NPL REPORT DQL-AS 002

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NPL
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Report

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Process Control Benefits of Continuous Monitoring using FTIR Spectroscopy at a Thermal Oxidiser Plant

Hugh Mortimer, Andy Brookes, Richard Camm, Marc Coleman & Rod Robinson

Executive Summary.

A study using on-line FTIR has been performed at a plant manufacturing modified oils that include linseed, castor, soya, and rape. Oxidative modification of these oils results in the release of a variety of VOCs from the aldehyde, carboxylic acid and ketone chemical groups. These species are abated by combustion to CO_2 and H_2O in a thermal oxidiser (TO) which has been routinely operated by the plant at maximum capacity to ensure no breakthrough. An FID is used to confirm this is the case during operation. On-line FTIR monitoring of both the inlet and outlet has enabled both speciation and quantification of the key VOCs. The data demonstrated, as expected, increases in CO_2, CO and H_2O concentrations across the TO, coupled with decreases in the concentrations of identified formic acid, acrolein, methanol and high aldehydes. In addition, it was also confirmed that both formic acid and ethene were produced as by-products of the combustion process. During the monitoring period a number of different oils were processed and the concentrations of the VOCs released were measured by the FTIR on the TO inlet. These measurements demonstrated how a TO maybe run below its maximum capacity without the risk of violation of the IPC licence. Calculations provided by the plant operator have estimated that implementation of such a process control regime could save £50k p.a. in operational costs and furthermore, help extend the lifetime of the current TO unit possibly saving an additional £500k.

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Approved on behalf of the Managing Director, NPL
by Stuart Windsor, Business Leader, Quality of Life Division

Case Study Rationale.

The measurement problem relates to the control of a thermal oxidiser at a plant involved in the manufacture of vegetable oil based products ranging from specialised lubricants to paint bases. The oxidation process causes considerable breakdown and cracking of the complex mixture of compounds in the oil. Typically a mixture of volatile organic compounds (VOC) containing aldehydes, acids and ketones is emitted. The thermal oxidation unit is used to abate these VOC emissions *via.* combustion. However, because the oils manufactured vary in composition the thermal oxidiser is used in such a way that it will cope with the most extreme abatement requirement (*i.e.* it is run at its maximum not optimum state). Operating the oxidiser in this inefficient way causes increased costs due to the increased air use and the reduction in the lifetime of the oxidiser.

The basic concept behind the field trial was to monitor the inlet and the outlet of the thermal oxidiser. On-line, real-time monitoring of the toxic species of importance would provide process information enabling the manufacturer to adjust the operating parameters so that the oxidiser could be optimally set for each oil batch. Consequently, this would yield a financial benefit with the assurance that there would be no increased risk of VOC break through.

It was estimated that the successful implementation of this control could result in the savings below:

- Avoiding replacement oxidiser £500,000
- Operating costs £50,000 per year

Process Description.

The batch reactors are in continuous use and batch times vary from 2-24 hours. The oil modification process involves passing air through the oils under temperature. By-product and decomposition product gases are produced and swept away with the surplus air. These waste products are typical of oil cracking (*e.g.* aldehydes and ketones) and are generally toxic. The range of oils and therefore decomposition gases is very wide, so the gas composition varies significantly.

The Environment Agency have stated that acrolein and formaldehyde are two of the main components that they require quantitative information on. The company has a request to be able to demonstrate best practise by running the unit at minimum temperature compliant with their authorisation. The company also want to identify a robust commercial analytical instrument that can reliably run on-line in the exhaust.

The gaseous emissions from the six reactors on site are combined into the thermal oxidiser inlet together with dilution air to maintain the emission levels below 25% of the lower explosive limit (LEL). This complex mixture of oxidised species is heated to between 600-1000 °C in the presence of air to combust these components to CO_2 and water. Incomplete oxidation sometimes occurs, resulting in a complex mixture of organic species being emitted from the thermal oxidiser unit.

In order to control these emissions the variety and concentration of components in the inlet and outlet streams need to be understood and correlated with the range of products

manufactured on the plant. The outlet from the thermal oxidiser is typically 180 – 250 °C and slightly above atmospheric pressure. The stream also contains significant levels of evolved water and CO_2. Typical conditions are shown in Tables 1 and 2

Inlet	
acrolein	1000-12000 ppm
formic acid	1000-3000 ppm
aldehydes	1000-3000 ppm
hydrocarbons	0-3000 ppm
carbon monoxide	300-500 ppm

Table 1 *Concentration ranges of key species on the inlet of the thermal oxidiser.*

Outlet	
Composition typical of **Inlet** feed- also includes formaldehyde	Varies between 5 - 2000 ppm.

Table 2 *Concentration ranges of key species on the outlet of the thermal oxidiser.*

Theory and Description of Measurements.

The aim of the case study was to provide data that would allow the identification of the minimum effective combustion temperature of the oxidiser for use under standard conditions, and also to identify appropriate parameters for use when key products are being manufactured so that the company can demonstrate compliance with its IPC authorisation.

The oxidiser exhaust gases were monitored using a BOMEM 9100 Fourier transform infrared (FTIR) spectrometer. The spectrometer was fitted with a 6.4m gas cell operated at 120 ^{o}C. A continuous gas sample was extracted from the sample points down a heated line, also heated to 120 °C, to the spectrometer using a Teflon-lined diaphragm pump. Infrared spectra were recorded approximately every 2 minutes at 1 cm^{-1} resolution using CAAP data acquisition software.

The instrument was calibrated using Protea's in-house vaporisation rig. Known volumetric flow rates of gaseous species were mixed into a nitrogen carrier, which passed the gasses through the analyser. Species which were liquid at RTP were vaporised into the matrix by

injection through heated capillaries. Concentrations were varied and calibration curves for the species of interest were calculated.

Prior to operation the FTIR and gas cell were thoroughly purged with dry nitrogen gas and background spectra were recorded. The apparatus used to monitor the oxidiser were configured as shown in Figure 1.

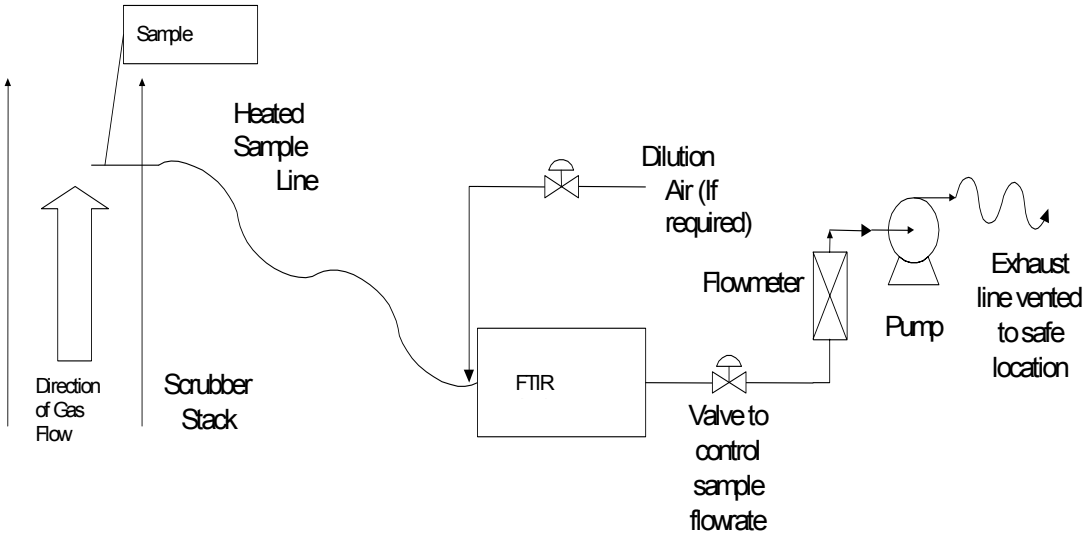


Fig. 1 *Schematic of apparatus configuration employed to monitor the thermal oxidiser.*

The logged spectra were analysed for the detected components using carefully selected spectral bands (Table 3). Detection limits for the analytes varied between 1 and 5 ppm under ideal conditions. The limits were sometimes higher in the presence of high concentrations of interfering analytes.

Inlet components	FTIR band	Exhaust components	FTIR band
Water	1893.00-1886.73	Water	1893.00-1886.73
Carbon Dioxide	2349.13-2285.0	Carbon Dioxide	794.14-789.8
Carbon Monoxide	2101.29-2096.47	Carbon Monoxide	2101.29-2096.47
Formic acid	1108.51-1102.72	Formic acid	1105.58-1102.98
Higher Acids	1190.0-1180.0	Higher acids	1172-1154
Acrolein	964.82-950.84	Formaldehyde	2783.56-2776.33
Methanol	1037.63-1027.02	Aldehydes	2715.78-2690.0
Aldehydes	2761.38-2670.25	Ethylene	953.73-944.34

Table 3 *Spectral bandwidths used for species quantification.*

Total VOC in both the inlet and exhaust was calculated by addition of the individual VOC concentrations. This value was expressed as mg/m^3 of toluene to allow comparison with FID data obtained by the plant during the trial.

Measurements.

The sample line was removed from the process at regular intervals to ensure that a build up of contamination in the line did not occur. On each occasion, the recorded concentrations fell to zero indicating that the line remained clean throughout the monitoring programme. The exhaust vent stack on the thermal oxidiser was monitored continuously over a two-day period during which the oxidation unit was in use. During the monitoring period, site staff varied the operating conditions of the oxidiser, in order to assess how these variations affected the emissions. Bulk gas flow through the thermal oxidiser inlet was measured continuously using Protea's logging flow meter 'ProFlow'. Exhaust flow measurements were obtained using a S-type pitot tube at frequent intervals throughout the monitoring period.

The inlet was monitored continuously over the period 15:24 on 16th April to 14:11 on 26th April 2002. The exhaust of the thermal oxidiser was monitored continuously over the period 17:54 on 15th April to 11:23 on 17th May 2002. Batch details are marked upon the concentration and mass profile charts and are also listed in Appendix 1.

Results.

Preliminary Monitoring.

Prior to the main field trial, a shorter trial was conducted to identify the main components present in the outlet. The results from this detailed that the component gases to be investigated would be CO, aldehydes, acids and VOC's. Component profiles for the preliminary monitoring period are shown below in Figure 2.

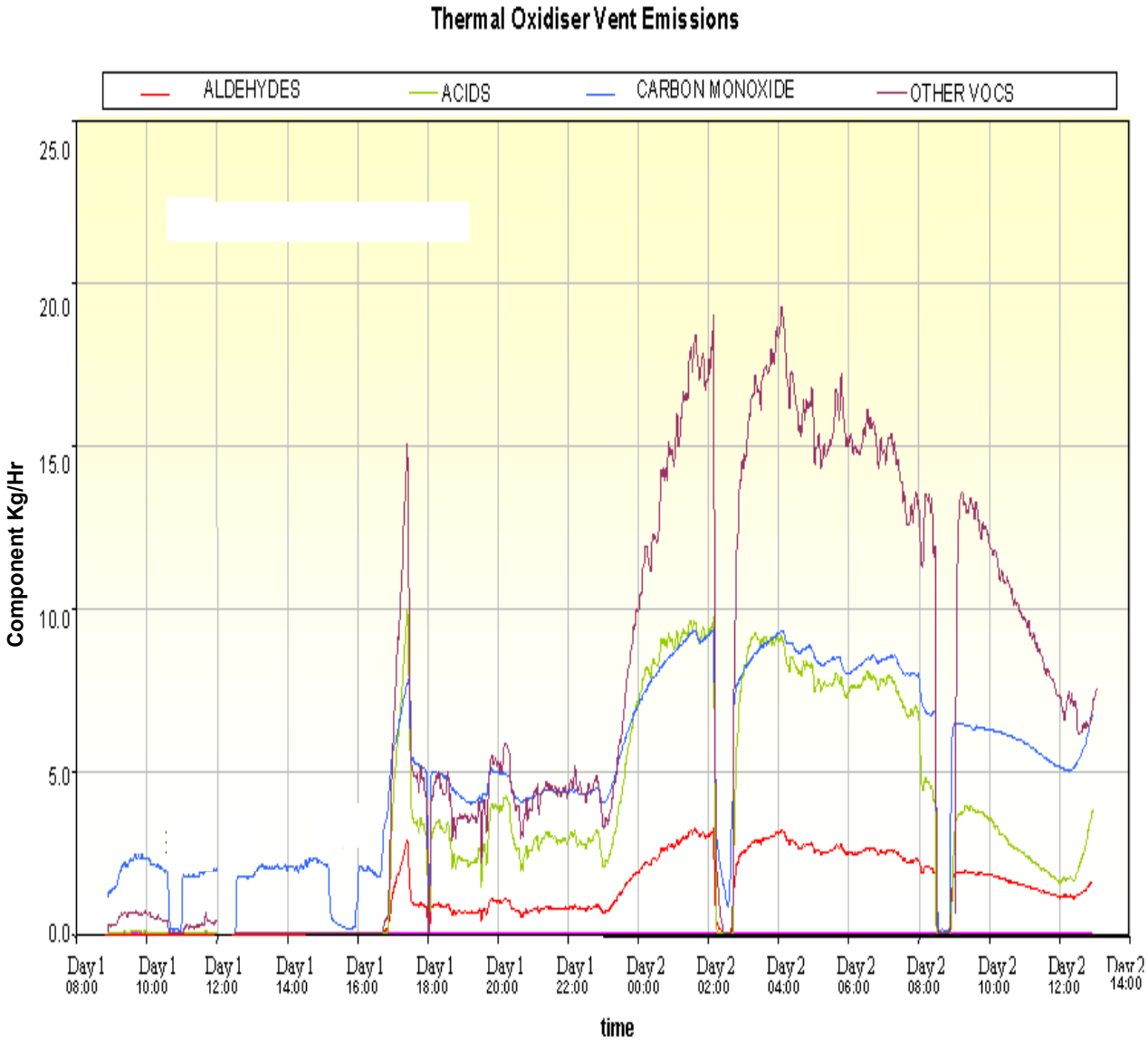


Fig. 2 *Results of the preliminary 2 day monitoring.*

Main Field Trial.

The average inlet flow was 5068Nm3/hr and the maximum was 6474Nm3/hr. Average concentration results for the whole monitoring period are shown in Table 4.

Component	Inlet Average mg/m3	Inlet Average Kg/hr	Outlet Average mg/m3	Outlet Average Kg/Hr
Water	924	4.7	12560	88
Carbon Dioxide	419	2.2	74963	526
Carbon monoxide	146	0.8	180	1.3
Formic acid	716	3.9	21	0.1
Higher acids	8.6	0.05	14	0.1
Formaldehyde	ND	ND	4.9	0.04
Higher aldehydes	201	1.1	4.6	0.03
Acrolein	164	0.9	ND	ND
Methanol	14.8	0.1	ND	ND
Ethylene	ND	ND	10.6	0.1

Table 4 *Average concentration in the inlet and outlet of the thermal oxidiser for total monitoring period.*

Profiles of concentration versus time and mass-flow versus time are shown in Appendix 2. Thermal oxidiser outlet results as total VOC in mg/m^3 of toluene, Kg/Hr Total VOC as toluene and cumulative mass of total VOC as toluene are presented below. Over the complete monitoring period 842kg of VOC expressed as toluene were emitted. The average and maximum emissions (expressed as mg/m^3 of Toluene and also Kg/Hr) over the complete monitoring period are given in the following table.

Component	Outlet Average mg/m3	Outlet maximum mg/m3	Outlet Average Kg/Hr	Outlet maximum Kg/Hr
Total VOC as Toluene	125	2371	0.9	16.6

Table 5 *Average and maximum outlet concentrations of total VOC as Toluene for the total monitoring period.*

The average and maximum emissions (expressed as mg/m^3 of Toluene and also Kg/Hr) calculated only during periods when production was occurring (i.e. excluding weekends and shutdowns) are shown in Table 6.

Component	Outlet Average mg/m3	Outlet maximum mg/m3	Outlet Average Kg/Hr	Outlet maximum Kg/Hr
Total VOC as Toluene	169	2371	1.2	16.6

Table 6 *Average and maximum outlet concentrations of total VOC as Toluene for the total monitoring period.*

Discussion.

Concentrations presented in the results section were calculated by the comparison of spectra recorded in CAAP to laboratory calibration curves. To add validation to these values a modelling algorithm developed at NPL has been used to fit a model to the measured spectrum. Consequently, a modelling concentration is derived which can be directly compared to that determined *via*. the calibration curve constructed by practical means.

The result of using the NPL developed algorithm to fit the model to a raw measured spectrum (recorded at 12:00 on 18/04/02 on the outlet) is shown in Figure 3. Obtaining a perfect fit is quite difficult and this is evidenced partly in the lower wavenumber region. However when the residuals are considered (raw measured – fitted model) it can be seen that these are no greater than the typical noise levels.

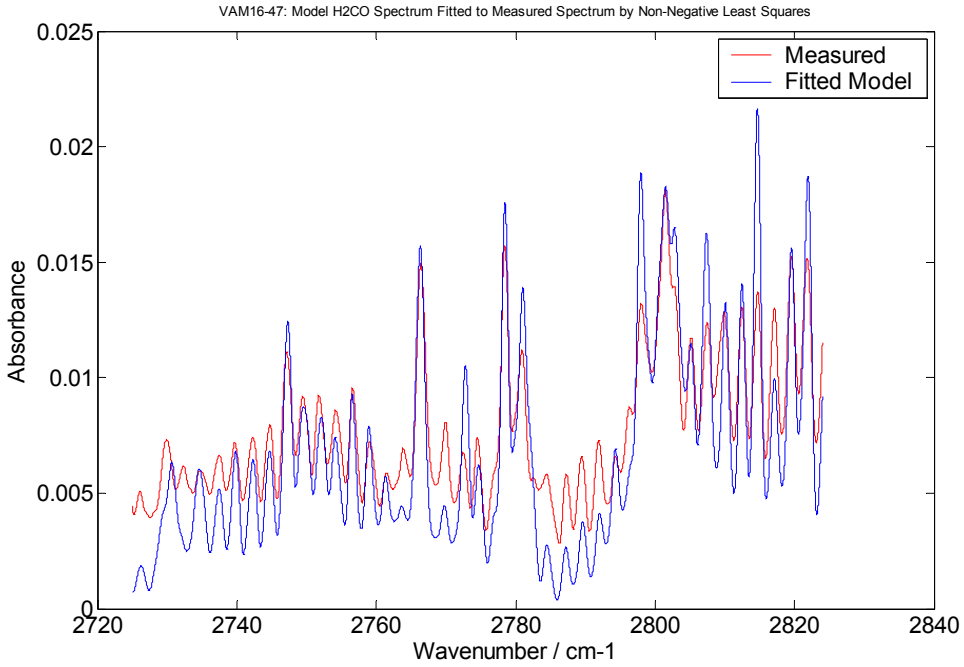


Fig. 3 *Fit of formaldehyde to outlet spectrum recorded at 12:00 on 18/04/02.*

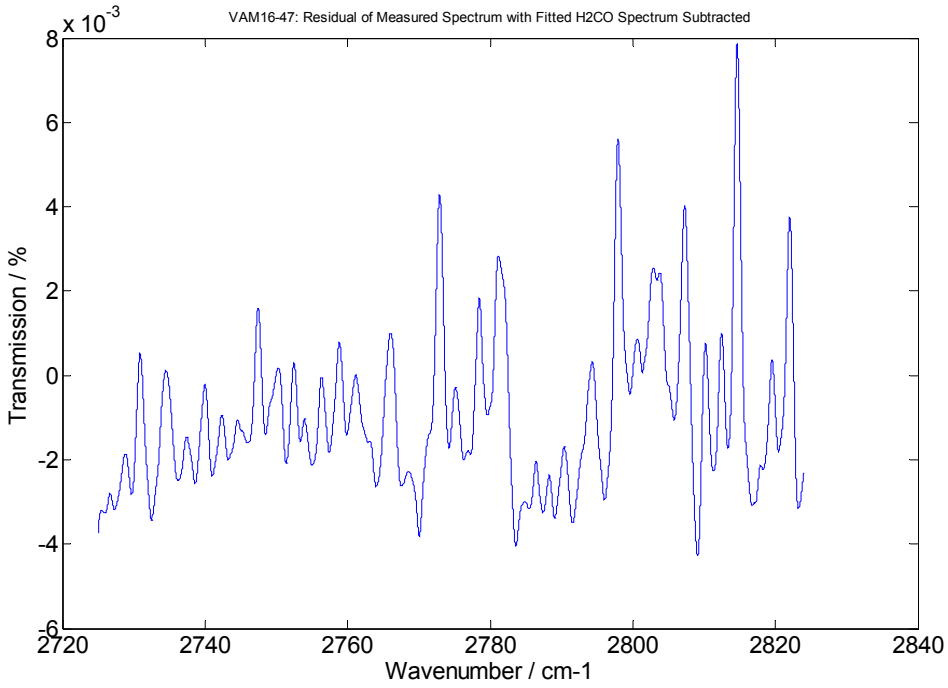


Fig. 4 *Residuals for subtraction of the fitted model from the raw spectrum in Fig. 3.*

The fit models a formaldehyde concentration of 4.9 ppm. Analysing the same raw measurement using the laboratory derived calibration curve yielded a concentration of 9.5 ppm. These values agree within the experimental measurement uncertainties. This is mainly a consequence of the fact that the concentrations are not far above the limit of detection for the instrument employed.

Conclusions.

The inlet and outlet to a thermal oxidiser used to abate VOC emissions, from an oil modification process have been monitored. Important data have been provided to the plant operator to facilitate future optimisation of the thermal oxidiser in terms of an uncertainty of the load caused for each different oil modification process employed on site. Whilst the previously employed in house FID provided real-time on-line data, there was no speciation possible. FTIR has provided speciation information important to the abatement problem and consequently a more efficient use of the thermal oxidiser.

This type of problem is generic and likely to be appropriate across a range of UK industries as thermal oxidisers, widely used as emissions abatement and power generation systems, become regulated under IPC legislation. This type of monitoring offers benefits to large process control companies needing to monitor emission as well batch management. The initial investment into spectrometric technologies, in this case FTIR spectroscopy, would in many cases be quickly paid back in the cost savings.

FTIR Spectroscopy has the potential to be used in a variety of different applications.

- Quality Control.
- Environmental monitoring.
- Process Control.

Economic and Operational Benefits.

In principle, the ideal generic solution to thermal oxidiser control would be to monitor both the inlet and the outlet. On-line, real-time data from the inlet would be used to determine the required operating parameters to set (temperature, air flow *etc.*). The abatement could then be confirmed using the outlet data, also enabling some fine-tuning in the unlikely event of any unexpected emission breakthrough.

Clearly, on this specific plant being able to move from the current situation where the thermal oxidiser is run at maximum capacity to ensure no breakthrough to running at a lower optimised capacity specific to each oil process would represent a significant economic benefit (see below). Moreover the lifetime of the equipment would also be increased, representing a further cost saving.

Possible Savings	
Operating cost savings approximately	£50,000 per year
Avoiding replacement oxidiser	£500,000

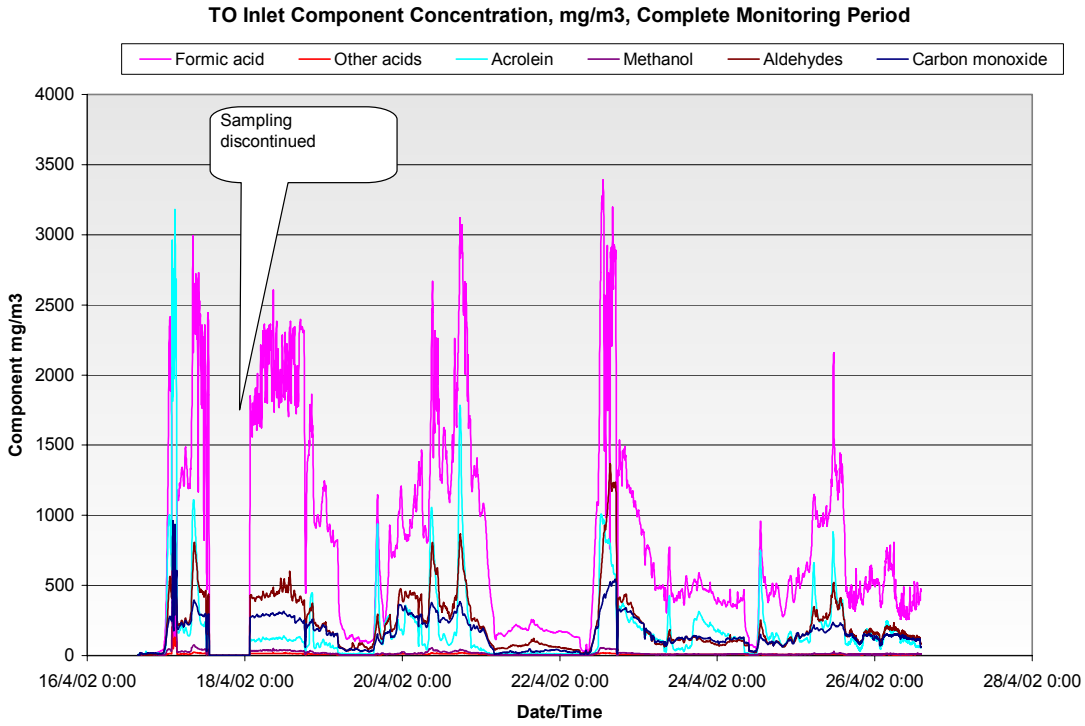
APPENDIX 1: Batch Details of the 70 Oils Processed.

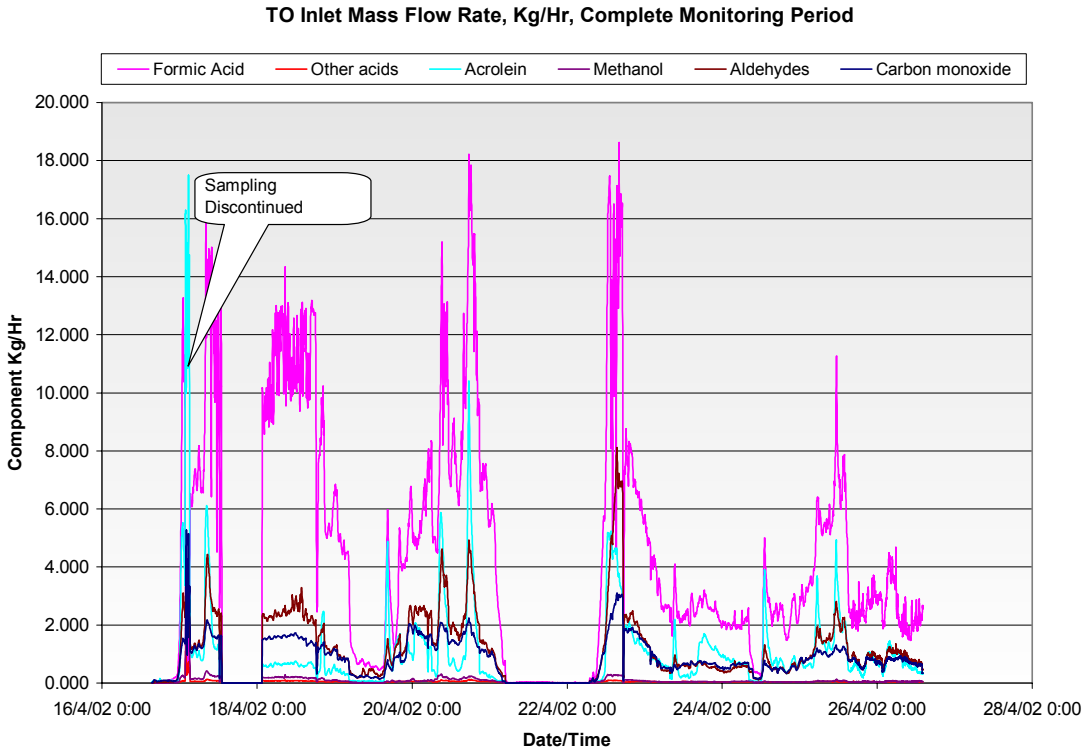
Start date/time	End date/time	Description	Oxidiser
16/4/02 16:27	19/4/02 5:58	Recovered vegetable oil	520
16/4/02 17:02	NR	Recovered vegetable oil	521
16/4/02 20:03	19/4/02 2:05	50p thickened rapeseed oil	522
17/4/02 4:01	19/4/02 5:58	50p thickened rapeseed oil	523
17/4/02 11:45	19/4/02 7:01	45-70p Blown linseed oil	524
18/4/02 11:47	NR	180-200p Blown castor Oil	525
19/4/02 11:44	20/4/02 8:04	15p Thickened Linseed Oil	524
19/4/02 16:45	20/4/02 1:05	Std boiled linseed oil	522
19/4/02 17:13	21/4/02 4:01	30p Boiled castor oil	523
19/4/02 23:12	21/4/02 4:01	Askes blown linseed oil	525
20/4/02 2:59	21/4/02 4:01	90p Thickened rapeseed oil	521
20/4/02 6:45	20/4/02 14:03	Std blown linseed oil	522
20/4/02 13:28	20/4/02 23:04	1p thickened linseed oil	520
22/4/02 7:13	23/4/02 16:02	Burnt rape	520
22/4/02 14:16	23/4/02 11:00	4-5p Thickened fish oil	523
23/4/02 5:05	24/4/02 0:02	10p Thickened linseed oil	524
23/4/02 10:17	24/4/02 15:00	Tall oil	522
23/4/02 13:28	NR	4-5p Thickened fish oil	523
24/4/02 9:01	25/4/02 16:01	65-80p Thickened linseed oil	520
24/4/02 13:43	26/4/02 5:01	500-600p Blown castor oil	524
24/4/02 18:03	29/4/02 15.00	60-70p Soya	525
25/4/02 0:58	26/4/02 11:29	65-80p Thickened linseed oil	521
25/4/02 8:03	29/4/02 10.45	65-80p Thickened linseed oil	523
25/4/02 14:46	NR	Tall oil	522
25/4/02 18:45	26/4/02 7:01	Askes boiled linseed oil	520
26/4/02 13:31	26/4/02 22:00	Std boiled linseed oil	521
26/4/02 13:45	30/4/02 14.30	60-70p thickened rape oil	524
29/4/02 14.00	29/4/02 22.00	Std Boiled Linseed oil	523
29/4/02 17.15	30/4/02 23.00	15p Blown linseed oil	525

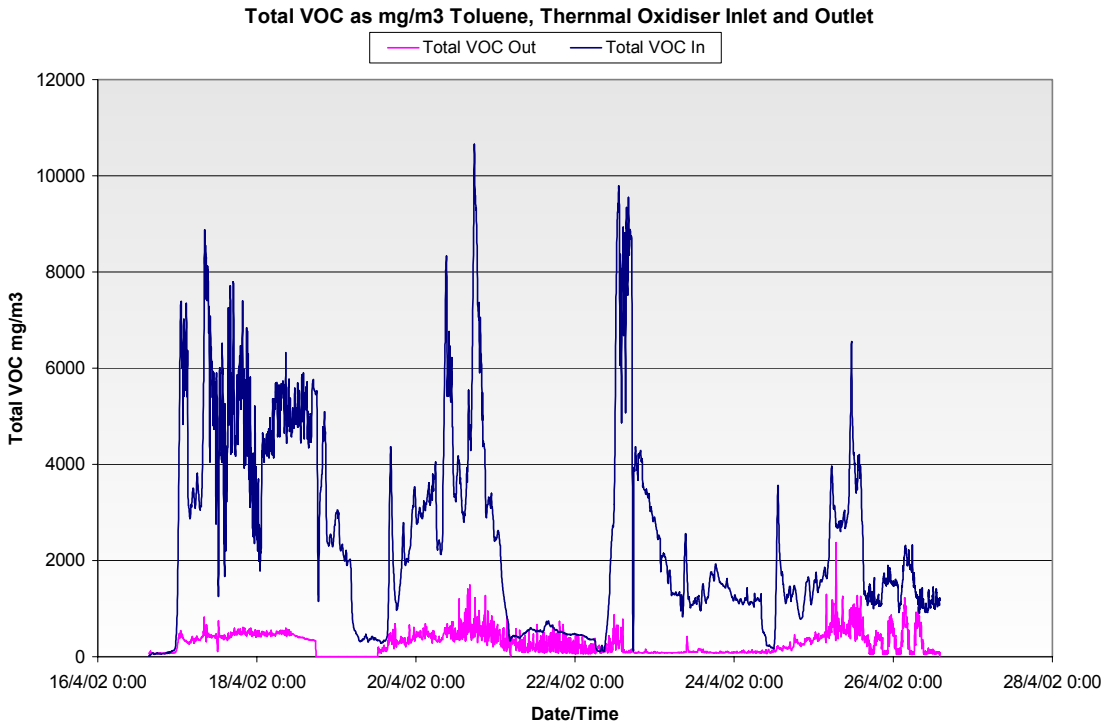
30/4/02 11.45	3/5/02 0.00	Recovered vegetable oil	520
30/4/02 12.00	3/5/02 1.00	Recovered vegetable oil	521
30/4/02 13.15	1/5/02 22.00	30p Blown Castor oil	522
30/4/02 16.15	1/5/02 3.00	Askes boiled linseed oil	523
30/4/02 22.30	2/5/02 4.00	45-55p Blown castor oil	524
1/5/02 12.00	1/5/02 23.00	Askes boiled linseed oil	523
1/5/02 12.30	NR	15p Blown castor oil	525
2/5/02 8.45	3/5/02 21.00	80p Blown castor oil	525
2/5/02 16.00	3/5/02 2.00	SHE No1 Pale boiled linseed oil	522
2/5/02 19.15	3/5/02 3.00	Taylors boiled linseed oil	523
3/5/02 11.15	3/5/02 18.00	Taylors boiled linseed oil	522
3/5/02 11.45	8/5/02 8.00	65-80p Thickened linseed oil	523
7/5/02 7.30	9/5/02 0.00	Blown castor oil	520
7/5/02 8.00	8/5/02 8.00	Thickened fish oil	522
7/5/02 12.00	10/5/02 2.00	Thickened linseed oil	525
7/5/02 17.45	9/5/02 16.00	Blown castor oil	521
8/5/02 7.00	9/5/02 8.00	Blown castor oil	524
8/5/02 10.30	9/5/02 12.00	Blown fish oil	522
8/5/02 20.15	10/5/02 6.00	Thickened linseed oil	523
9/5/02 14.15	10/5/02 22.00	Refined rape	524
9/5/02 20.00	10/5/02 22.01	Thickened linseed oil	522
10/5/02 8.45	10/5/02 22.02	Thickened fish oil	520
10/5/02 8.45	10/5/02 22.03	Thickened fish oil	521
10/5/02 8.45	10/5/02 22.04	Thickened linseed oil	523
10/5/02 17.15	10/5/02 22.05	Blown ground nut oil	525
13/5/02 8.15	NR	Thickened linseed oil	522
13/5/02 8.15	13/5/02 17.00	Thickened fish oil	520
13/5/02 8.15	13/5/02 18.00	Thickened fish oil	521
13/5/02 8.15	14/5/02 3.00	Thickened linseed oil	523
13/5/02 8.15	NR	Blown ground nut oil	525
13/5/02 17.00	13/5/02 21.30	Blown linseed oil	524
14/5/02 8.00	15/5/02 20.00	Thickened linseed oil	522

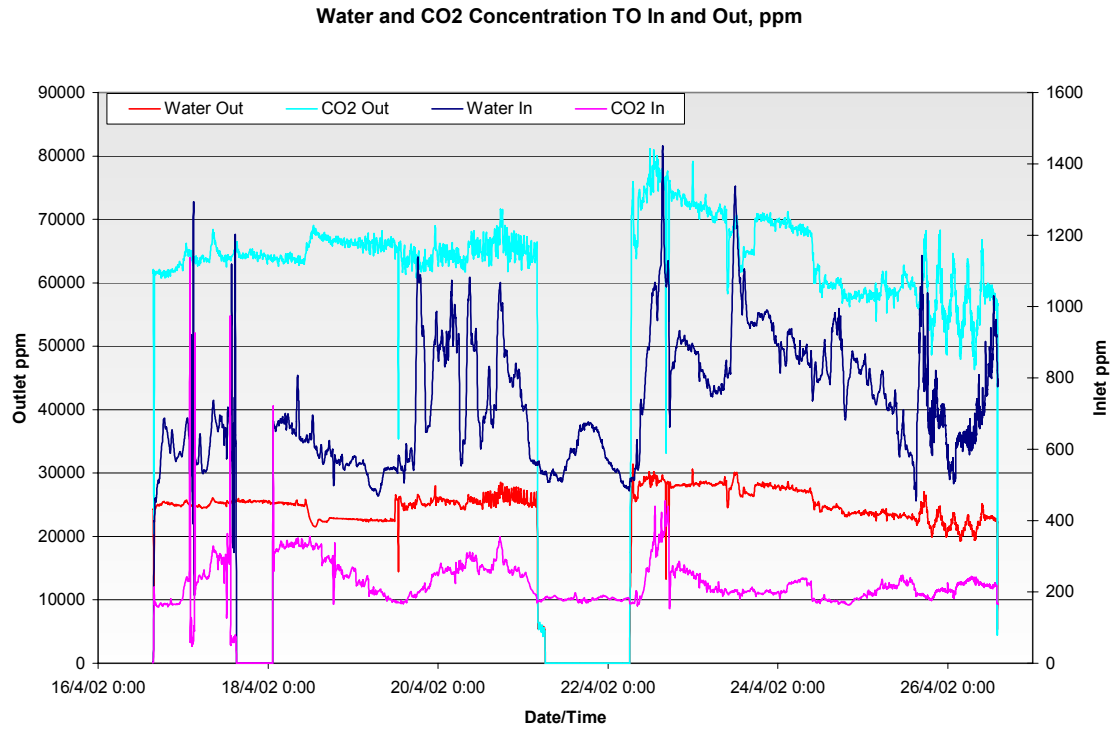
14/5/02 13.15	17/5/02 1.00	Recovered vegetable oil	520
14/5/02 13.30	17/5/02 4.00	Recovered vegetable oil	521
14/5/02 15.45	16/5/02 8.00	Blown castor oil	523
15/5/02 11.00	16/5/02 10.00	Blown fish oil	524
16/5/02 11.45	NR	Thickened linseed oil	525
16/5/02 16.45	17/5/02 1.00	High temp boiled linseed oil	523
16/5/02 17.15	NR	Std boiled linseed oil	522
16/5/02 23.45	NR	Thickened linseed oil	524

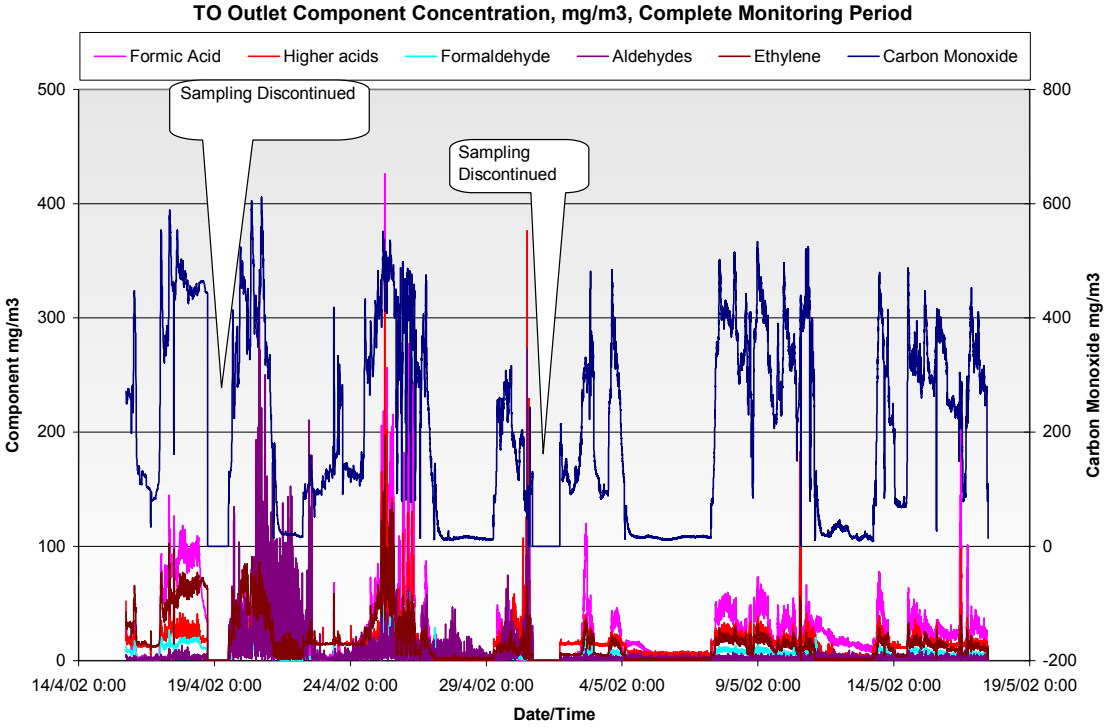
APPENDIX 2: Concentration and Mass Profiles.






Total VOC as mg/m3 Toluene, Thernmal Oxidiser Inlet and Outlet
Total VOC Out
Total VOC In
12000
10000
8000
6000
4000
2000
0
Total VOC mg/m3
16/4/02 0:00
18/4/02 0:00
20/4/02 0:00
22/4/02 0:00
24/4/02 0:00
26/4/02 0:00
28/4/02 0:00
Date/Time


Water and CO2 Concentration TO In and Out, ppm
Water Out
CO2 Out
Water In
CO2 In
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
Outlet ppm
1600
1400
1200
1000
800
600
400
200
0
Inlet ppm
16/4/02 0:00
18/4/02 0:00
20/4/02 0:00
22/4/02 0:00
24/4/02 0:00
26/4/02 0:00
Date/Time


TO Outlet Component Concentration, mg/m3, Complete Monitoring Period
Formic Acid
Higher acids
Formaldehyde
Aldehydes
Ethylene
Carbon Monoxide
Sampling Discontinued
Sampling Discontinued
Component mg/m3
Carbon Monoxide mg/m3
500
400
300
200
100
0
800
600
400
200
0
-200
14/4/02 0:00
19/4/02 0:00
24/4/02 0:00
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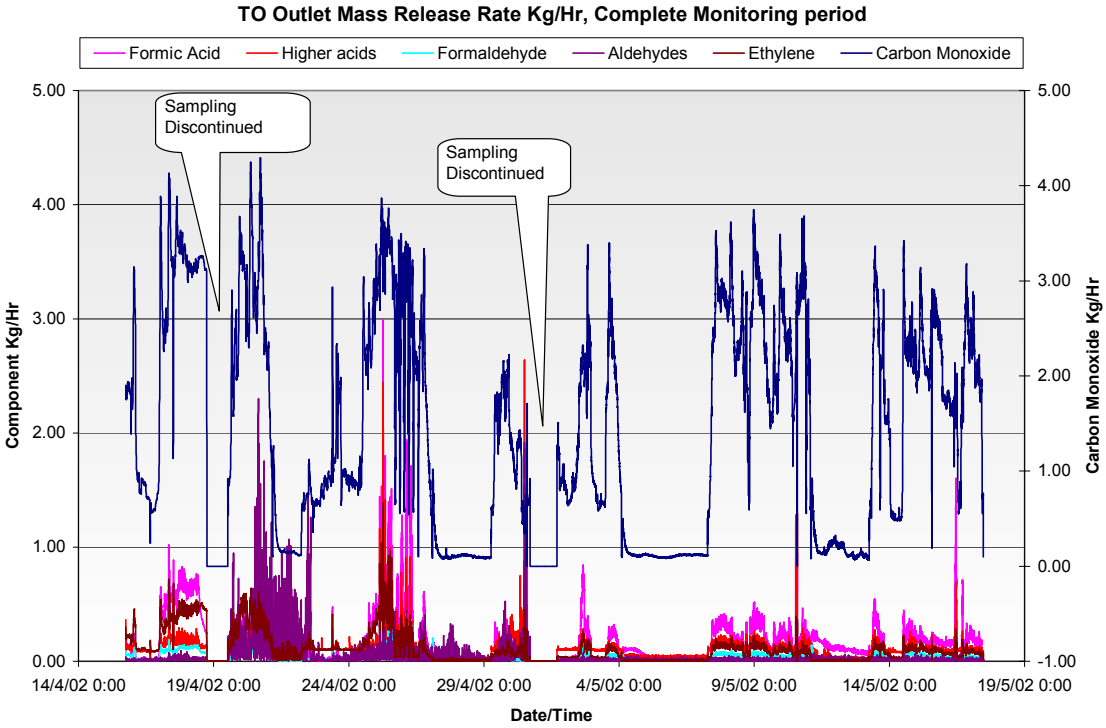
TO Outlet Mass Release Rate Kg/Hr, Complete Monitoring period
Formic Acid
Higher acids
Formaldehyde
Aldehydes
Ethylene
Carbon Monoxide
Sampling Discontinued
Sampling Discontinued
Component Kg/Hr
Carbon Monoxide Kg/Hr
5.00
4.00
3.00
2.00
1.00
0.00
5.00
4.00
3.00
2.00
1.00
0.00
-1.00
14/4/02 0:00
19/4/02 0:00
24/4/02 0:00
29/4/02 0:00
4/5/02 0:00
9/5/02 0:00
14/5/02 0:00
19/5/02 0:00
Date/Time