

DETERMINATION OF ALCOHOL ETHOXYLATE COMPONENTS IN SEWAGE SLUDGE

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Abstract - An analytical method has been developed for the determination of alcohol ethoxylate (AE) components in sewage sludge. The method has been extensively ring tested in several industrial laboratories and the concentrations in sludge samples from a number of EU countries has been obtained. The method is based on a methanol soxhlet extraction of centrifuged sludge, which is then cleaned up using an alumina column, followed by derivatisation with naphthoyl chloride and a further alumina column clean-up. The extract is analysed using high performance liquid chromatography with fluorescence detection. Using the method, sludges from several European Sewage Treatment Plants (STP) were analysed. The concentration of the AEs, which are primarily linear, in digester inlet averaged 1164 ug g^{-1} ($550 - 2947 \text{ ug g}^{-1}$) and in outlet sludges the mean value obtained was 189 ug g^{-1} (range $59 - 437 \text{ ug g}^{-1}$) respectively. Removal of the AEs by anaerobic digestion at the STP averaged 82% (range 61 - 93%). The mean concentration of AEs found in all the outlet sludges analysed was 167 ug g^{-1} ($<22 - 468 \text{ ug g}^{-1}$). The interlaboratory relative standard deviation of the procedure was around 40% for the digester sludges analysed. The method

developed provides a more accurate estimate of the environmental level of AE components compared to the existing colorimetric approaches. Still the method will over-estimate the concentration of alcohol ethoxylates in sludges due to the non-specific nature of the detection. However, it is sufficiently robust and accurate to give good estimates of alcohol ethoxylates in sludges and hence maximal concentrations in soils.

Keywords Alcohol ethoxylates, AE, analysis, biodegradation, sludge

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INTRODUCTION

In several earlier papers (Waters and Feijtel, 1995, van de Plassche et al, 1997, van de Plassche et al, 1999) the results of an assessment of the environmental risks associated with four major groups of surfactants was described. In such assessments the predicted or measured concentrations of chemicals in relevant environmental compartments (eg aquatic, terrestrial, etc) are compared with those that are shown to have no effect on representative organisms in order to establish the existence of adequate safety margins (AIS, 1989).

As part of that exercise, a joint industry AISE/CESIO Task Force (TF) 'Monitoring and Environmental Surfactant Analysis' was charged with the development and application of specific methodology for the environmental monitoring of the major surfactants under consideration i.e. linear alkylbenzene sulphonates (LAS), alcohol ethoxylates (AE), alcohol ethoxylated sulphates (AES), alcohol sulphates (AS), secondary alkane sulphonates (SAS) and soap. The principle route of exposure in the environment was considered to be the aquatic compartment, hence the methodologies developed and used were designed for aqueous samples.

At the Limelette workshop, on the risk assessment of detergent chemicals, (AISE-CESIO,1995) the conclusions reached for the Dutch risk assessment were that for the four surfactants (LAS, AS, AES, AE) assessed, there were no significant risks posed for the aquatic environment. However, the meeting also noted that while the data generated from the Dutch exercise were sufficient for derivation of soil PECs, further information for the terrestrial environment was desirable. Hence the TF has further developed the analytical screening methodology, originally developed for the aquatic environment to allow for the determination of alcohol ethoxylate components in sewage sludge, which is the primary input of such chemicals onto soil via sludge application to agricultural land.

This paper describes the results of that development and the experiences of using the method. The emphasis was on linear-type of alcohol ethoxylate components which are the largest volume non-ionic surfactants used in household cleaning products disposed of via sewage treatment plants.

MATERIALS AND METHODS

Materials and Methods

Chemicals and Standards

The commercial surfactants Genapol® C100 (a coconut based linear alcohol ethoxylate with a mixture of C₁₂ and C₁₄ alkyl chain lengths and an average of 10 ethoxy units) and Genapol® T110 (a tallow based linear alcohol ethoxylate with a mixture of C₁₆ and C₁₈ alkyl chain lengths and an average of 11 ethoxy units) were supplied by Clariant GmbH, Germany. The organic solvents, methanol, acetonitrile, chloroform, acetone, dichloromethane, and cyclohexane were all HPLC grade. The ammonium acetate used in the HPLC mobile phase was supplied by Aldrich. The derivatization reagents 1-naphthoyl chloride and 1-methylimidazole were obtained from Aldrich and used as received.

Note, it is recommended that fresh derivatization reagents are used as the chemicals can have a relatively short shelf life due to their susceptibility to hydrolysis.

Materials

Alumina-N SPE cartridge, 0.5 g/6 ml or 2 g/12 ml, were used, as obtained from a variety of suppliers.

Sample Collection

An AISE/CESIO surfactant monitoring programme was set up in 1997 at several activated sludge treatment plants in the UK, Germany, the Netherlands, Italy and Spain and several trickling filter plants in the UK. Details of the sewage treatment plants are given in Table 1. Several sludge samples were collected to represent the various types of sewage sludge generated in Europe and included a co-settled sludge, anaerobic digester inlet- and outlet sludge, Klam press sludge and lagoon sludge. A general description of the various sludges is given below :

Co-settled sludge (ca., 3-5 wt% dried solids) which typically consists of primary settled sludge (ca., 5-7 wt% dried solids) combined with the humus clarifier or secondary settler sludge (ca., 0.5 wt% dried solids).

Anaerobic digester inlet sludge which is typically a thickened co-settled sludge (ca., 7-9 wt% dried solids) that has been mixed with a polymer and/or passed over a belt press or through a gravity settling tank.

Anaerobic digester outlet sludge (ca., 4-6 wt% solids) that has typically a 10 to 15 day sludge retention time.

A sampling programme was agreed by the Task Force for collection of grab samples of sludge. The liquid sludge samples (namely the co-settled sludge and digester inlet and outlet sludge) were collected directly in glass vessels and preserved on site with 8% formalin (40% aqueous

formaldehyde solution) to prevent biodegradation during transport and storage. All the samples were typically extracted within a week of collection.

Sample extraction

The liquid sludge samples (e.g., co-settled-, digester inlet- and outlet sludge samples) were centrifuged (e.g., at 6000 rpm for 30 minutes) to generate solid pellets. The centrifuged sludge solids were transferred to methanol pre-extracted, pre-weighed Soxhlet thimbles and Soxhlet extracted for four to six hours using 150 ml of HPLC grade methanol. Drying of the sludges samples prior to extraction is not recommended as there is the potential for loss of the shorter ethoxylate chain AE components.

The resulting Soxhlet extracts were evaporated to dryness using a rotary evaporator set at 60°C, though occasionally, depending on the sample, a water/oil residue would remain. To remove the aqueous phase from this oil/water mixture the residue was resolvated in several 10 ml aliquots of acetone and evaporated. The resulting water free oily mixture or dried residue was resolvated in a known volume of HPLC grade methanol to give the appropriate sludge concentration in the organic solvent for AE analysis. At this stage it is possible to spike the extract with AE to assess the recovery of the analytical procedure. The levels used are shown in Table 2.

For the intralaboratory evaluations the resolvated methanol extracts were evaporated to dryness and distributed as dried residues which were subsequently stored at -15°C until analysis.

Solid Phase Extraction (SPE) sample concentration and clean-up

An alumina SPE sample concentration/clean up step was used to prepare the samples prior to HPLC fluorescence analysis. The dried extracts, equivalent to about 0.2 g of dry sludge, obtained from the sludge Soxhlet extraction procedure were resolvated in a known volume of a dichloromethane(DCM)/methanol (100:5 v/v) solution or chloroform to give the appropriate sludge concentration for the SPE procedure. Depending on the sample residue the use of a sonic bath may be required for the resolvation step.

One ml of the DCM/methanol solution was placed on an alumina-N SPE cartridge, previously conditioned with 20 ml DCM/MeOH (100:5 v/v) at a flow rate of 2-3 ml/min. It is important that the conditioned cartridge is not allowed to dry out prior to the application of the extract. The analytical recovery of the clean-up procedure was determined using an appropriate volume of a 1 mg/ml Genapol® methanol stock solution (1:1 mixture of Genapol® C100 and T110) which was added to the extract on top of the column prior to commencing the SPE method.

The alcohol ethoxylates were eluted from the cartridge with 20 ml of DCM/MeOH (100:5 v/v), either in separate portions or as one wash and the eluate collected in 150 ml glass round bottom flasks, rotary evaporated to near-dryness at 50 - 60°C under a gentle stream of nitrogen, transferred to reaction vials with methanol (4 x 1 ml) and taken to dryness. The resulting dried residue was derivatized with 20 µl 1-naphthoyl chloride, 50 µl 1-methylimidazole (the imidazole being used to remove the HCl generated in the reaction and as a catalyst for analytical acetylations (Connors and

Pandit, 1978) and 830 μl HPLC grade acetonitrile. The reagents and extract were mixed on a rotamixer and then placed in an oven at 60°C for 30 minutes. After cooling, the derivatization reaction was quenched with 100 μl of methanol and the final 1 ml solution mixed on a rotamixer. (Note : alternatively 10 μl of 1-naphthoyl chloride, 25 μl of 1-methylimidazole, 915 μl HPLC grade acetonitrile and 50 μl of methanol may be used, for which similar results have been obtained).

The derivatized extract was evaporated to dryness under a gentle stream of nitrogen at 60°C and resolvated in 3 ml DCM/cyclohexane (1:1 v/v) using a sonic bath. The resolvated extract was placed on an alumina-N SPE cartridge (0.5 g/6 ml, Bond Elute cartridge from Varian or a 2 g/12 ml Isolute from Jones Chromatography or Supelco) which had been conditioned with 20 ml DCM/cyclohexane (1:1 v/v) at a flow rate of 2-3 ml/min. It is important that the conditioned cartridge was not allowed to dry out prior to the application of the extract. Without applying any vacuum, the alumina cartridge was washed with 2 x 5 ml DCM/Cyclohexane (1:1) to remove the less polar derivatized impurities and excess derivatization reagents. The AEs were eluted from the alumina cartridge with 15 ml DCM/MeOH (100:5 v/v) and collected in a glass vial. The eluate was evaporated to dryness at 60°C under a gentle stream of nitrogen and resolvated in 1000 μl acetonitrile (or 1000 μl acetonitrile:methanol 1:1) with the aid of a sonic bath and transferred to 2 ml HPLC vials for HPLC analysis. Derivatized eicoson-1-ol should be added to the residue prior to the re-solvation step as an internal standard for the HPLC injection procedure and to account for any in-run sensitivity changes that may be encountered with very “dirty” samples. Depending on the level of AEs the derivatized sample may need to be diluted to allow quantification.

Preparation of AE calibration standards

As the AEs do not have an appreciable UV absorbance above 200 nm or any fluorescence activity, a derivatization step is required for UV or fluorescence detection (Lux and Schmitt, 1996). An external calibration method was used to quantify the AE concentration and the calibration standards underwent a similar derivatization procedure as that used in the SPE sample clean-up method outlined above. The standards were derivatized using 1-naphthoyl chloride and 1-methylimidazole. The calibration standards were prepared by transferring a known volume of a 100 mg/ 100 ml Genapol® methanol stock solution (1:1 mixture of Genapol® C100 and T110) in a glass reaction vial. The methanol was evaporated to dryness under a gentle stream of nitrogen at 60°C. The standards were derivatized using 20 µl 1-naphthoyl chloride, 50 µl 1-methylimidazole and 830 µl acetonitrile as described above. The reaction was finally quenched with 100 µl of methanol and the resulting 1000 µl solution transferred to an HPLC vial for HPLC analysis.

HPLC Analysis

The sludge extracts and calibration standards were both analysed using reverse phase HPLC fluorescence. The chromatographic separation was performed with a gradient methanol, ammonium acetate, acetonitrile eluent at a flow rate of typically 2 ml/min using a C18 analytical column (typically a 250 x 4 mm, 10 µm, Waters µ-Bondapak column) and an injection volume of typically 20 µl. The following gradient programme was generally used:

Eluent A : methanol:0.05m ammonium acetate (25:75 v/v)

Eluent B : acetonitrile:methanol (50:50 v/v)

Gradient programme

Time	%A	%B
0.0	50	50
6.0	25	75
36.0	0	100
50.0	0	100
55.0	50	50

Detection was by fluorescence at an excitation wavelength of 300 nm, emission wavelength of 385 nm and a slit width of 10 nm.

A typical standard chromatogram is shown in figure 1.

Quantitation of the AE components in the samples was undertaken by integrating the total peak area over the range of AE components of interest, namely the C12 to C18 AE (see Figure 1). Under the reverse phase conditions used, AEs were separated mainly by the length of the alkyl chain, though a partial splitting of the range of ethoxymers in each homologue peak was achieved as the alcohol had separated from the monoethoxylated alcohol, and the di and polyethoxylated alcohols.

Integration

Assessment of the chromatograms obtained from the various samples, showed that the samples were grouped, approximately into those that were simple, (figure 2) and those that were very complex, (figure 3). Integration of the former is easily achieved using a base-line approach, in a similar fashion to the

standards. However, the complex chromatograms, could be assessed a number of different ways, with varying degrees of over-estimation of the alcohol ethoxylates present. The method chosen by the TF was to use a base-line which probably over-estimates the total alcohol ethoxylates, see figure 3, this approach is referred to as the common base-line method. The other approach adopted, see later, was to integrate the total peak area between and including the elution of the C12 polyethoxylated alcohols to the C18 polyethoxylated alcohols. This area was directly compared with that obtained for the known concentrations of the AE external calibration standards.

SCOPE AND LIMITATIONS

Commercial AE surfactants are each complex mixtures of components with a range of alkyl and ethoxymer chain lengths. Many different grades are in use in consumer cleaning products. The results reported here are for the composite mixture of AE components resulting from that use.

The analytical method described is an HPLC screening method with fluorescence detection capable of determining alcohol ethoxylate components in the range of C12 - C18 alkyl chain lengths with an ethoxylate chain of EO4 up to approximately EO20 in sludge samples. The detection limit is approximately $10 \mu\text{g g}^{-1}$ of total AEs in dried sludge.

An initial ring test of the methodology by the TF members, using a common methanol extract of a sludge sample from Huyton STP (UK), was carried out. In the ring test, two different clean-up procedures involving either the use of alumina and silica columns prior to the derivatisation step or

the use of two alumina columns, one before and one after the derivatisation step, were evaluated. In general, the latter procedure provided cleaner, better quality chromatograms with less interfering peaks in the region of interest. Consequently, there were less complications in the identification and quantification of AE peaks, thereby resulting in lower AE levels (see Table 3). There was better recovery of AEs from the initial alumina column than from the second alumina column (after derivatisation), due to loss of the alcohols and lower ethoxylated (EO <3) materials. However, overall the recovery throughout the whole procedure was acceptable, i.e. >80%. This clean-up procedure was therefore preferred in the monitoring exercise of European STPs.

Positive interferences may arise from the presence of alkylphenol ethoxylates (APE), branched AE and some alcohol EO/PO nonionics. The interference from APE will depend on the source of the sludge. Thus STP's with a very high industrial input, may, in some countries, contain a peak(s) in the retention time window just before the C12 peak elutes. The extent of this interference will, obviously, depend on the concentration of the APE, and in most circumstances may be avoided through careful adjustment of the integration parameters. This is illustrated by Kiewiet et al, 1995, where a simpler clean-up stage allows more of the APEs to pass through to the final sample.

It is very important, that a number of blanks are generated to ensure that the peaks being measured in the final sample, are derived from the original STP samples. Thus solvent blanks as well as procedure blanks should be generated.

It is clear from the above discussions, that the samples and quantification require an experienced analyst. Collecting the samples, extracting the AEs and the final analytical step, are all prone to errors from interferences, contamination and incorrect interpretation. It is essential that these are minimised and that the best analytical practices are observed throughout the procedures described. Subsequent to the initial ring test a monitoring exercise was carried out in five countries, Italy, Netherlands, Spain, Germany and the UK, details of the STPs are given in Table 1. In the latter two countries, the samples were shared by a number of the participating laboratories, resulting in two further ring tests. The results from these exercises, are shown in Table 4 and are discussed in the RESULTS section.

RESULTS

The results of the monitoring exercise carried out in a number of European countries to assess the fate of AE components in the digester of sewage treatment plants and hence into the terrestrial environment, are shown in Tables 4 and 5. Ten laboratories of the joint AISE/CESIO Task Force participated and applied the agreed methodology to determine the levels of AE components in sludges from a number of European STPs. Most of the STPs selected had a known history concerning performance and concentrations of surfactants in the different STP compartments (Holt et al, 1998, Matthijs et al, 1999, Schöberl, 1994 and 1995). The percentage and type of industrial input to the influents received at these plants varied considerably, see Table 1.

The main objective of the exercise was to assess the typical levels of AE components in anaerobically digested sludge, which may be applied to land. Primary sludge and/or digester sludge samples were also collected from some STPs in order to assess the removal of AE components during the anaerobic digestion. Certain countries (e.g. UK) also apply primary sludge directly to soil. Based on the data for primary and digested sludges, the concentrations of AE components in sludge amended soils can be predicted.

The levels of AE components (Table 4) for the ranges of both the digester inlet and outlet samples were in reasonably good agreement considering the varying age and efficiency of the European STPs selected for the study and the wide variability in amount and type of industrial input received. Where levels of AE components were measured in digester inlet and outlet sludges, the mean values obtained were 1164 ug g^{-1} ($550 - 2947 \text{ ug g}^{-1}$) and 189 ug g^{-1} (range $59 - 437 \text{ ug g}^{-1}$) respectively. Removal of the AE components by anaerobic digestion at the STP averaged 82% (range 61 - 93%). The mean concentration of AE components found in all the outlet sludges was 167 ug g^{-1} ($<22 - 468 \text{ ug g}^{-1}$). The interlaboratory relative standard deviation of the procedure was around 40% for the digester sludges analysed. Typical chromatograms for the digester sludge inlet and outlet are given in figures 4-5.

The ultimate anaerobic biodegradation obtained in this study, is in good agreement with that obtained for typical AE components in a modified ECETOC anaerobic biodegradation test (Madsen et al, 1995; Salanitro and Diaz, 1995), which yielded >75% ultimate anaerobic biodegradation.

The average recovery of appropriate standard additions of Genapol® C100/T110 through the analytical procedure was 93% (Table 5). Analyses performed on the same samples on different days showed reproducible results for most extracts (e.g. Huyton, UK). A wide variability was, however, seen for extracts of samples from one of the STPs, i.e. Mitchel Laithe, UK, which had a high trade influent of approximately 35-40%, which is mainly from the wool scouring and dye industry.

DISCUSSION AND CONCLUSIONS

Analytical Methodology

The method described has been extensively assessed and tested by the AISE-CESIO Analytical Task Force members. It is generally capable, depending on the sample, when used by an experienced analyst, of giving good clean chromatograms, with a minimum of interferences from other sources. It will always be prone to over-estimating the level of AE components in sludges, due to the non-specific nature of the detection technique. However, for the purposes it was developed, to aid risk assessment, it is considered sufficiently robust and accurate. The method is capable of detecting levels below 20 - 30 mg/kg in the original sludge and uses commonly available equipment and procedures.

The crucial stage of the method is the integration. As already indicated the approach adopted is to use all the peak area obtained with the elution of the C12 and the end of the C18 peaks. However,

the baseline must be carefully drawn, the common-baseline approach has been found to be the best compromise by the Task Force (see Figures 2 and 3).

The lower ethoxylated alcohols, EO 0-3, are lost during the initial pre-concentration stage and while washing the second alumina column. This material can be trapped in the eluate and subsequently analysed, this approach is the subject of further work by Task Force members. The results reported in this paper have not been normalised to account for this loss but only include the EO 4+ components.

The general approach described in this paper, is capable of being applied to waters. The application to effluents from STPs with a detection limit of 10 - 20 ug/l has been described in Cassani et al, 1998.

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Table 1 : Details of the STPs which provided sludge samples for the monitoring exercise

Country	Name of STP	STP details	Population served	Influent - % Industrial input (principle source)
UK	Huyton	Trickling filter.	80,000	21
	Mitchell Laithe	Activated sludge and trickling filter (1:2).	350,000	35-40
Germany	München II	Activated sludge, primary elimination	680,000	30
	Stahnsdorf	Activated sludge	200,000	25
	Buchenhofen	Activated sludge	700,000	50
Italy	Torino	Activated sludge	1,500,000	50
	Monza	Activated sludge	450,000	30
Spain	Viveros Madrid			
Netherlands	De Meern	Activated sludge	30,000	<10
	Bennekom			
	Eindhoven	Activated sludge	750,000	30
	Horstenmeer	Activated sludge	160,000	20
	Karlingse Veer	Activated sludge	300,000	20
	Steenwijk	Activated sludge	98,000	<10

Table 2 : Spiking levels of alcohol ethoxylates into sludge samples for recovery experiments

Sludge description	Weight equivalent of solid sludge per ml of resolvated extract (g/ml) ^A	Genapol® C100/ Genapol® T110 added to 1 ml extract (ug) ^B
Co-settled sludge	0.1	200
Anaerobic digester inlet sludge	0.1	200
Anaerobic digester outlet sludge	1.0	50

^AWeight equivalent of sludge after resolution of Soxhlet extract in appropriate volume of chloroform and/or DCM/methanol 100:5 v/v)

^BConcentration of nonionic spike added to extract to determine analytical recovery

Table 3 : Summary of first ring test - comparing different procedures (using total peak area)

Laboratory	Double alumina method (mg/kg)	Alumina/silica method (mg/kg)
1	448, 581	721, 803
2	256	388
3	284	-
4	496, 382	776, 746
5	70 - 100	330, 450
7	190	>430
8	334	-
9	358, 202	858

Table 4 : Concentration and removal of AE in dried sludges from European STPs (worst case integration approach)

STP	Date of sampling	Digester Inlet ($\mu\text{g g}^{-1}$ sludge)	Digester Outlet ($\mu\text{g g}^{-1}$ sludge)	Removal (%)	No of labs engaged
Germany					
München II	2-6 Dec 96	555	86	85	5
Stahnsdorf	13-17 Jan 97	1111	437	61	5
Buchenhofen	17-21 Feb 97	550	59	89	5
Italy					
Torino	28 Jan 97		36		1
Monza	7 Feb 97		33		1
UK					
Mitchell Laithe	7-17 Feb 97	2947	203	93	5
Huyton		1178	223	81	2
Netherlands					
De Meern			124		1
Bennekom			48		1
Eindhoven			<22		1
Horstenmeer			468		1
Karlingse Veer			353		1
Steenwijk			115		1
Spain					
Viveros Madrid		641	124	81	1

Table 5 : Recovery of Genapol C100/T110 spikes through the analytical procedure

STP	Digester Inlet Sludge (% recovery)	Digester Outlet Sludge (% recovery)
Germany		
München II	94 (s = 33, n = 5)	80 (s = 44, n = 5)
Stahnsdorf	98 (s = 48, n = 5)	110 (s = 41, n = 5)
Buchenhofen	97 (s = 33, n = 4)	71 (s = 32, n = 4)
Italy		
Torino		63, 67
Monza		62
UK		
Mitchell Laithe	104, 56	
Huyton	99, 99	76, 137
Netherlands		
De Meern		83
Bennekom		80
Eindhoven		80
Horstenmeer		87
Karlingse Veer		71
Steenwijk		102

Figure 1 Standard Chromatogram

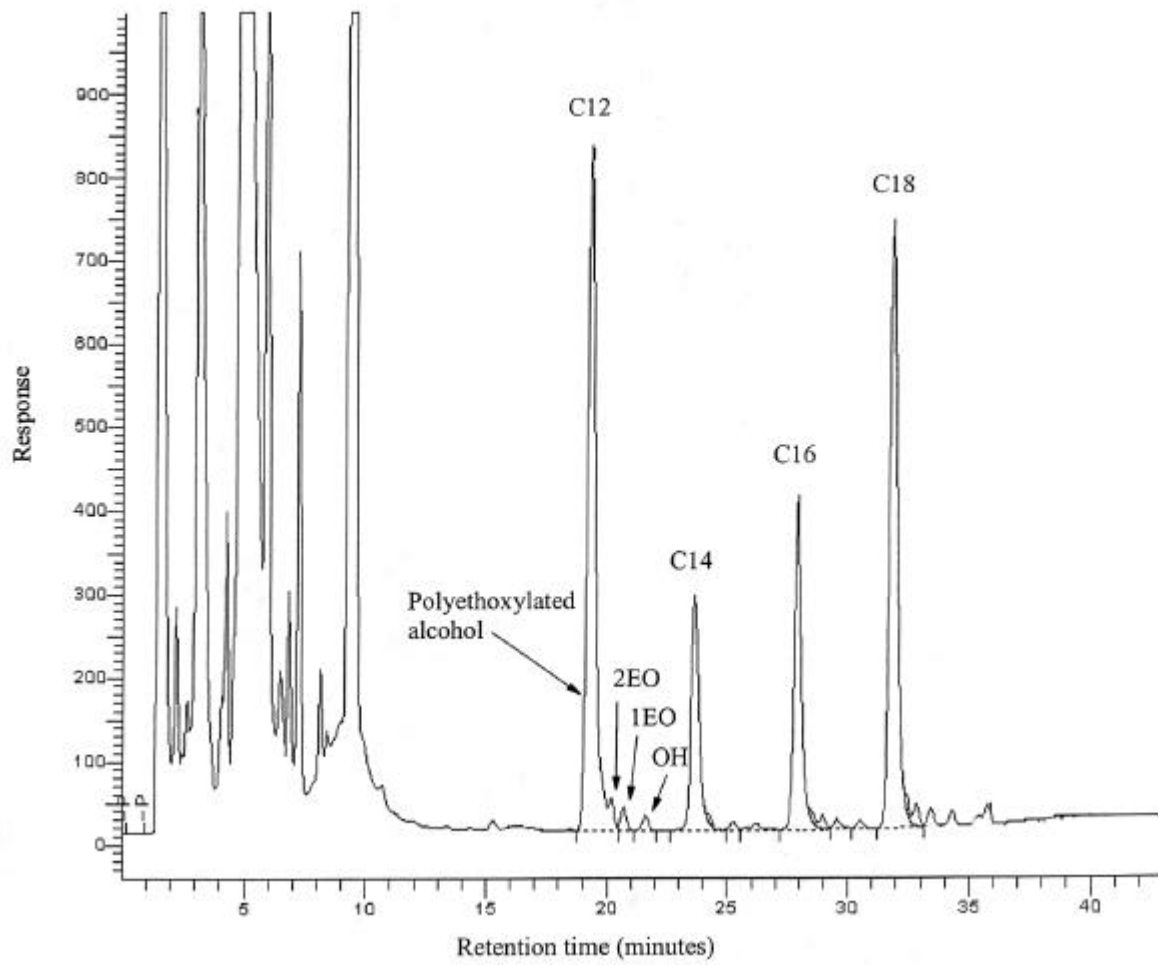


Figure 2 Simple chromatogram

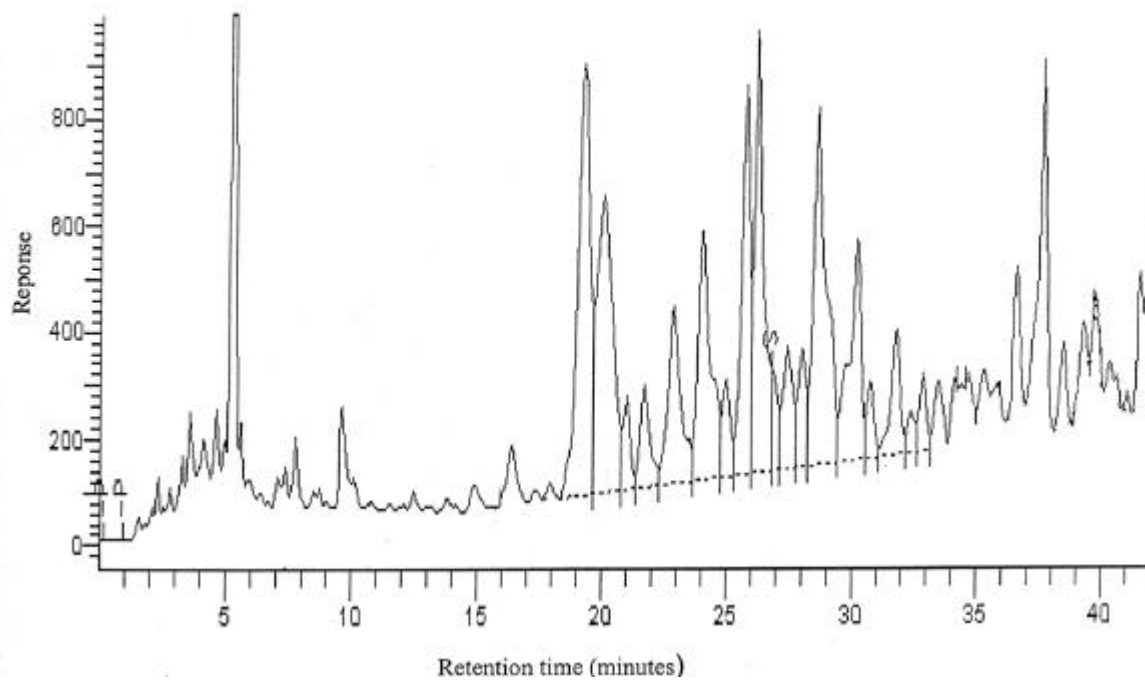


Figure 3 Complex chromatogram

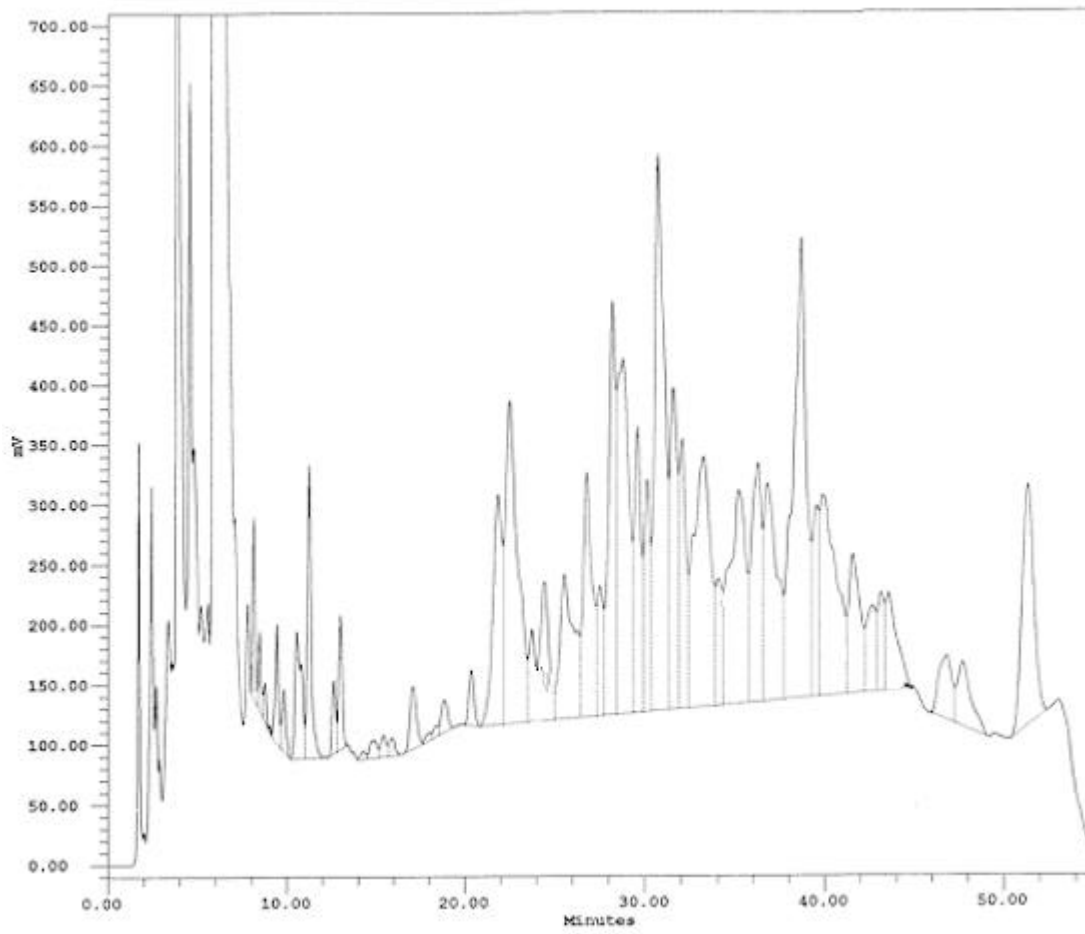


Figure 4 Sludge Inlet

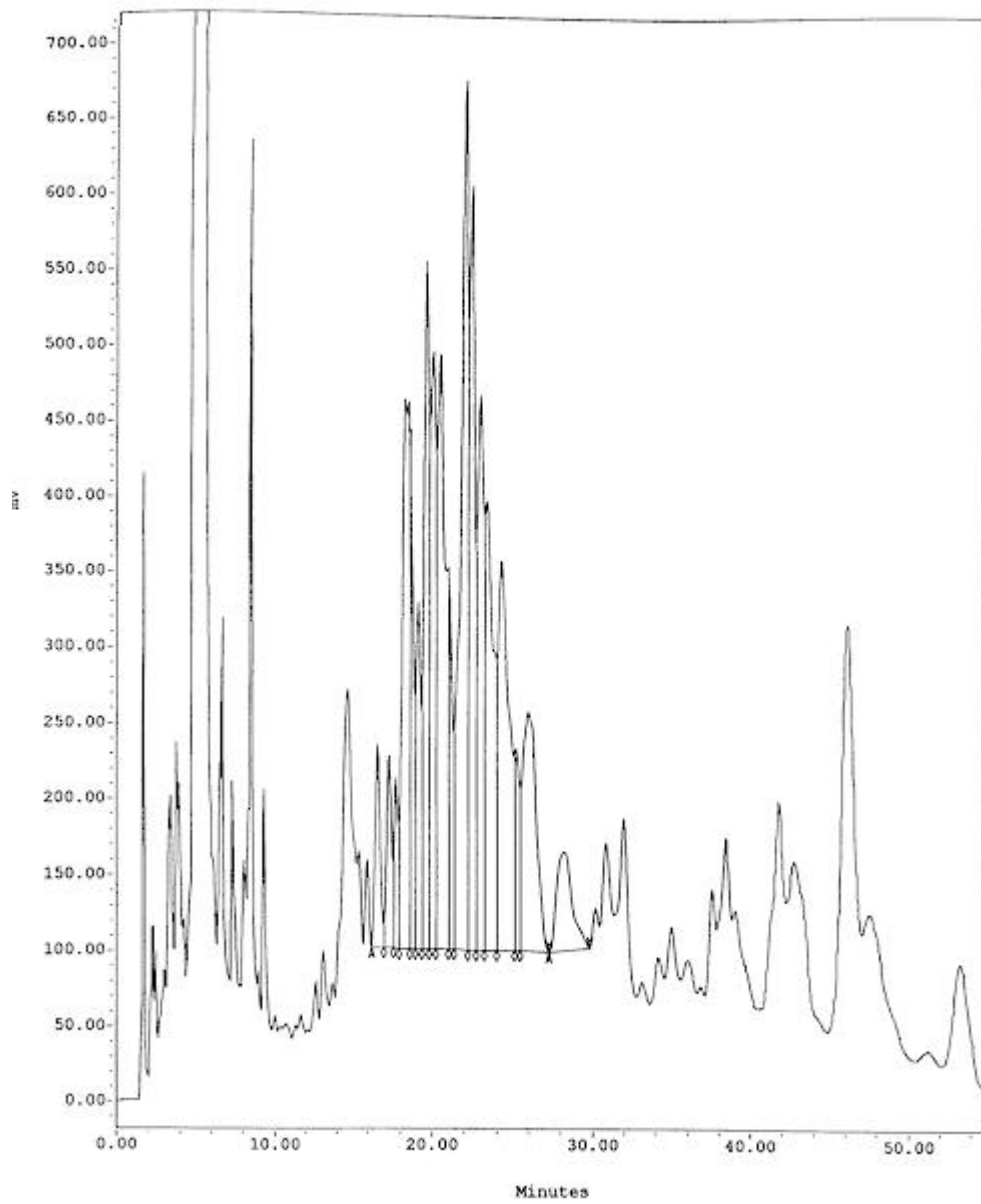


Figure 5 Sludge outlet

