried for 16 h at 120°C. The conditioning procedure approximates plant treatment of activated carbon and ensures no fouling agents were present on the Haycarb.

The AR grade frothing agents obtained from Acros were PPG, average molecular weight 425, catalog number 19215-5000; α-terpineol, 98%, mixture of isomers, catalog number 42005-5000; and 4-methyl-2-pentanol (MiBC), ≥99%, catalog number 14938-0025. PPGME was obtained from Hoechst chemicals.

The pre-treated carbon was ground by hand to <45 μm, and contacted with a solution of frothing agent. The solution/carbon ratios used were: PPG and PPGME, 100 ml of solution of 80 g $l^{-1}$ reagent, 10 g of Haycarb; α-terpineol, 100 ml of 1:1 ethanol:water solution of 50 g $l^{-1}$ reagent, 0.5 g of Haycarb; MiBC, 400 ml of 1.25 g $l^{-1}$ reagent, 0.5 g of Haycarb. The beakers were placed in a water bath set at 20°C and the solutions stirred. After 24 h the carbon was separated by filtration and stored under vacuum in a desiccator containing silica gel until required for analysis.

The liquid from the filtration was analysed for residual frothing agent by various analytical techniques, thus permitting the amount of frothing agent adsorbed to be calculated. The quantities adsorbed were 29.8, 30.9, 16.9, and 14.1% for PPG, PPGME, α-terpineol and MiBC, respectively.

TD-py-GC-MS of the samples was performed using a Geofina hydrocarbon meter (GHM) furnace. The frothing agents were coated onto sodium sulfate, approximately 10% w/w, or adsorbed on Haycarb, and heated from 150–500°C at 25°C $\text{min}^{-1}$, with a final hold time of 5 min at 500°C. The volatile products from the thermal desorption pyrolyser were cryogenically focussed onto a capillary column by immersing a loop (approximately 10 cm long) into liquid nitrogen. Separation of the volatile components was achieved by removing the liquid nitrogen trap and injecting onto a Hewlett Packard 5809 (series I) gas chromatograph fitted with a Hewlett Packard, HP-5ms, 30 m × 0.25 mm i.d. × 0.25 μm phase thickness. Helium was used as both pyrolysis and carrier gas (linear velocity 60 cm $\text{s}^{-1}$), and injections were split approximately 90:1. The oven was programmed from 40 to 280°C at 6°C $\text{min}^{-1}$ where it was held isothermally for 15 min. Eluting compounds were monitored by a Hewlett-Packard 5970 mass selective detector in the electron impact (EI) mode. Typical mass spectrometer operating conditions were electron multiplier voltage 2350 V, emission current 220 μA, electron energy 70 eV and source temperature 220°C.

Thermal analysis experiments were performed using a Netzsch STA-409 simultaneous TG-DTA apparatus. 10 mg samples were heated at 10°C $\text{min}^{-1}$ in an alumina crucible (6 mm internal diameter and 4 mm in depth) in an argon atmosphere flowing at 60 ml $\text{min}^{-1}$. The evolved gases were carried by a transfer line heated to 200°C to either a Balzers thermostar quadrupole mass spectrometer, or to a Bruker IFS 55 FTIR spectrometer fitted with a MCT (Hg–Cd–Te) detector.

The MS data was usually recorded in the selective ion monitoring (SIM) mode, which enabled the evolution of a specific amu value to be followed as a function of temperature. The FTIR data was recorded in the Gram Schmidt (GS) mode, which showed infrared activity for all gases between 4000 to 650 $\text{cm}^{-1}$ as a function of time (and hence temperature), as well as recording the spectrum of the evolved gases at a specific temperature.

## 3. Results and discussion

### 3.1. Thermal behaviour of the frothing agents

The first measurements were made using TD-py-GC-MS, since this technique enabled the unambiguous identification of evolved gases. The total ion chromatogram for the pyrolysis of PPG shown in Fig. 2 has an initial carbon dioxide peak followed by a series of peaks that differ by a constant atomic mass. These peaks appear to be due to differing chain length (where *n* equals the number of repeating monomer units), and therefore molecular weight, boiling off from the isomeric mixture. The molecular weights of PPG detected were 134, 192, 250, 308, 366, 424, 482, 540, and 598 g $\text{mol}^{-1}$ for $n$ equal to 2–10, respectively. The ion chromatogram for PPGME was very similar, with molecular weights of 148, 206, 264, 322, 380, 438, and 496 g $\text{mol}^{-1}$ for $n = 2$–8, respectively. The relative peak area (%) of each peak was multiplied by its molecular weight, and then this sum was averaged for all the peaks. An average molecular weight of 390 g $\text{mol}^{-1}$ was calculated for PPG, and 292 g $\text{mol}^{-1}$ PPGME. Although the result for PPG is

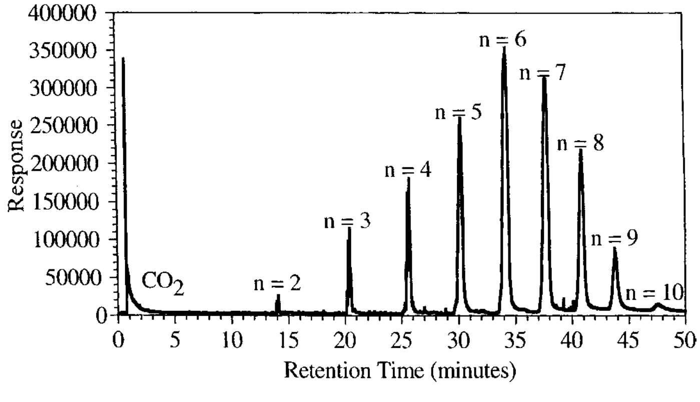

Fig. 2

Table 1
Pyrolysis gases of α-terpineol heated from 150–500°C at 25°C min$^{-1}$ in an inert atmosphere

| RT (min) | Relative peak area (%) | Gas evolved |
|---|---|---|
| 7.17 | 1.84 | α-Terpinene |
| 7.36 | 1.75 | σ-*iso*-Propyltoluene |
| 7.45 | 9.37 | Limonene |
| 8.19 | 0.98 | 3-Carene |
| 8.90 | 3.37 | *iso*-Terpinolene |
| 11.44 | 80.8 | α-Terpineol |
| 11.59 | 1.91 | α-Terpinyl acetate |

Table 2
Mass losses and corresponding temperature ranges of PPG, PPGME, α-terpineol, and MiBC heated at 10°C min$^{-1}$ in an argon atmosphere

| | Frothing agent | | | |
|---|---|---|---|---|
| | PPG | PPGME | α-Terpineol | MiBC |
| Mass loss (%) | 94.6 | 94.9 | 96.7 | 36.6 |
| Temperature (°C) | 249–338 | 144–292 | 171–198 | 85–112 |

close to the expected value of 425 g mol$^{-1}$, it is slightly lower indicating that some minor thermal degradation of the PPG may have occurred. This possibility has been previously reported [5]. The manufacturers given value for PPGME is actually 250, which is lower than the experimentally determined value. Degradation is thus unlikely to have taken place.

In the total ion chromatogram (TIC) of the α-terpineol pyrolysis seven peaks were detected. The identity, retention time, and relative peak area of the gases evolved is presented in Table 1. The main gas evolved was α-terpineol along with some limonene (the dehydration product of α-terpineol). Other gases of structure similar to α-terpineol also evolved in minor quantities. The total ion chromatogram from the TD-py-GC-MS analysis of MiBC displayed only one peak due to the evolution of MiBC, indicating that this compound boils off without change. Hence, of the four frothing agents examined, three boiled off apparently unchanged. Pine oil was the only compound that showed any thermal degradation on heating, consisting of 10% degradation due to dehydration of the parent compound, and another 10% from some other minor decomposition compounds.

The thermal decomposition of the four frothing agents were each studied by TG-EGA, at a heating rate of 10°C min$^{-1}$ under an argon atmosphere. The evolved gases were analysed by MS and FTIR spectroscopy. The TG curve of each frothing agent consisted of one broad mass loss. The mass losses and their corresponding extrapolated onset/offset temperatures are presented in Table 2. The maximum rate of mass loss for PPG, PPGME, and α-terpineol occurred at 315, 226, and 171°C, respectively. All the frothing agents contained no residue in the sample crucible after analysis, indicating all had boiled off. The low percentage of MiBC and the actual TG curve show that it commenced evaporation before the analysis had started. The TG curve of the PPG, together with the GS curve (obtained from the FTIR analysis) and the SIM (obtained from the MS data) are shown in Fig. 3. It demonstrates that the evolved gas emission

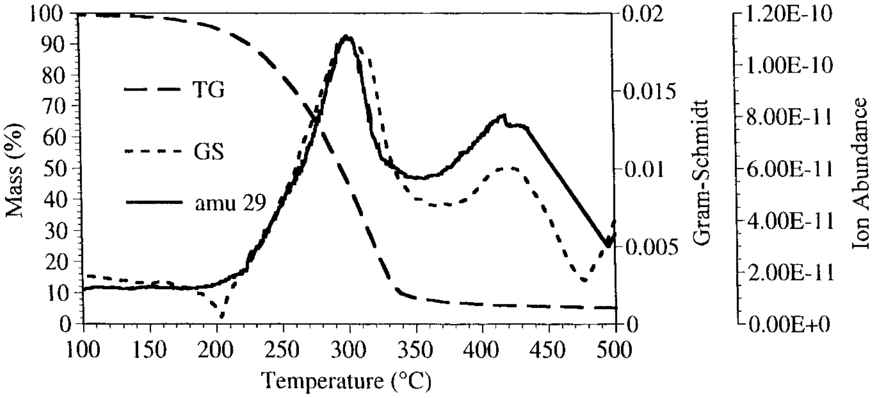

Fig. 3

extended beyond the temperature range of the mass loss, and so gave two peaks in the GS and SIM curves. All the other evolved PPG products displayed similar curves as amu 29 and are not shown here. These observations could be explained by the volatile material condensing in the MS transfer line, where they would evolve as a function of time, not temperature. This could not be avoided, as the transfer line was operated at the maximum temperature of 200°C, and this was clearly insufficient to volatilise the higher molecular weight components. The infrared spectrum of the gases evolved from the mass loss displayed all the characteristic peaks of the PPG in the liquid state. The behaviour of the other three frothing agents was similar, with the FTIR spectrum dominated by bands typical of the volatilised starting compound.

### *3.2. Thermal behaviour of the frothing agents adsorbed on activated carbon*

TD-py-GC-MS was used to identify the gases evolved from each frothing agent adsorbed on activated carbon when heated in an inert atmosphere from ambient to 1000°C. Each pyrolysis experiment produced numerous gases, and for simplicity gases with a peak area less than 10% of the largest peak were excluded from the study. The remaining gases were identified using a mass spectra database and manual interpretation. The gases produced for each pyrolysis, along with their retention time and relative peak area (%), are presented in Table 3. For PPG, propanal had the largest relative peak area, followed by 3-ethoxy pentane, 3,3-oxybis-2-butanol, and PPG ($n = 2$–8). The volatile components from the PPG were identified by comparison to the non-adsorbed PPG TIC. For PPGME, 3,3-oxybis-2-butanol had the largest relative peak area, followed by dipropylene glycol, PPGME ($n = 4$), propanal, and 2-methyl-2-pentenal. The PPGME volatile compounds were identified by comparison to the non-adsorbed PPGME total ion chromatogram, and the dipropylene glycol was identified by comparison to the adsorbed PPG total ion chromatogram. For α-terpineol, 3,3-oxybis-2-butanol had the largest relative peak area, followed by propanal, and 2-ethyl-4-methyl-1,3-dioxolane. Finally, for MiBC, the most abundant gas evolved was unchanged MiBC, and all other gases were minor in comparison.

For the TG analysis, a blank experiment was conducted which involved heating the pre-conditioned carbon from ambient temperature to 1000°C without adsorbed frothing agent. A mass loss of 1.4% was observed from 25–520°C, and a second mass loss of 4.5% occurred above 520°C. TD-py-GC-MS showed that the evolved gases up to 520°C were water vapour, CO and $CO_2$. The latter two gases may have arisen from the decomposition of surface species such as carboxyl groups. The gases evolved above 520°C were CO, $CO_2$ and $H_2$, which were probably formed from the reaction of residual water vapour with the carbon.

The TG curves along with their GS and MS curves for the four frothing agents adsorbed on activated carbon are presented in Figs. 4–7. The TG curves showed three mass losses, two of which were associated with the properties of the carbon as indicated by the blank experiment. One of the mass losses, in the temperature range 200–400°C, was due to the adsorbed frothing agent. The mass losses and their extrapolated onset/offset temperatures for each sample are presented in Table 4. For PPGME, α-terpineol and MiBC, the mass loss occurred some 100°C higher than for the frothing agents alone, and indicated that the adsorption process had delayed the evolution of the volatile material. This may be due to the molecules being trapped in the internal pore structure of the carbon, thus delaying the diffusion process to the surface, or to a significant interaction between the active sites on the surface of the carbon and the molecule.

The amount of frothing agent adsorbed on the carbon is given in Table 5, based on the analytical data described in the experimental section, together with the actual mass loss observed adjusted for the 1.4% mass loss determined in the blank experiment. It can be seen that for PPG and PPGME the observed mass loss is some 5–6% less than might be expected if all the adsorbed frothing agent had completely decomposed to volatile components. This suggests that some of these frothing agents had formed non-volatile products, which were therefore retained on the carbon. This might explain why the activity of regenerated used carbon never manages to regain the full activity of a new carbon. There is less of a problem with MiBC, with only a 0.7% difference between the observed and expected mass loss value, and for α-terpineol the value observed is slightly higher than expected indicating

Table 3
Gases evolved from the pyrolysis of PPG, PPGME, α-terpineol, and MiBC adsorbed on activated carbon

| Peak | RT (min) | Relative peak areas (%) | Gas evolved |
|---|---|---|---|
| PPG-AC | | | |
| 1 | 1.07 | 18.3 | Propanal |
| 2 | 2.67 | 12.2 | 3-Ethoxy pentane |
| 3 | 3.23 | 6.18 | Pentane |
| 4 | 3.82 | 2.77 | Di-*iso*-propyl ether |
| 5 | 7.24–9.05 | 11.9 | 3,3-Oxybis-2-butanol |
| 6 | 13.8–14.9 | 6.94 | PPG ($n = 2$) |
| 7 | 19.7–21.0 | 6.31 | PPG ($n = 3$) |
| 8 | 24.0–26.3 | 9.00 | PPG ($n = 4$) |
| 9 | 29.5–30.7 | 6.13 | PPG ($n = 5$) |
| 10 | 33.4–34.8 | 8.61 | PPG ($n = 6$) |
| 11 | 37.0–38.3 | 8.85 | PPG ($n = 7$) |
| 12 | 40.3–41.4 | 2.78 | PPG ($n = 8$) |
| PPGME-AC | | | |
| 1 | 1.04 | 8.87 | Propanal |
| 2 | 2.75 | 5.95 | 2-Ethyl-4-methyl-1,3-dioxolane |
| 3 | 2.87 | 4.74 | Dimethyl-1,4-dioxane |
| 4 | 3.03 | 4.58 | 2,5-Dimethyl-1,4-dioxane |
| 5 | 3.26 | 3.78 | 2,5- and 2,6-dimethyl dioxene |
| 6 | 3.56 | 8.59 | 2-Methyl-2-pentenal |
| 7 | 4.05 | 2.75 | 2-*iso*-Propoxy-1-propanol |
| 8 | 4.84 | 1.80 | 2-Methyl-2-cyclopenten-1-one |
| 9 | 7.52–9.50 | 22.6 | 3,3-Oxybis-2-butanol |
| 10 | 13.84–14.24 | 2.99 | PPGME ($n = 3$) |
| 11 | 14.40–15.25 | 14.52 | Dipropylene glycol |
| 12 | 19.92–21.04 | 12.9 | PPGME ($n = 4$) |
| 13 | 24.99–26.02 | 5.93 | PPGME ($n = 5$) |
| α-Terpineol-AC | | | |
| 1 | 0.94 | 2.10 | Propene |
| 2 | 1.23 | 15.0 | Propanal |
| 3 | 1.40 | 3.56 | Propanol |
| 4 | 2.62 | 3.77 | Toluene |
| 5 | 2.87 | 9.46 | 2-Ethyl-4-methyl-1,3-dioxolane |
| 6 | 3.00 | 7.61 | Isomer of above peak |
| 7 | 3.14 | 6.61 | 2,5-Dimethyl-1,4-dioxane |
| 8 | 3.37 | 5.13 | 2,5- and 2,6-dimethyl dioxane |
| 9 | 3.53 | 3.46 | *Trans*-2,6-dimethyl-*p*-dioxane |
| 10 | 3.61 | 5.60 | 2-Methyl-2-pentanal |
| 11 | 4.07 | 2.84 | Di-*iso*-propyl ether |
| 12 | 4.89 | 2.50 | 2-Methyl-2-cyclopenten-1-one |
| 13 | 7.67–8.93 | 27.8 | 3,3-Oxybis-2-butanol |
| 14 | 14.45–14.96 | 4.84 | Dipropylene glycol |
| MiBC-AC | | | |
| 1 | 1.23 | 2.48 | 4-Methyl-1-pentene |
| 2 | 1.28 | 3.37 | 2,3-Dimethyl-1-butene |
| 3 | 2.37 | 5.09 | 4-Methyl-2-pentanone |
| 4 | 3.11 | 87.6 | MiBC |
| 5 | 3.51 | 1.42 | 2-Hexanol |

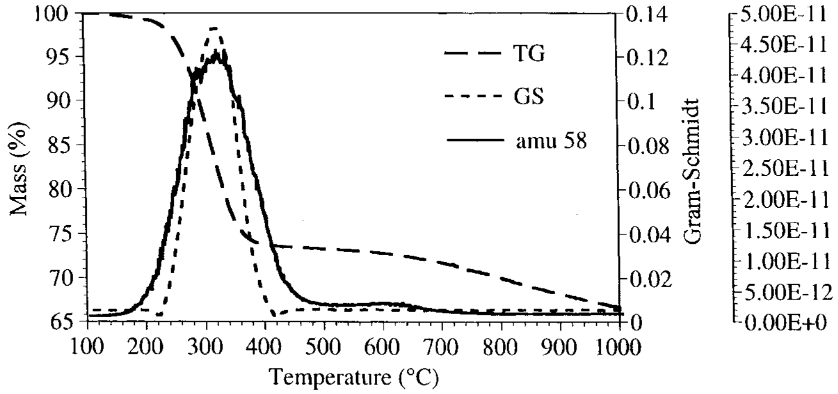

Fig. 4

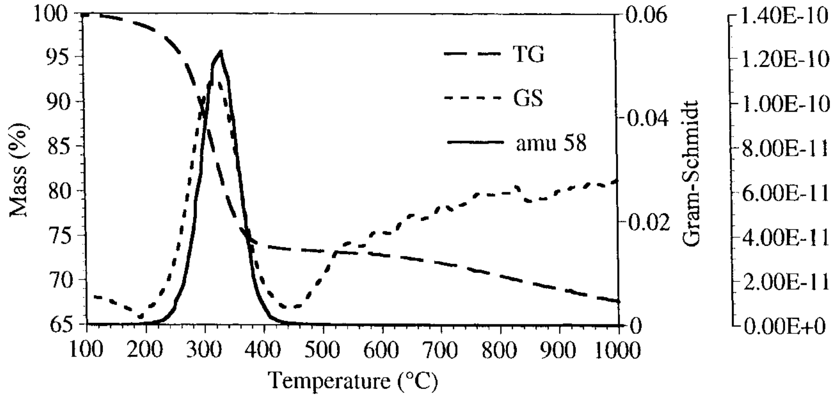

Fig. 5

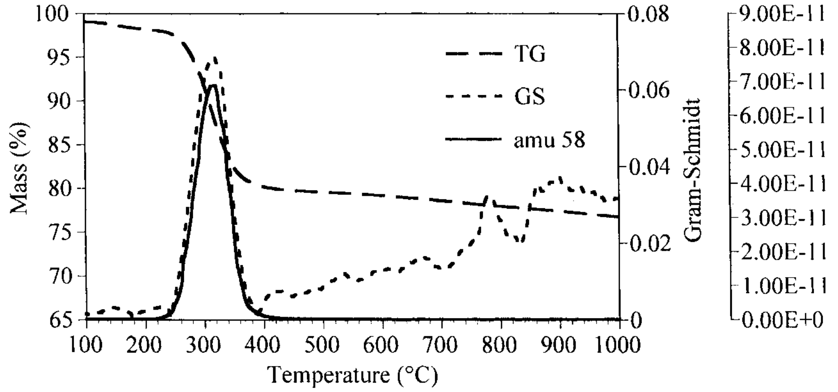

Fig. 6

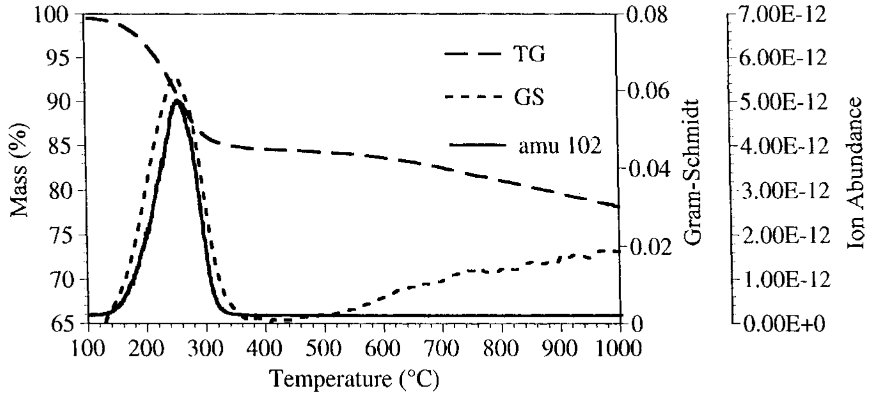

Fig. 7

that all the products are gaseous and have been evolved.

The gases evolved from each frothing agent adsorbed on activated carbon were studied by SIM from ambient to 1000°C in argon atmospheres. The gases evolved were monitored via their molecular ions, which had been previously identified by the TD-py-GC-MS analyses. Qualitative analysis was only possible due to interfering fragment ions and/or isotope ions.

All the ions monitored in the SIM analyses of PPG, PPGME, and α-terpineol displayed the same curve, that is one broad peak, coinciding with the TG curve. In Figs. 5–7 are shown the chromatograms for amu 58, which also is the molecular ion for propanal. In Fig. 8 is shown the SIM analysis of MiBC, in which the monitored amu is 102, which is the molecular ion for MiBC.

Table 4
Mass losses and their temperatures for PPG, PPGME, α-terpineol, and MiBC adsorbed on Haycarb

| | Frothing agent | | | |
|---|---|---|---|---|
| | PPG | PPGME | α-Terpineol | MiBC |
| Mass loss (%) | 25.9 | 24.4 | 18.6 | 14.8 |
| Temperature (°C) | 258–351 | 255–363 | 275–357 | 186–311 |

Table 5
Experimental versus theoretical mass losses for PPG, PPGME, α-terpineol, and MiBC adsorbed onto Haycarb

| | PPG | PPGME | α-Terpineol | MiBC |
|---|---|---|---|---|
| Experimental | 24.5 | 23.0 | 17.2 | 13.4 |
| Theoretical | 29.8 | 30.9 | 16.9 | 14.1 |

Table 6 gives the relative peak area of the gases evolved from each SIM analysis. The relative peak area of each gas evolved has been expressed as a percentage. That is, the ion abundance (in amps per degree Celsius) of each gas was divided by the sum of the ion abundances for both mass losses. Therefore a semi-quantitative analysis of each gas can be compared between the mass losses. A number of gases detected in the TD-py-GC-MS analyses were not detected in the TG-MS analyses. For the PPG analysis these were the PPG gases ($n = 4$–8); for PPGME these were 2-*iso*-propoxy-1-propanol, 3,3-oxybis-2-butanol, PPGME ($n = 3$–5), and dipropylene glycol; and for α-terpineol these were 2-methyl-2-pentanal, di-*iso*-propyl ether, 3,3-oxybis-2-butanol, and dipropylene glycol. The lack of detection of these compounds is probably due to their condensation in the transfer tube between the TG and MS, as observed in the analysis of the frothing agents alone.

The component in the evolved gas stream with the largest relative peak area for the decomposition of PPG and PPGME was propanal, and all other peak areas were small by comparison. The gases with the largest relative peak areas for the decomposition of α-terpineol were propene and propanal, and any other detected gases were small by comparison. In the MiBC analysis, 4-methyl-1-pentene and 2,3-dimethyl-1-butene had the largest relative peak area (these

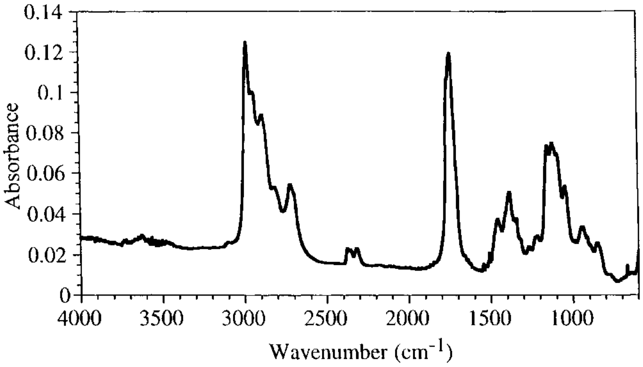

Fig. 8

Table 6
Estimated ion abundance of the evolved gases from the PPG, PPGME, α-terpineol, and MiBC SIM analyses heated at 10 °C min$^{-1}$ in an argon atmosphere

| Amu | Abundance (%) | Gas |
|---|---|---|
| PPG | | |
| 58 | 88.4 | Propanal |
| 72 | 6.61 | Pentane |
| 102 | 0.85 | Di-*iso*-propyl ether |
| 116 | 2.00 | 3-Ethoxy pentane |
| 134 | 0.74 | PPG ($n = 2$) |
| 162 | 0.67 | 3,3-Oxybis-2-butanol |
| 192 | 0.72 | PPG ($n = 3$) |
| PPGME | | |
| 58 | 93.7 | Propanal |
| 96 | 1.80 | 2-Methyl-2-cyclopenten-1-one |
| 98 | 1.22 | 2-Methyl-2-pentenal |
| 114 | 1.34 | 2,5- and 2,6-dimethyl dioxene |
| 116 | 1.91 | 2-Ethyl-4-methyl-1,3-dioxolane<br>Dimethyl-1,4-dioxane<br>2,5-Dimethyl-1,4-dioxane |
| α-Terpineol | | |
| 42 | 46.3 | Propene |
| 58 | 43.1 | Propanal |
| 60 | 6.32 | Propanol |
| 92 | 2.13 | Toluene |
| 96 | 0.70 | 2-Methyl-2-cyclopenten-1-one |
| 114 | 0.51 | 2,5- and 2,6-dimethyl dioxane |
| 116 | 0.87 | 2-Ethyl-4-methyl-1,3-dioxolane<br>2,5-Dimethyl-1,4-dioxane<br>*Trans*-2,6-dimethyl-*p*-dioxane |
| MiBC | | |
| 84 | 78.4 | 4-Methyl-1-pentene-2,3-dimethyl-1-butene |
| 100 | 12.6 | 4-Methyl-2-pentanone |
| 102 | 9.06 | MiBC<br>2-Hexanol |

gases have the same molecular weight and thus do not have separate ion signals). However, it should be noted that the high ion abundance of any of the ions monitored by the MS may also be due to the detection of ions from the fragmentation of higher molecular weight gases

The GS chromatogram shown in Fig. 4 is very similar to the MS ion chromatogram displayed in the same figure, and both coincide with the TG curve.

The infrared spectrum of the mass loss is presented in Fig. 8. The spectrum shows all the characteristic peaks of PPG plus significant peaks at 2816, 2721 and around 1750 cm$^{-1}$. The peaks at 2816 and 2721 cm$^{-1}$ are very characteristic stretching vibrations of the aldehydic C–H contained in aldehydes. The large peak around 1750 cm$^{-1}$ is very characteristic of carbonyl stretching. Similar comments can be made about the FTIR spectra of the other three frothing agents. In general, the FTIR technique was only capable of detecting characteristic bands of the unchanged evolved frothing agent, and not all that useful for detecting any of the other numerous gases that were evolved.

## 4. Conclusions

The evidence presented here indicates that the four frothing agents studied displayed one mass loss on heating which for PPG, PPGME and MiBC was associated with being boiled off unchanged. α-terpineol showed some decomposition. When adsorbed on activated carbon, each sample again showed one mass loss associated with the decomposition of the frothing agent, but now there were numerous gases evolved in this one temperature range. Thus the activated carbon had a significant effect on the thermal decomposition of the frothing agents. Although the decomposition temperature increased by 100°C for PPG, PPGME, α-terpineol and MiBC when adsorbed on carbon, the decomposition temperature of below 300°C was still well within the range of decomposition used in regeneration kilns in gold plants. However, there was some PPG and PPGME (and to a lesser extent MiBC) which did not volatilise, suggesting that some residual decomposition product remained on the carbon. This may be one of the reasons why reactivated carbon never regains the activity of a new carbon.

The evolved gas profiles from the decomposing frothing agents adsorbed on carbon were sufficiently distinctive to act as diagnostic probes for the presence of contaminants on plant sample of activated carbon. In practice, it is reasonable to look for the major gases evolved, such as propanal which was formed in the decomposition of PPG, PPGME and α-terpineol. Another dominant gas was 3,3-oxybis-2-butanol, which was evolved from PPGME and α-terpineol. MiBC was the only frothing agent that was not significantly affected by adsorption on carbon, and MiBC was still the major product evolved on heating, and hence the most useful gas for detecting its presence.

Comparison of the three different analytical techniques indicated that the TD-py-GC-MS technique was required for unambiguous gas identification. This was mainly because many gases were evolved in the same temperature range, and so these gases needed to be separated from one another by GC in order to obtain an MS record that could be easily interpreted. The TG-MS technique provided mass loss data and temperature range of gas evolution, and made it possible to monitor (once the identity of the gases had been established by the TD-py-GC-MS technique) the evolved gases as a function of temperature. The TG-FTIR technique did not require data from other techniques, but on the other hand only the major components could be readily identified.

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## References

[1] S.R. La Brooy, J.W. Hosking, D.M. Muir, M. Ruane, I. Smith, W.D. Hinchliffe, Gold-Mining, Metallurgy and Geology, Australasian Institute of Mining and Metallurgy, Melbourne, Australia, 1984, pp. 257–269.

[2] S.R. La Brooy, A.R. Bax, in: Proceedings of the 13th Australian Chemical Engineering Conference, E.A. Books, St. Leonards, Australia, 1985, pp. 187–191.

[3] S.R. La Brooy, A.R. Bax, D.M. Muir, J.W. Hosking, H.C. Hughes, A. Parentich, Gold 100, Vol 2: Extractive metallurgy of gold, South African Institute of Mining and Metallurgy, Johannesburg, 1986, pp. 123–132.

[4] M. Ruane, W.D. Hinchliffe, J.W. Hosking, D.M. Muir, Carbon-in-Pulp Gold Processing Technology (Project No. 10), Western Australian Mining and Petroleum Research Institute, Report No. 2, Perth, Western Australia, 1983.

[5] K. Vo Van, S.L. Malhotra, L.D. Blanchard, (a) J. Appl. Polymer Sci. 18 (1974) 2671; (b) J. Macromol. Sci-Chemistry, A8 (5) (1974) 843.