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EVALUATION OF THE AMBIENT AIR QUALITY ANALYSIS OF HCL, H_2S AND NH_3 FROM ENHANCED EVAPORATION SPRAY SYSTEM PONDS ON THE HIGHVELD OF SOUTH AFRICA

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EVALUATION OF THE AMBIENT AIR QUALITY ANALYSIS OF HCL, H_2S AND NH_3 FOR ENHANCED EVAPORATION SPRAY SYSTEM (EESS) PONDS

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SUMMARY

Enhanced evaporation spray system ponds are an inexpensive method for waste water storage and removal. The spray system involves the spraying of the waste water via spray pipes that hang over the waters surface into the ambient environment. However, since such waste water storage and removal is used by large industry and specifically the metal refining industry the water contains chemicals that when are evaporated cause some disturbances in the surrounding ambient atmosphere.

This document focuses specifically on three gases, HCL (hydrochloric acid mist), H_2S (hydrogen sulphide) and NH_3 (ammonia). These three gases that evaporate from the waste water, are the major gases of concern with regards to EESS ponds in the platinum refining industry. The corrosive effects are visible on surrounding steel structures as well as a distinctive unpleasant odour. This study also highlights the emphasis on proper ambient air quality analysis as well as safety measures for workers in the vicinity of the evaporation ponds.

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CHAPTER ONE

INTRODUCTION

1. INTRODUCTION TO COMPANY X EESS PONDS

Company X currently makes use of four Enhanced Evaporation Spray System (EESS) Ponds. The purpose of these ponds is to allow for the evaporation of effluent from the metal refineries. There are two effluent streams that feed the ponds, with one being an acid stream and the other an alkaline stream. Since these streams mix in the ponds various atmospheric gases are given off due to the various chemical processes that occur.

These gases from the EESS ponds are the main area of concern in terms of ambient atmospheric quality. In particular, the gases that are of concern and are to be analysed for are NH_3, H_2S and HCL. The Department of Agriculture, Conservation, Environment and Land Affairs (DACEL) requires Company X to obtain analysis of the mentioned gases at current production levels, and then modelled to test assumptions for an increased production level. The research conducted was to analyse the gas concentrations in the surrounding area of the ponds, then model the results using two different models [1,2] and then relating the results to the chemical water composition.

The corrosive effects of the gases were to be identified on various metals and provided to Company X. The outcomes of the research are to provide Company X with information on the current effects of the three gases as well as the effects on human health and corrosive effects on various metals.

1.1 BACKGROUND

The ambient air quality in the vicinity of industrial processes has recently become a greater area of concern, and affects on the surrounding population because of the recent restructuring of the National Air Quality legislation. The refinement of certain metals requires the use of EESS ponds for water waste storage from the process. These ponds contain various industrial effluents that may alter the natural ambient air of the surroundings upon evaporation. They are located at the end of a refinement process and are lined to prevent leakage. The ambient air and water quality is to be analysed by accredited consultants, with the results modelled on two different air quality models.

The analysis of the ponds water for pH, chlorides, metals and ammonium compounds is to be conducted. Once the water analysis has been conducted analysis of the ambient air around the ponds must be undertaken. Ideally the water and air analysis should be performed on the same day.

Atmospheric data such as moisture, wind direction and speed, and temperature will also be conducted using a portable weather station. The results from the analysis are then modelled using the HAWK[1] and TAPM[2] (The atmospheric pollution model), and the corrosion effects from the measured gases will then be identified. The international best practice for the evaporation ponds as well as ambient air quality monitoring is to be looked at in further detail. The research was performed as required by Company X to conform with DACEL requirements of monitoring the area around the EESS ponds.

1.2 AIMS AND OBJECTIVES

- Obtain a water analysis from the EESS ponds for the various parameters mentioned above (independent consultants will be used).
- Obtain an ambient air analysis for the area around the EESS ponds for the gases mentioned above (independent consultants will be used).
- Provide details on the human health effects of the three gases and the legislation pertaining to the study
- The results from the analysis will then be modelled using the HAWK[1] and TAPM models.
- The corrosion effects from the gases is to be briefly identified (corrosion tables will be used) on 304L, 316L, 317L stainless steel, mild steel and zinc.

1.3 RESEARCH METHODS

Independent consultants analysed the EESS pond water and ambient air around the ponds. A portable weather station was used to obtain meteorological data, which was be provided by, the University of Pretoria. The analysis information was then modelled at the University of Pretoria using the TAPM model and an independent consultant modelled the same results on the HAWK model. The ambient air quality will then be able to be correlated with the water quality.

Air quality analyses:

The Department of Agriculture, Conservation, Environment and Land Affairs (DACEL) were interested in the HCl concentrations at approximately 500m and 200m from the ponds. Analyses of the ambient air were taken at approximately 20m from the ponds. Since there are four ponds that make up a large square, analysis on the four sides at the mentioned distances was undertaken. A total of 35 samples over 3 cycles for the area around the ponds was analysed as indicated in table 6.

Water analysis:

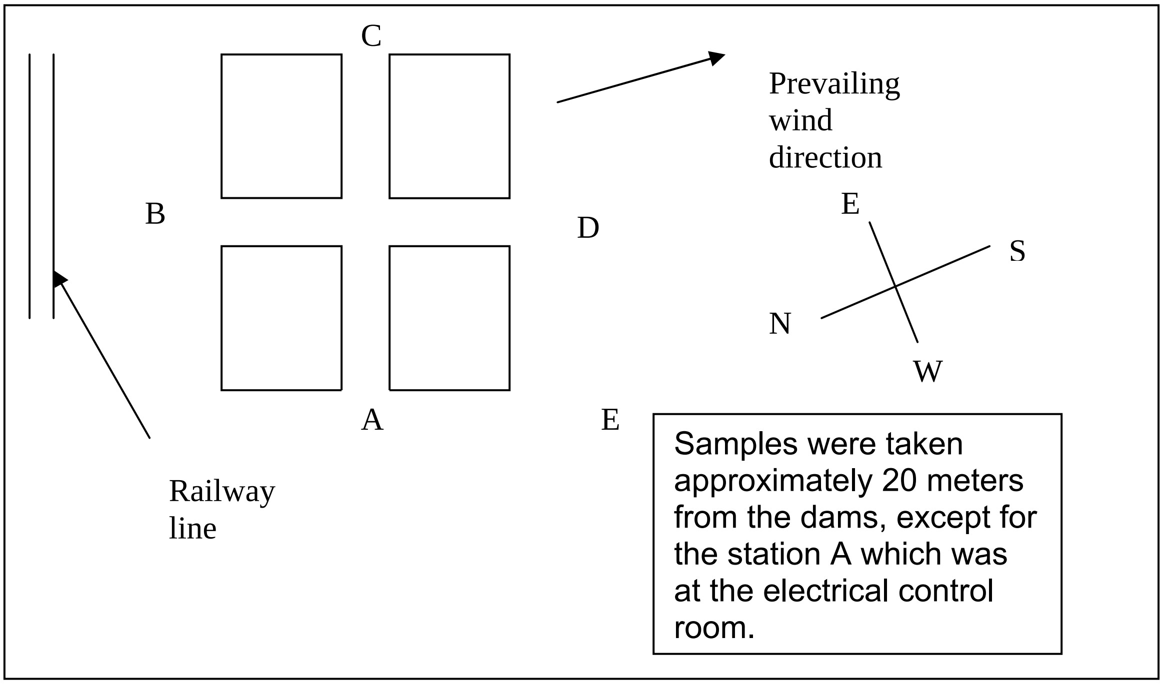
A representative sample on the ponds was to be analysed. Since the composition of the water in the ponds varies with depth, and since only the surface of the water evaporates, and therefore affects the ambient air, a full profile and analysis of the water was to be undertaken.

1.4 IMPORTANCE OF RESEARCH

EESS ponds are a convenient method for the containment of the refinery effluent. Unfortunately they are not always environmentally friendly, especially with ambient air quality. There are various environmental consequences that may result from the air pollution which negatively impact on the surrounding areas, such as the effect of respiratory problems and possible corrosion effects. Fortunately if correctly used, the EESS ponds may be operated without any significant environmental damage. The importance of this research is to identify the current possible problems affecting the environment and identifying methods to improve on the ambient air quality analyses as well as safety measures that should be commissioned.

1.5 SETTING

The following diagram depicts the research area:



Samples were taken approximately 20 meters from the dams, except for the station A which was at the electrical control room.

Figure1: Outlay of Ponds

The area studied is situated in reasonably isolated area from urbanisation. There is a large mine dump situated south of the ponds and a Spoornet railway line situated north of the EESS ponds. Urbanisation is at an approximate distance of one kilometre north of the ponds and the remaining surrounding area between the ponds and the other non-urban areas belonging to Company X.

The Various co-ordinates for the area are GPS: 26˚ 13, 02 S, 28˚ 26, 86 E with the Elevation; 1585m. This information is required for the computer modelling.

1.6 REPORT STRUCTURE

The report is structured as follows:

- Human health effects and legislation for the three gases are identified and discussed in chapter 2
- The corrosion effects of the gases on three different types on stainless steel, on mild steel and zinc are identified in chapter 3

- The results obtained from the study are identified in chapter 4
- A discussion of the results is provided in chapter 5, with recommendations provided in chapter 6

CHAPTER 2

HUMAN HEALTH EFFECTS

2.1 AMMONIA

Concentrated ammonia in the air can irritate people's eyes, skin, and breathing passages, and can damage body tissues over time. Direct contact with concentrated ammonia solutions can burn the skin. Ammonia has such an unpleasant odor that most people avoid exposures that would cause health effects. Ammonia has not been found to cause cancer or birth defects (Toxic release inventory).

Water-soluble, ammonia is rapidly absorbed in the upper airways, with the result of damaging upper airway epithelia. Moderate concentrations (50-150 ppm) can lead to severe cough and mucous production; higher concentrations (>150 ppm) may cause scarring of the upper and lower airways.

A consequence of these inflammatory responses, in some cases, is reactive airways dysfunction syndrome (RADS) and associated persistent airway hyper-responsiveness. At higher concentrations, sufficient ammonia may bypass the upper airways to cause lower lung inflammation and pulmonary edema. Massive exposure to ammonia can be fatal (Donham, et al, 1995).

2.2 H_2S

Hydrogen sulphide is a colourless gas and has a distinct rotten eggs smell. Significant HS poisoning usually occurs by inhalation. Local irritant effects, along with arrest of cellular respiration, may follow. H_2S forms a complex bond to iron in mitochondrial cytochromes, thereby arresting aerobic metabolism in an effect similar to cyanide toxicity (Gayman, 2000).

Low-level exposures usually produce local eye and mucous membrane irritation, while high-level exposures rapidly produce fatal systemic toxicity. As a cellular poison, H_2S affects all organs, particularly the nervous system. The spectrum of illness depends on the concentration and duration of exposure, with high concentrations (>800 ppm) causing sudden death. H_2S concentrations above 150 ppm, however, may overwhelm the olfactory nerve so that the victim may have no warning of exposure, and therefore is a gas that must be monitored and controlled where possible (Gayman, 2000).

2.3 HCL

Hydrogen Chloride is a colorless to slightly yellow gas, with a strong odor. It is a corrosive chemical and contact can severely irritate and burn the skin and eyes with possible eye damage and loss of sight and can irritate the lungs causing coughing and/or shortness of breath. Higher exposures can cause a build-up of fluid in the lungs (pulmonary edema), a medical emergency, with severe shortness of breath and may also affect the liver and kidneys (Hazardous substances fact sheet, 2001).

CHAPTER 3

LEGISLATION

3.1 The AQM Acts effect on monitoring the EESS ponds

The new Air Quality Management Bill has recently become enacted by parliament. The new legislation dramatically introduces new approaches to Air Quality Management in South Africa. It sets new frameworks with management plans, monitoring and enforcement provisions.

The frameworks that are to be in place according to the legislation are national norms and standards. Above the norms and standards (limits for the various chemicals) standards for air quality monitoring, management planning and information management are to be introduced. The legislation therefore encompasses air quality in its totality and according to the legislation, effective air quality monitoring is essential and international best practise is to be adhered to. The ambient air monitoring conducted at the EESS ponds by the consultants will be compared in chapter 5.

An air quality management plan will be required for the EESS ponds with regards to the future usage of the ponds as well as the current reduction of the emissions. Since the spray system of the ponds is to be removed, a significant reduction in the emissions will be evident. The legislation requires the license that must be obtained by government, must specify on-site ambient air quality measurement and reporting requirements. Therefore on-site monitoring equipment will be required on the EESS site.

Standards for the various pollutants of interest will only be available as from July 2005 (DEAT), and since no environmental standards for the three pollutants, HCL, H_2S and NH_3 the environmental standard of TLV/50 were used on the advice of the independent consultants to Company X (OH&AP). I order to adhere to the new legislation the recommendations that follow in chapter 6 are to be adhered to as well as formulating an Air Quality Management Plan for the EESS ponds.

CHAPTER 4

CORROSION EFFECTS

4. INTRODUCTION

Corrosion of metals is directly dependant on temperature and concentration of the corrosive agent. The higher the temperature and concentration the higher the corrosive effects. Water also increases the corrosive effects of some agents by forming a solution. HCL provides corrosive effects as a liquid (dissolved in water) and as a dry gas as identified by Bermudez and Rabald below. Ammonia and H_2S must be in aqueous form to be able to show any corrosive effects on the various metals in this research.

4.1 HCL WET

Stainless steel

304L (Cr 18.8%, Ni 10%, C< 0.03%), 316L (Cr 17.5%, Ni 13%, C< 0.03%, Mo 2.6%), 317L (Cr 17-19%, Ni 9-12%, C max 0.1%).

Corrosion resistance:	304L,	316L
HCl dilute acid:	good,	very poor. (www.nsi-be.com)

Moisture in the presence of HCL is a corrosion catalyst.

Research into the erosion-corrosion of stainless steels 304L and 316L with an aqueous solution of 10%wt HCL in the presence of α-Al_2O_3 particles. It was identified that the stainless steels 304L and 306L suffered corrosion by the corrosion-affected erosion mechanism. (Bermudez, et al, 2003)

According to the BCTB-301 (British Control Tables) inorganic gases corrosion tables both HCL and H_2S are corrosive on steel, with ammonia not being corrosive on steel at the SV (specific volume) of 661.7368; 701.06644; and 1410.8728 respectively. Unfortunately the type of steel was not specified in the tables.

4.2 AMMONIA

304L:

Ammonia: resistant at 673-773 K and at 25323-35452 kPa of ammonia at all concentrations. Ammonia corrodes stainless steel in extreme conditions such as 361 K and at a pressure of 5858 kPa. The ammonia must also be in liquid form (Rabald, 1968). At a temperature range from 288 – 366 K type 304L has excellent resistance to ammonia gas (Schweitzer, 1995).

316L:

At an average temperature of between 297 and 323 K 316L stainless steel corrodes at less than 5 x 10^{-5} m per year at a concentration of 50% and is therefore fully satisfactory. At a temperature range from 288 – 366 K type 304L has excellent resistance to ammonia gas (Schweitzer, 1995).

317L:

It is resistant to ammonia at room temperature in a saturated solution. It is also resistant to a 10% solution of ammonia and experiences a corrosion rate of < 1 x 10^{-4} m/year. 317L is not particularly resistant to 25% solution of ammonia and therefore the corrosion rate is < 1 x 10^{-3} m/year (Rabald, 1968).

Mild steel (carbon steel):

Carbon steel has excellent resistance to ammonia gas in the temperature range of 288 – 313 K (Schweitzer, 1995). It is also resistant to 25% solution of the attacking agent and has a corrosive rate of 5-6 g/m^2 per day (Rabald, 1968).

Zinc:

The formation of zinc corrosion products in solutions is primarily determined by the pH of the solution. In alkaline solutions pH 5 – 13.5 corrosion films are formed. At a pH<6 and pH>12.5 the films are rather lose (Zhang, 1996). With ammonium salt solutions the oxide film was found to form at higher bulk pH values due to the dissociation of NH_4^+ ions (Zhang, 1996). Therefore the higher the concentration of ammonia and water vapour in the atmosphere the higher the possibility of the pH being increased and therefore zinc corrosion.

4.3 HCL gas dry

304L:

The resistance of 304L stainless steel to HCl gas varies from resistant to unusable from 258 – 573 K. Corrosion rates at 258 K is 6 x 10^{-5} m/year; at 313 K is 2 x 10^{-5} m/year and at 523 K is 1 x 10^{-3} m/year (Rabald, 1968).

316L and 317L:

The resistance of 316L and 317L stainless steels varies between resistant to unusable from room temperature to 813 K.

Table 1: HCL gas (dry) resistance to 316L and 317L

K	Agitation	m/year
353	None	2 x 10^{-4}
477	Rapid	1 x 10^{-4}
753	Rapid	2 x 10^{-4}

Mild steel (carbon steel):

Table 2:The resistance of mild steel also varies between room temperature to 573 K. Corrosion rates:

Medium	K	Corrosion
Dry HCl	258	5 x 10^{-5} m/year
Dry HCl	313	2 x 10^{-4} m/year
Dry HCl	423	Slight corrosion

With the addition of water to the HCl gas an aqueous solution is formed. This solution greatly affects stainless steal at any temperature at nearly all concentrations i.e. the corrosion effects on the steels are greatly increased. The average corrosion rate for a 0.5% HCl solution at 308 K is approximately 4 x 10^{-3} m/year (Rabald, 1968).

Table 3: Corrosion rate with HCL on mild steel

Steel	20% HCl (293 K) m/year
Mild Steel	38 x 10^{-3}
17% Chromium	35 x 10^{-3}

18% Chromium 8% Nickel	25×10^{-3}

Zinc:

Zinc when in contact with acidic and strong alkaline solutions, it corrodes rapidly. Very dilute concentrations of acids accelerate corrosion rates beyond the limits of usefulness. Alkaline solutions of moderate strength are much less corrosive than corresponding concentrations of acid, but are still corrosive enough to impair the usefulness of zinc. Therefore in the presence of water vapour the HCl gas will for an acidic solution and therefore corrode the zinc.

4.4 H_2S

Stainless steel:

Good to poor resistance in the temperature range; room temperature – 773 K, in a solution or gas medium.

Table 4: Corrosion rates in m/year (Rabald, 1968)

Corrosion medium	**K**	**304L**	**316L**	**Remarks**
98% H_2S + air + N_2	305	$< 3 \times 10^{-6}$	$< 3 \times 10^{-6}$	Type 304:risk of crevice corrosion; type 316:slight pitting

Type 304L experiences good resistance of $< 2 \times 10^{-2}$ m penetration /year from 288 - 473 K. Type 316L experiences excellent resistance of $< 2 \times 10^{-3}$ m penetration /year from 288 – 344 K and then good resistance of $< 2 \times 10^{-2}$ m penetration/year from 344 – 473 K.

If the dry hydrogen sulphide comes in contact with water vapour to from wet hydrogen sulphide then type 304L the resistance of this steel become unsatisfactory at all temperatures and type 316L provides good resistance at all relevant temperature ranges (Schweitzer, 1995).

Mild steel:

Mild steel provides resistance < 2 x 10^{-2} m penetration/year to hydrogen sulphide from 211 K to room temperature, provided that it is free from water. 1-3 % water increases the attack ten-fold and brings the risk of stress corrosion (Rabald, 1968).

Zinc:

Hydrogen sulphide (H_2S) is also harmless because insoluble zinc sulphide (ZnS) is formed (www.corrosion-doctors.org).

CHAPTER 5

RESULTS

5 ANALYSIS

The ambient air analysis was performed during normal evaporation on the EESS dams. The spray towers were not operational during the sampling. NIOSH methodologies were used for the survey instead of ambient air monitoring methodology. Samples were taken approximately 20m from the ponds, located at points A, B, C, D and E as indicated on figure 1. Station A was located at the electrical control room at a distance of approximately 25m from the centre of the 4 ponds.

The findings are given in table 5 and are as follows (OH & AP consultants);

Table 5: Sampling Data (OH & AP consultants)

Ammonia	**Cycle 1 (21:00 – 9:51) (µg / m^3)**	**Cycle 2 (10:00–22:51) (µg / m^3)**	**Cycle 3 (23:00 – 7:55) (µg / m^3)**	**Average Concentration**
Sample pos A	<0.86	<0.84	-	<0.85
Sample pos B	<0.99	<0.99	<1.42	<1.13
Sample pos C	3.62	<1.65	<2.37	2.54
Sample pos D	<0.28	<0.43	<0.62	<0.44
Sample pos E	<0.78	-	-	<0.78
Hydrogen Sulphide				
Sample pos A	67.56	283.75	-	175.66
Sample pos B	90.48	108.07	127.44	108.66
Sample pos C	242.32	-	466.45	354.39
Sample pos D	139.86	157.88	1289.04	528.92
Sample pos E	401.34	-	-	401.34
Hydrochloric Acid				
Sample pos A	<8.59	<8.44	-	<8.25
Sample pos B	<9.90	<9.6	<14.16	<11.22
Sample pos C	<12.07	<16.56	<23.66	<17.43
Sample pos D	<2.84	<4.26	<6.16	<4.42
Sample pos E	<7.87	-	-	<7.87

- The hydrogen sulphide concentration was higher than the proposed standard at the sampling points C,D.
- The ammonia and hydrochloric acid mist concentrations were below the detection limit for most of the samples taken.

The above findings were a result of comparing the measured concentrations to TLV/50 recommended standards.

5.1 SIMULATION RESULTS

TAPM was configured to the following: 25 grid points for west-east and north-south and an outer grid spacing 30000m, 3100m, 1100m and 400m from the centre on the EESS ponds with 20 vertical grid levels. This provides modelling data for the area around the ponds at the various above mentioned distances, 30000m, 400m etc. The above distances were chosen to provide dispersion data as close to the ponds while maintaining the grid nest ratios of 3.0, 3.33 and 3.0 as recommended by TAPM. TAPM's inputs were maintained as standard for this study. The modelling data is provided in tables 9 - 12.

- CONC:- concentration at the selected grid point, ponds centre
- CMAX:- maximum concentration on the grid, total area modelled
- CLOC:- local maximum concentration for a 5 × 5 sub-grid region surrounding the selected grid point

The concentration maximums for table 6 were calculated for the concentration at the ponds area centre. The hourly maximum is the highest value for any hour, daily values were calculated for the day with the maximum hourly value, and the total value was calculated for all 96 hours. The weather data used by TAPM corresponds to table 13.

Table 6: TAPM model summary for the source centre

GAS	CONCENTRATION Maximums (μg/m^3)	DISTANCE (m)
HCL (hourly)	9.84	30000
HCL (daily)	9.84	30000
HCL (total)	9.84	30000
HCL (hourly)	9.84	3100

HCL (daily)	9.84	3100
HCL (total)	9.84	3100
HCL (hourly)	11	1100
HCL (daily)	9.88	1100
HCL (total)	9.85	1100
HCL (hourly)	11	400
HCL (daily)	9.88	400
HCL (total)	9.85	400
H_2S (hourly)	100	30000
H_2S (daily)	100	30000
H_2S (total)	100	30000
H_2S (hourly)	334.7	3100
H_2S (daily)	314.7	3100
H_2S (total)	310.325	3100
H_2S (hourly)	349.7	1100
H_2S (daily)	315.49	1100
H_2S (total)	311.76	1100
H_2S (hourly)	338.7	400
H_2S (daily)	315.325	400
H_2S (total)	312.56	400
Ammonia (hourly)	1.1	30000
Ammonia (daily)	1.1	30000
Ammonia (total)	1.1	30000
Ammonia (hourly)	1.1	3100
Ammonia (daily)	1.1	3100
Ammonia (total)	1.1	3100
Ammonia (hourly)	1.1	1100
Ammonia (daily)	1.1	1100
Ammonia (total)	1.1	1100
Ammonia (hourly)	1.1	400
Ammonia (daily)	1.1	400
Ammonia (total)	1.1	400

Table 7: TAPM model summary for the maximum concentration on the grid area

GAS	**CONCENTRATION MAXIMUM (µg/m^3)**			
	30000m	3100m	1100m	400m
HCL	9.84	12	16	24
H_2S	326.7	417.7	524.7	776.7
Ammonia	1.1	1.1	2	3

Company X did not require the results of the HAWK model to be compared with the TAPM results in this study, the results from the HAWK model were also confidential to the independent consultants and Company X.

WEATHER STATION DATA

A weather station was set up by sample position E. The parameters that were measured were time, wind speed, wind direction, temperature (˚C), pressure (bar), humidity and incoming solar radiation (W/m^2). The weather station data is provided in table 13. From the graphs it is evident that there were temperature changes over the time period of the analysis according to the natural day/night changes, as well as natural wind speed changes from day to night[5] of maximum temperature peaks during mid-day and wind speed fluctuations during the 24 hour course.

WATER ANALYSIS

The water analysis was performed by an independent consultant on the same days as the air analysis and the results are given in annexure 2. Averages of the chemical compounds of interest of the four ponds:

1. Chloride: 69202.5 mg/l
2. Sulphate: 35017.16 mg/l
3. Free and saline ammonia as NH_4: 140.41 mg/l

CHAPTER 6

DISCUSSION

6. AMBIENT AIR ANALYSIS

The ambient air analysis was performed by independent consultants, using NIOSH methodologies. These methodologies lead to the confusion on whether the non-enclosed ambient air would require such type of sampling which is not required by the Air Quality legislation. The ambient air analysis was also conducted using outdated equipment, which upon inspection was not operating at all. This provides some doubt in the sampling analysis performed by the independent consultants. A repetition of the sampling was not performed due to time and financial constraints.

The equipment used were gas and dust absorbing tubes (HCL, H_2S, and NH_3) that were connected to constant airflow sampling pumps with low flow adapters, Gillian and SKC. Unfortunately it was the low flow sampling pumps that were not functioning. With the ever advancing field for technology newer and better equipment is available that provides real time data for ambient air pollution. Portable as well as fixed air quality monitoring instrumentation are available for the analysis of the three gases of interest as well for many other gases. The international trend is to no longer use gas and mist absorbing tubes with low flow pumps and to rather use more advanced air quality monitoring instrumentation.

Upon further inspection of the sampling equipment on the site, it was noticed that there were only two sampling units and not four as was required, which does not correspond to the sampling analysis provided by the consultants. The sampling units were also placed at a distance of 20m from the ponds and not at 500m and 200m as was required by the government institution. The relevance of the sampling analysis once again is in question as the sampling distances differ substantially.

To obtain proper ambient air analysis measurements of the ambient air directly above the waters surface is required for accurate modelling, which may have been obtained with the use of portable instruments. Unfortunately, again this advice was ignored by the consultants.

The independent consultants used by Company X indicated a total lack of knowledge and interest in the ambient air analysis of the EESS ponds as was indicated by the equipment used and the approach to the methodology that was required. Nonetheless the results were used and an emission rate was calculated for input into the model[1] by using the gas concentrations provided by the consultants and multiplying by the total volume per time sampled. This will give the units of mass per time. TAPM only required the gas concentration as an input.

It was noticed that the corrosive effects of the gases differ on different metals. HCl wet was noticed to be corrosive on 304L steel effected 316L steel very poorly. 304L steel, mild steel has excellent resistance to ammonia at the temperature range during the study, with 316L and zinc exhibiting corrosion. Ammonia must be in the aqueous form for corrosion to take place. HCl dry was identified to be more corrosive as temperature increases, with mild steel exhibiting the more resistance to HCl dry. H_2S was identified to have poor corrosive effects with the metals in the study at the temperature range of 293 to 308 K during the study.

6.1 TAPM / WATER RELATION

The air analysis nevertheless provided a baseline for the Modelling on TAPM and Hawke models. The water analysis was compared with the actual air analysis to provide a relation between the concentration of the chemical compounds in the water which would evaporate and form the relevant chemical gases of interest.

Due to the sampling points of the air analysis not being directly above the water surface of the ponds, a direct relation to the specific pond can not be observed and therefore the averages of the compounds in the 4 ponds are used. A relation between the water compound concentration and the air concentration was established.

Table 8: Water/air compound concentration relation

Compound (water)	**Concentration mg/l (pond)**	**Compound (air)**	**Concentration µg/m^3 (air)**
Chloride	69 202,5	HCL	9.838
Sulphate	35 017,16	H_2S	313.794
NH_4	140.41	NH_3	1.148
• The ammonia and hydrochloric acid mist concentrations were generally below the detection limit for most samples taken • The detection limit was not provided by the consultants			

From the above table the general assumption that the above water concentrations will give the above air concentrations. The above (table 8) air concentrations and the results from TAPM were almost exact at a distance of 30000m from the source. At a distance of 400m TAPM indicated that the gas concentrations maximums were about 2.5 times larger. Generally TAPM's results indicated the same concentration values at the different distances. The concentration of the gases that should have been predicted by TAPM should show a trend of decreasing concentration with an increase in distance from the source.

TAPM is recommended for when the horizontal radius of influence lies between 5000m and 30000m with 20000m being a typical value flat terrain (Hurley, 2002). The gas concentration maximums values are therefore much larger because of this limitation of TAPM, as it is not able to process the terrain accurately and also not able to use the meteorological data as effectively.

It is also identified that at 30000m the concentration of NH_3, and remains constant over time and there is a slight peak in the H_2S concentration approximately every 24h with HCL having peaks at approximately 35h and 72h. This increase is seen to happen at the early hours of the morning when the surface air is denser. At 3100m only the ammonia concentration remains constant over time, with the HCL, H_2S concentrations varying over time. The concentrations of these gases reach a maximum approximately every 24h. There is a significant decline in the graph of H_2S at 3100m which could be attributed to the bypass acid stream having an influence at this time.

At 1100m the HCL concentration exhibits peaks, with the maximum concentration occurring approximately every 24h. The H_2S concentration follows the same trend as the HCL concentration at 3100m and the initial downward spike is attributed to the bypass stream which has a significantly lower concentration of sulphate. The ammonia concentration remains constant with only two peaks at 48 and 72h which may be attributed to the higher concentration of the bypass stream during that specific time.

At 400m from the source the ammonia concentration peaks approximately every 24h. The HCL concentrations display peaks over the time period with two CLOC peaks. H_2S displayed two CLOC peaks with a slight decrease at the beginning of the study. A full detailed comparison with the modelling results and the water concentrations was not possible due to the lack of information provided by Company X with regards to the process. Information on when effluent was pumped into the ponds and the analysis of the streams at that time would be required to properly relate the modelled results to the water concentrations. The simulation peaks obtained from TAPM may be attributed to the general process operations and surface wind directions and speeds. A higher gas concentration would be observed during pond top up from the process, exhibiting a higher peak and during low wind speeds and direction there would be a lack of gas dispersion resulting in higher gas concentration peaks.

The plume of a pollution source is an integral part of air quality modelling as it shows where the major pollutants are dispersing to or over. An indication of where the problems may occur is therefore provided so that possible remediation or preventative action may occur. According to TAPM the entire area for 30000m is observes the same pollution concentration even if the wind blows in only one direction. This is another limitation of TAPM and therefore is not as good a model for air quality dispersion modelling.

The sampling of the ambient air was performed on the 23rd, 24th and 25th of November 2004. The water sample from the ponds was only received by the chemical labs on the 2nd of December 2004. No information on whether a sample from each pond was taken on each day of the ambient air sampling, or whether a number of once off samples where taken on one day. It is important to have a water analysis for the three days of study to be able to correlate correctly the ambient concentrations to the water concentrations.

Upon consultation with an experienced water analysis consultant it was advised that the water should be profiled from the bottom up. This is required to accurately determine the actual concentration of the various pollutants at the various layers in the water. From the information provided by the labs it is evident that the water was not profiled at all. No information on the equipment used to extract a sample of water was provided or the method used to extract the water sample from the ponds.

The equipment used would greatly affect the representativeness of the sample. Ideally low flow pumps and high quality bladders should be used and the sample should be taken at the centre of the ponds as well as where the feed stream enters the ponds. If such parameters where not used then the water analysis from the chemical lab is questionable.

6.2 INTERNATIONAL BEST PRACTICE

Unfortunately there is not specific base line international best practice on EESS ponds. A general requirement for waste water bodies are that they be lined to prevent leaching into the underground water compartments (EPA, 1995). Company X’s EESS ponds are double lined and are fitted with leak detection equipment (Addendum to scoping report, 2003). The EESS ponds water level is kept at an approximate 3m with the total depth of the pond being approximately 4-5m. This extra 1.5m above the water surface also provides a safety measure in case of extreme rain (Storm water BP, 1999). Therefore Company X complies with international best practice with regards to the design of the ponds.

The international best practise for the analysis of ambient air does not involve the use of gas and mist absorbing tubes with low flow sampling pumps. Fixed air quality monitoring stations which use electrochemical cells or gas chromatography or laser analysis are the current international best practice instruments. These instruments have various accreditations such as TUV, MCERT’s and many other different types of accreditation which enables the user to have the utmost confidence that the results obtained from these types of instruments are extremely accurate and there is no need to always use a chemical laboratory.

Portable analysers are also greatly used internationally dew to their ease of use as well as the quality of the results, with the convenience of being able to move the instrument around and use it in different applications. Most portable instruments use electrochemistry to obtain concentration results which allows for simple maintenance.

The international best practice with regards to water analysis is to properly profile the water from bottom to top by using low flow pumps. These pumps are used because the water turbidity is kept at a minimum, which is very important when obtaining a sample from the bottom of a water body. High quality bladders for the retention of the water sample are also required, and ideally the water sample should be analysed in a laboratory within 1 day to prevent possible chemical reactions.

International best practice was not adhered to when the sampling of the ambient air was undertaken and since no information was provided with the water sampling analysis it is not possible to comment of whether international best practice was adhered to.

CHAPTER 7

RECOMMENDATIONS

To provide a descriptive ambient air quality analysis of a large water body to then model the results and then further relate the gaseous air concentrations to the water concentrations the following recommendations are given:

1. A complete profile of the water from the bottom to the top would be required to identify the various compositions at the various levels. The use of low flow pumps as well as high quality bladders are to be used. This is important so that the air concentrations can be related properly to the concentrations of the water and also, relate the concentrations to the process which feeds the water into the ponds. The water samples should then be taken to a lab for analysis as quickly as possible.

2. The equipment used to perform the air analysis must be of a high standard. The level of technology with regards to air quality analysis has greatly improved and real time data is now possible for ambient and stack emissions. A fixed monitoring station to be set up around the EESS ponds to measure the three gases of interest is recommended. A constant measurement of the gases will then be available for modelling, possible process modification and safety reasons.

3. To monitor on the surface of a water body it is required to obtain a sample of the air directly above the surface and not a certain distance away from the water. This greatly influences the concentration as well as the modelling results.

4. Due to the high level of certain gases in the proximity of the EESS ponds, it is recommended that people that work within the area of the ponds, carry gas detection instruments as a health precaution. The instruments should detect ammonia, hydrogen sulphide and oxygen[3]. A small portable instrument to measure HCL is not economically viable, therefore an oxygen sensor is recommended. If there is a pollutant gas in a specific area the

oxygen level would be lower than normal. The sensor will trigger an alarm indicating that there is a gas present in the air which could be harmful.

5. A detailed air monitoring campaign for the three gases should be performed, using this sampling campaign as a basis.

6. A corrosion study on the metals surrounding the ponds should also be conducted for Company X's reference

NOTES

[1] Independent consultants modelled the analysis data on the HAWK model.

[2] The TAPM model was supplied by the University of Pretoria.

[3] Instrumentation for this application may be obtained from GLA technologies.

[4] Consultation with Professor Hannes Rautenbach

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ANNEXURE 1

(Tables and Graphs)

Table 13: Weather station data

St No	Year	J.Day	Time	Wnd Spd (m/s)	Wnd Dir	Temp Deg C	Hum %	Pressure	Incomming radiation (W/m2)
110	2004	328	850	0	0	19.9	69.9	845	
110	2004	328	900	0.163	190.7	20.88	65.34	844	
110	2004	328	910	0.03	195.1	21.21	63.7	843	
110	2004	328	920	0.18	88.8	20.53	65.07	843	
110	2004	328	930	3.286	38.95	18.18	71.8	843	
110	2004	328	940	3.422	37.58	18.56	70.7	843	987.1
110	2004	328	1010	3.795	38.64	22.107	59.04	843	998.21
110	2004	328	1020	3.425	23.24	22.432	58.21	843	1027.7
110	2004	328	1030	3.627	37.48	22.533	60.7	843	1044.6
110	2004	328	1040	3.806	30.39	22.934	60.66	843	1120.2
110	2004	328	1050	3.751	51.25	23.432	61.75	842	1067.2
110	2004	328	1100	4.436	26.93	23.499	59.58	842	1087.4
110	2004	328	1110	3.867	35.71	23.675	59.28	842	964.73
110	2004	328	1120	4.502	30.17	23.638	59.21	842	1088.2
110	2004	328	1130	3.901	42.03	23.819	59.38	842	1104.2
110	2004	328	1140	3.941	24.26	24.194	53.55	842	928.1
110	2004	328	1150	3.588	38.93	23.999	54.72	842	1098.3
110	2004	328	1200	4.53	20.3	24.737	51.01	842	1099.4
110	2004	328	1210	4.517	38.64	24.887	47.42	841	1110.1
110	2004	328	1220	5.214	30.76	25.299	45.73	841	1100.7
110	2004	328	1230	5.076	32.26	25.427	48.98	841	905.86
110	2004	328	1240	5.226	22.82	25.697	46.45	841	933.62
110	2004	328	1250	6.383	8.16	25.917	42.35	841	1010
110	2004	328	1300	5.483	14.61	26.351	42.05	841	889.64
110	2004	328	1310	5.471	10.12	26.557	41.27	841	1063.9
110	2004	328	1320	6.075	8.84	26.52	39.68	841	1096.6
110	2004	328	1330	6.134	356.1	26.851	36.84	840	1123.8
110	2004	328	1340	6.267	347.8	27.323	35.1	840	1056
110	2004	328	1350	5.788	333.9	27.432	33.08	840	957.71
110	2004	328	1400	5.575	355.4	27.391	34.58	840	800.22
110	2004	328	1410	5.982	351.4	27.103	33.65	840	864.14
110	2004	328	1420	6.116	338.7	27.547	35.32	840	366.64
110	2004	328	1430	5.437	337.6	26.406	34.28	840	801.57
110	2004	328	1440	5.26	354.1	27.08	33.83	840	903.54
110	2004	328	1450	4.956	326.6	27.502	33.01	840	562.44
110	2004	328	1500	4.722	341.3	27.435	33.42	840	811.89
110	2004	328	1510	4.677	339.6	27.216	32.64	840	582.13
110	2004	328	1520	6.916	3.788	27.564	33.57	840	524.25
110	2004	328	1530	5.526	3.878	27.231	33.63	840	680.12
110	2004	328	1540	5.155	347.1	27.58	30.82	839	524.56
110	2004	328	1550	4.147	350.7	27.533	32.54	839	541.23
110	2004	328	1600	4.629	338.8	27.359	31.86	839	477.79
110	2004	328	1610	3.786	327.5	27.639	32.45	839	330.84
110	2004	328	1620	4.171	346.8	27.011	33.49	839	165.02
110	2004	328	1630	3.989	353	26.904	33.57	839	342.08

110	2004	328	1640	4.217	346.6	26.992	31.84	839	305.12
110	2004	328	1650	4.411	341	27.263	31.21	839	276.98
110	2004	328	1700	4.78	353.9	27.255	29.47	839	253.62
110	2004	328	1710	4.362	345.5	27.423	28.84	839	200.76
110	2004	328	1720	4.647	351.2	27.344	27.93	839	196.24
110	2004	328	1730	4.163	351.9	27.123	27.81	839	131.02
110	2004	328	1740	4.91	347.3	27.069	27.29	839	89.678
110	2004	328	1750	4.313	352.5	26.737	27.51	840	120.21
110	2004	328	1800	3.942	347.2	26.78	27.81	840	41.204
110	2004	328	1810	4.283	20.87	26.482	34.97	840	11.013
110	2004	328	1820	7.09	50.73	23.95	64.86	840	6.6442
110	2004	328	1830	7.77	52.92	22.102	76.2	840	5.929
110	2004	328	1840	7.29	50.11	21.758	75.1	841	-2.1631
110	2004	328	1850	7.5	57.26	21.299	74.5	841	-3.0384
110	2004	328	1900	6.251	53.81	21.016	74.4	841	-5.1922
110	2004	328	1910	6.013	55.23	20.742	75.6	841	-5.2015
110	2004	328	1920	5.879	59.6	20.383	72.2	841	-4.7827
110	2004	328	1930	5.214	53.62	20.091	69.91	841	-4.6394
110	2004	328	1940	4.12	54.65	19.805	70.4	841	-4.6898
110	2004	328	1950	3.915	52.38	19.667	70.9	841	-4.9838
110	2004	328	2000	3.635	52.73	19.517	71.4	841	-4.715
110	2004	328	2010	4.203	52.06	19.285	70.7	841	-4.5023
110	2004	328	2020	3.765	50.54	19.174	70.5	841	-4.5023
110	2004	328	2030	3.776	51.22	18.966	71.1	842	-4.4681
110	2004	328	2040	3.979	53.17	18.876	71.8	842	-4.1466
110	2004	328	2050	2.044	40.58	18.667	73.2	842	-4.5534
110	2004	328	2100	1.967	37.26	18.358	74.1	842	-4.3408
110	2004	328	2110	2.319	37.96	18.344	74.7	842	-4.0437
110	2004	328	2120	2.432	41.78	18.307	75.6	842	-3.7528
110	2004	328	2130	2.115	37.6	18.249	77.1	842	-3.3244
110	2004	328	2140	2.805	32.26	18.426	76.7	842	-2.8396
110	2004	328	2150	2.984	38.92	18.628	76.6	842	-3.0397
110	2004	328	2200	2.567	46.62	18.438	78.5	842	-2.924
110	2004	328	2210	3.869	32.56	18.447	76.6	842	-2.2735
110	2004	328	2220	4.009	34.08	18.851	75.3	842	-2.8551
110	2004	328	2230	4.103	32.49	18.823	74.9	842	-2.6581
110	2004	328	2240	4.718	20.32	18.811	74.7	842	-2.3235
110	2004	328	2250	3.964	345.7	18.698	74.3	842	-3.2335
110	2004	328	2300	3.648	345.9	18.247	75	843	-3.0147
110	2004	328	2310	2.955	335.5	18.169	75.1	843	-3.6968
110	2004	328	2320	2.194	328.7	18.066	76.7	843	-3.7127
110	2004	328	2330	2.266	330.6	17.908	76.8	843	-3.2374
110	2004	328	2340	2.427	297.9	18.087	74.4	843	-2.9842
110	2004	328	2350	2.729	270.3	18.272	72.9	843	-2.4493
110	2004	328	2400	2.329	271.4	18.613	70.3	843	-2.6401
110	2004	329	10	1.837	314.3	18.564	69.96	843	-2.9373
110	2004	329	20	1.638	291.2	18.531	67.64	843	-2.7652
110	2004	329	30	1.583	291.1	18.848	64.38	843	-2.7464
110	2004	329	40	1.382	332.2	18.993	64.62	843	-4.1572
110	2004	329	50	2.255	343.8	18.535	65.46	843	-3.8631

110	2004	329	100	2.501	351.7	18.207	66.42	843	-3.788
110	2004	329	110	1.916	357.3	18.114	66.13	843	-4.3823
110	2004	329	120	1.41	6.333	17.827	67.22	842	-4.4261
110	2004	329	130	1.142	357.7	17.833	67.42	842	-5.3614
110	2004	329	140	0.616	334.6	17.42	67.89	842	-5.9369
110	2004	329	150	0.33	24.34	17.378	68.47	842	-4.889
110	2004	329	200	1.222	95.1	17.538	71.3	842	-3.6378
110	2004	329	210	1.816	89.7	17.133	76.3	842	-3.4845
110	2004	329	220	1.578	78	16.907	81.2	842	-3.8848
110	2004	329	230	0.899	93.2	16.717	79.6	842	-3.9661
110	2004	329	240	1.02	106.9	16.687	78.1	842	-3.4907
110	2004	329	250	1.117	85.6	16.766	79.1	842	-3.3249
110	2004	329	300	1.512	59.09	16.64	79.2	842	-3.3033
110	2004	329	310	1.482	65.76	16.469	80.4	842	-3.5727
110	2004	329	320	1.435	46.84	16.248	82.9	842	-3.698
110	2004	329	330	1.505	44.24	15.869	85.1	842	-3.2758
110	2004	329	340	1.916	57.69	15.751	86.7	842	-3.1475
110	2004	329	350	1.993	58.29	15.716	87.5	842	-3.4041
110	2004	329	400	2.288	61.79	15.539	87.3	842	-3.1194
110	2004	329	410	2.71	62.13	15.543	87.3	842	-2.916
110	2004	329	420	3.22	55.11	15.63	86.2	843	-2.9973
110	2004	329	430	2.807	61.28	15.589	86.5	843	-3.0099
110	2004	329	440	2.208	59.04	15.532	87.2	843	-3.5449
110	2004	329	450	2.312	56.13	15.314	88	843	-2.9222
110	2004	329	500	2.338	61.81	15.204	89	843	-1.3454
110	2004	329	510	2.512	67.38	15.258	90.2	843	2.4748
110	2004	329	520	2.948	63.35	15.389	91	843	11.076
110	2004	329	530	2.501	48.99	15.45	91.1	843	35.642
110	2004	329	540	2.416	45.78	15.126	91.4	843	67.887
110	2004	329	550	3.225	49.53	15.205	91.1	843	98.548
110	2004	329	600	3.257	45.61	15.419	90.8	843	129.37
110	2004	329	610	3.111	47.35	15.689	90.1	843	160.91
110	2004	329	620	3.234	55.1	16.032	89.5	843	198.68
110	2004	329	630	2.69	50.06	16.252	88.6	843	231.25
110	2004	329	640	3.048	52.53	16.717	87.7	844	263.49
110	2004	329	650	3.647	49.23	16.979	87.4	844	335
110	2004	329	700	3.454	51.12	17.341	86.9	844	299.18
110	2004	329	710	3.39	43.41	17.728	86.5	844	285.73
110	2004	329	720	3.514	53.88	18.041	85.2	844	274.79
110	2004	329	730	3.797	38.26	18.755	83.1	844	279.03
110	2004	329	740	3.498	32.43	18.966	81.6	844	287.3
110	2004	329	750	3.824	31.87	19.409	78.6	844	303.54
110	2004	329	800	4.208	29.35	19.83	77.1	844	448.7
110	2004	329	810	4.265	25.94	20.217	75.7	844	463.38
110	2004	329	820	3.413	12.49	20.4	74	844	442.14
110	2004	329	830	4.43	8.06	20.684	72.3	844	772.45
110	2004	329	840	4.737	3.164	21.36	70.1	844	738.43
110	2004	329	850	5.033	4.217	21.518	67.89	844	830.89
110	2004	329	900	5.038	13.92	21.552	65.43	844	933.85
110	2004	329	910	4.093	356.7	22.154	64.1	844	933.97

110	2004	329	920	4.317	2.118	22.19	63.66	844	532.39
110	2004	329	930	4.616	7.32	21.782	61.76	844	669.39

110	2004	329	940	3.82	7.69	22.145	59.96	844	976.3
110	2004	329	950	4.169	9.12	22.841	59.13	844	989.36
110	2004	329	1000	4.435	1.561	23.169	58.57	844	834.07
110	2004	329	1010	3.939	355.1	23.134	56.52	844	977.75
110	2004	329	1020	4.701	355.5	23.586	54.72	844	1112
110	2004	329	1030	4.745	0.133	23.928	53.13	844	1066.8
110	2004	329	1040	3.941	359.8	23.945	53.26	844	772.18
110	2004	329	1050	3.69	337	24.052	48.89	844	894.94
110	2004	329	1100	4.054	343.7	24.379	50.65	844	1109.3
110	2004	329	1110	3.82	346.5	24.607	46.86	844	985.32
110	2004	329	1120	3.013	359.9	24.797	47.45	844	1084.6
110	2004	329	1130	4.421	351.4	25.144	41.24	844	1114.4
110	2004	329	1140	3.746	335.7	25.361	37.53	843	1131.9
110	2004	329	1150	2.605	353.2	25.66	38.22	843	968.39
110	2004	329	1200	3.823	23.8	25.646	42.59	843	1041.3
110	2004	329	1210	3.522	341.4	25.564	38.16	843	1108.2
110	2004	329	1220	3.946	10.53	26.336	36.85	843	1091.7
110	2004	329	1230	3.904	15.81	26.665	36.83	843	1085.2
110	2004	329	1240	4.43	341.9	26.459	35.61	843	766.26
110	2004	329	1250	3.829	13.59	26.646	35.19	843	1037.7
110	2004	329	1300	4.052	345.5	26.433	33.67	843	1086.6
110	2004	329	1310	4.269	350.6	26.83	33.17	843	1090.4
110	2004	329	1320	3.573	344.1	26.949	32.22	843	1051.7
110	2004	329	1330	4.593	356	27.5	32.19	842	422.52
110	2004	329	1340	3.964	2.874	27.025	33.13	842	425.75
110	2004	329	1350	3.671	11.68	26.528	33.45	842	389.01
110	2004	329	1400	3.552	26.05	26.368	33.71	842	945.01
110	2004	329	1410	4.152	12.6	27.309	31.91	842	474.5
110	2004	329	1420	3.428	9.22	27.314	32.34	842	885.25
110	2004	329	1430	5.109	356.6	27.726	30.82	842	706.22
110	2004	329	1440	3.99	330.8	27.645	30.29	842	418.76
110	2004	329	1450	3.374	13.21	27.415	31.15	842	409.83
110	2004	329	1500	3.385	20.22	27.195	31.55	842	643.36
110	2004	329	1510	4.183	350.4	27.832	30.5	842	772.99
110	2004	329	1520	4.468	354.2	27.939	30	842	655.3
110	2004	329	1530	4.668	353.8	28.297	30.21	841	213.9
110	2004	329	1540	2.301	29.67	27.362	31.15	841	513.59
110	2004	329	1550	1.977	38.82	27.442	30.44	841	598.64
110	2004	329	1600	4.868	340.3	28.291	29.5	841	529.76
110	2004	329	1610	4.202	355.1	28.003	29.84	841	493.94
110	2004	329	1620	4.265	358.8	28.43	29.76	841	446.86
110	2004	329	1630	5.209	10.19	28.222	30.58	841	379.35
110	2004	329	1640	4.946	358.6	28.061	29.79	841	372.03
110	2004	329	1650	4.778	357	28.028	29.38	841	332.63
110	2004	329	1700	4.103	7.28	28.004	29.44	841	292.81
110	2004	329	1710	4.204	2.24	27.923	29.29	841	250.17
110	2004	329	1720	4.513	358.1	28.023	29.2	841	212.65
110	2004	329	1730	4.726	0.508	27.748	29.81	841	176.36

110	2004	329	1740	4.056	8.11	27.698	30.96	841	139.78
110	2004	329	1750	3.567	9.05	27.471	31.41	841	106.05
110	2004	329	1800	4.169	0.44	27.371	30.42	841	76.329
110	2004	329	1810	3.382	1.825	27.242	30.83	841	45.654
110	2004	329	1820	3.549	3.258	26.858	30.89	841	23.683
110	2004	329	1830	3.307	3.598	26.5	32.27	842	5.4253
110	2004	329	1840	3.313	7.55	26.272	32.5	842	-1.4377
110	2004	329	1850	2.894	12.49	26.021	33.07	842	-5.1762
110	2004	329	1900	2.34	27.84	25.783	35.41	842	-7.4741
110	2004	329	1910	1.988	32.95	24.922	38.58	842	-7.7493
110	2004	329	1920	1.596	20.94	24.718	38.08	842	-6.9834
110	2004	329	1930	1.673	355.7	24.612	35.79	842	-7.6711
110	2004	329	1940	1.593	348.3	24.038	37.26	842	-7.9336
110	2004	329	1950	1.443	334.1	23.509	39.35	842	-8.9588
110	2004	329	2000	0.776	339.1	22.747	40.13	842	-8.0402
110	2004	329	2010	0.841	44.1	22.753	45.31	843	-7.0657
110	2004	329	2020	0.587	119.2	22.408	48.75	843	-6.8128
110	2004	329	2030	0.807	130.9	21.826	48.07	843	-6.4565
110	2004	329	2040	0.148	15.51	21.879	43.8	843	-6.7254
110	2004	329	2050	0.79	79.3	21.882	51.7	843	-4.543
110	2004	329	2100	0.699	100.2	21.792	52.39	843	-4.6868
110	2004	329	2110	0.116	93.7	21.764	50.09	843	-5.1777
110	2004	329	2120	0.919	52.2	21.612	54.65	843	-4.8091
110	2004	329	2130	1.173	74.2	21.394	61.14	843	-4.1685
110	2004	329	2140	1.433	71.8	21.484	60.84	843	-3.9967
110	2004	329	2150	1.643	58.88	21.226	63.03	843	-4.2689
110	2004	329	2200	1.721	49.01	20.977	60.95	843	-4.5597
110	2004	329	2210	1.225	25.86	20.21	62.94	844	-5.2258
110	2004	329	2220	1.428	49.77	19.775	63.77	844	-3.8936
110	2004	329	2230	1.468	40.97	20.581	63.68	844	-3.8654
110	2004	329	2240	0.919	40	20.44	65.5	844	-4.6065
110	2004	329	2250	0.87	40.02	20.448	66.35	844	-4.9255
110	2004	329	2300	0.416	2.425	20.15	67.15	844	-5.6573
110	2004	329	2310	0.671	353.2	19.912	68.99	844	-4.0623
110	2004	329	2320	0.738	28.6	19.981	70.4	844	-4.0685
110	2004	329	2330	0.051	47.96	19.963	71.2	844	-4.0998
110	2004	329	2340	0	0	19.602	72.6	844	-3.5775
110	2004	329	2350	0.504	156.5	19.491	73.3	844	-3.6933
110	2004	329	2400	0.908	190.8	19.045	74	843	-3.3713
110	2004	330	10	0.695	193.6	18.862	73.7	843	-3.7439
110	2004	330	20	0.432	199.6	18.415	74.6	843	-3.9443
110	2004	330	30	1.01	189.6	18.266	75.9	843	-3.3751
110	2004	330	40	1.543	191.1	17.961	77	844	-2.7871
110	2004	330	50	1.813	210.5	17.981	77	844	-3.3908
110	2004	330	100	0.928	213.5	17.819	77.7	844	-5.0894
110	2004	330	110	0.259	34.01	17.347	80.8	844	-4.348
110	2004	330	120	0.653	13.74	17.436	84.4	844	-3.5722
110	2004	330	130	0.148	10.95	17.646	83.9	844	-3.7536
110	2004	330	140	0	0	17.704	80.5	844	-3.8037
110	2004	330	150	0.348	110.5	17.484	79.1	844	-5.1174

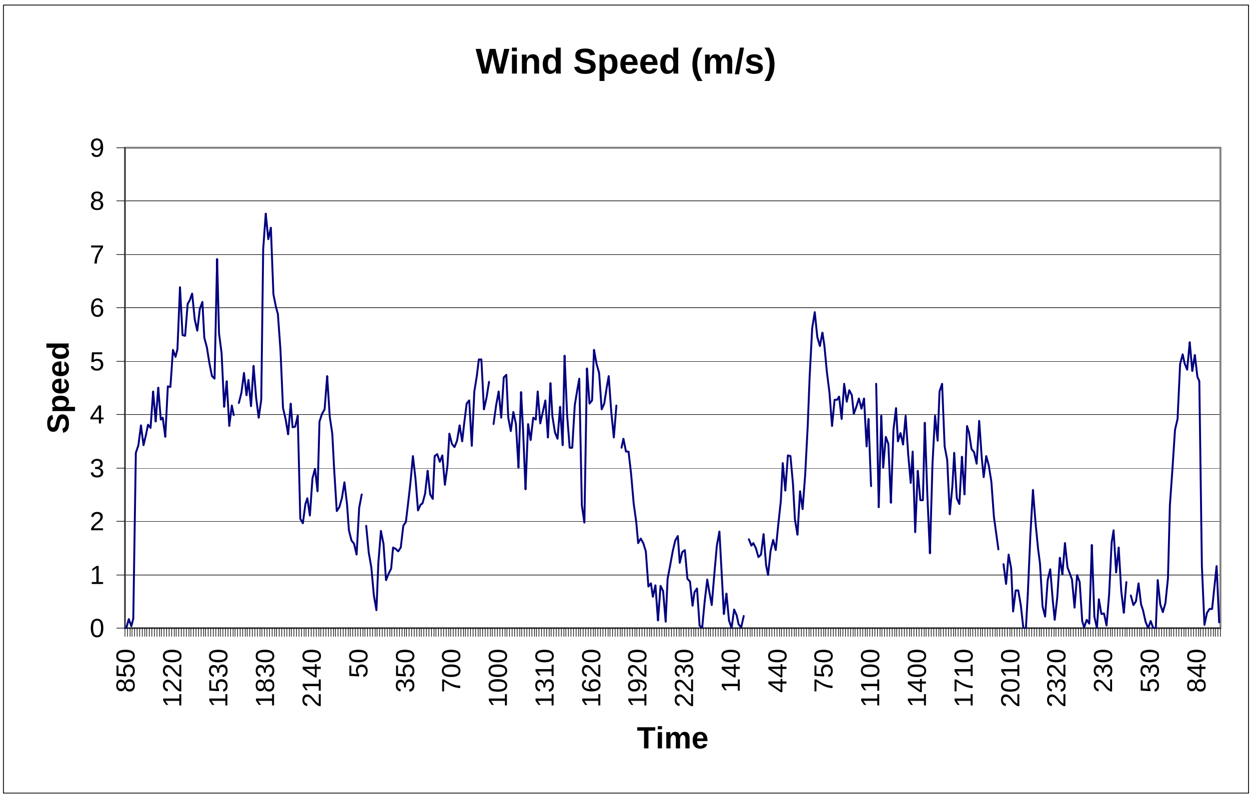
110	2004	330	200	0.24	143.3	17.092	80.2	844	-4.4574
110	2004	330	210	0.068	119.8	17.168	81.9	843	-5.0048
110	2004	330	220	0.007	101.8	16.755	84.3	843	-4.6575
110	2004	330	230	0.227	93.1	16.332	85	843	-4.0413
110	2004	330	240	1.661	82.3	16.637	86.1	843	-1.0134
110	2004	330	250	1.551	74.8	17.521	88	843	-1.5389
110	2004	330	300	1.595	76.4	17.18	90.2	843	-1.6891
110	2004	330	310	1.498	76.8	17.244	90.7	844	-2.1113
110	2004	330	320	1.331	68.35	17.39	91.3	844	-2.2521
110	2004	330	330	1.382	61.51	17.355	92.1	844	-2.2521
110	2004	330	340	1.758	53.99	17.252	92.5	844	-2.6649
110	2004	330	350	1.18	53.17	17.006	92.9	844	-3.2686
110	2004	330	400	1	51.86	16.879	93.4	844	-3.0935
110	2004	330	410	1.454	46.88	16.884	94.7	844	-2.6868
110	2004	330	420	1.651	38.51	16.776	95.2	844	-2.9652
110	2004	330	430	1.46	34.32	16.57	96.2	844	-2.5461
110	2004	330	440	1.943	34.16	16.783	96	844	-2.252
110	2004	330	450	2.389	29.38	16.883	96.2	844	-1.6797
110	2004	330	500	3.086	28.07	16.997	96.1	844	-0.26587
110	2004	330	510	2.578	29.12	17.126	96.6	844	3.6377
110	2004	330	520	3.234	29.35	17.104	96.4	844	14.313
110	2004	330	530	3.222	32.34	17.106	96	844	40.684
110	2004	330	540	2.699	40.48	17.208	95.3	844	66.977
110	2004	330	550	2.041	39.81	17.086	95.1	844	96.051
110	2004	330	600	1.751	33.65	16.943	94.9	844	128.98
110	2004	330	610	2.568	31.48	17.123	95	844	151.33
110	2004	330	620	2.229	37.84	17.53	94.3	844	188.83
110	2004	330	630	2.862	40.06	17.885	93.3	844	241.05
110	2004	330	640	3.791	40.96	18.199	92.5	845	260.18
110	2004	330	650	4.704	31.61	18.699	90.8	845	279.02
110	2004	330	700	5.621	26.11	18.938	90.7	845	264.54
110	2004	330	710	5.922	22.6	18.904	90.8	845	217.24
110	2004	330	720	5.449	14.2	18.791	90.7	845	195.61
110	2004	330	730	5.29	26.05	18.657	90.6	845	369.49
110	2004	330	740	5.538	27.73	19.057	89	845	378.29
110	2004	330	750	5.294	12.46	19.272	86.9	845	592.13
110	2004	330	800	4.798	23.8	19.775	85.1	845	537.1
110	2004	330	810	4.416	4.111	20.423	83.5	845	483.43
110	2004	330	820	3.781	9.87	20.341	82.1	845	606.39
110	2004	330	830	4.278	7.32	20.858	79.6	845	690.52
110	2004	330	840	4.28	349.5	21.745	76.6	845	740.08
110	2004	330	850	4.334	344.7	22.241	74.2	845	772.03
110	2004	330	900	3.918	343.4	22.469	72.5	845	809.75
110	2004	330	910	4.577	350.4	22.973	70.3	845	841.24
110	2004	330	920	4.246	345.9	23.379	68.77	845	849.89
110	2004	330	930	4.457	2.492	23.718	67.29	845	887.88
110	2004	330	940	4.366	352.9	24.424	63.2	845	920.27
110	2004	330	950	4.016	1.296	24.719	60.64	845	936.68
110	2004	330	1000	4.15	352	25.578	58.14	845	954.37
110	2004	330	1010	4.302	353.3	25.39	58.04	845	968.13

110	2004	330	1020	4.116	341.3	25.798	51.72	845	1000.1
110	2004	330	1030	4.302	348.4	26.332	46.44	845	1016
110	2004	330	1040	3.4	5.035	26.608	45.26	845	1021.9
110	2004	330	1050	3.919	354.1	27.016	42.23	845	1042.3
110	2004	330	1100	2.661	336.2	27.37	42.17	845	1044.5
110	2004	330	1110	4.574	351.3	27.509	37.91	845	1056.5
110	2004	330	1120	2.27	352.6	27.94	33.15	845	1050
110	2004	330	1130	3.975	330.3	27.989	35.39	845	1060.2
110	2004	330	1140	3.008	336.8	28.111	32.64	845	1072.6
110	2004	330	1150	3.581	342	28.137	32.46	845	1078.4
110	2004	330	1200	3.45	335.6	28.512	30.5	844	1075.5
110	2004	330	1210	2.35	288.7	28.878	30.3	844	1057.6
110	2004	330	1220	3.717	302.9	29.551	31.1	844	1048.8
110	2004	330	1230	4.126	342.2	29.377	31.57	844	1058.7
110	2004	330	1240	3.5	317.5	29.594	30.93	844	1050.6
110	2004	330	1250	3.658	318.3	30.254	30.04	844	1040.7
110	2004	330	1300	3.436	346.3	29.913	30.26	844	1032.9
110	2004	330	1310	3.976	308.3	30.219	29.48	844	1022.5
110	2004	330	1320	3.265	295.2	30.246	29.46	843	990.02
110	2004	330	1330	2.718	357.4	30.039	29.3	843	975.16
110	2004	330	1340	3.304	314	30.475	25.79	843	829.2
110	2004	330	1350	1.799	320.8	31.188	24.43	843	931.45
110	2004	330	1400	2.953	328.2	31.015	23.32	843	911.65
110	2004	330	1410	2.396	296	31.295	22	843	887.26
110	2004	330	1420	2.395	295.1	31.466	20.99	843	884.77
110	2004	330	1430	3.85	283.5	31.926	20.39	843	846.66
110	2004	330	1440	2.483	292.8	32.012	20.41	843	799.7
110	2004	330	1450	1.397	242.5	32.017	20.69	842	767.94
110	2004	330	1500	3.083	274.5	31.92	20.96	842	759.32
110	2004	330	1510	3.981	294	31.966	19.96	842	720.44
110	2004	330	1520	3.507	300.3	32.037	19.39	842	686.75
110	2004	330	1530	4.44	293.2	32.402	19.91	842	659.1
110	2004	330	1540	4.574	299.9	32.134	18.85	842	606.54
110	2004	330	1550	3.405	332	32.31	21.35	842	570.66
110	2004	330	1600	3.147	334.7	31.996	23.79	842	537.26
110	2004	330	1610	2.131	328.9	31.356	24.22	842	506.18
110	2004	330	1620	2.65	317.7	31.942	18.96	842	449.52
110	2004	330	1630	3.279	295.8	32.368	17.57	842	412.45
110	2004	330	1640	2.437	309	32.256	18.35	842	375.99
110	2004	330	1650	2.32	321.5	32.166	18.53	842	341.42
110	2004	330	1700	3.211	336.6	32.093	19.3	842	304.36
110	2004	330	1710	2.507	318.2	32.072	18.9	842	256.98
110	2004	330	1720	3.784	332.6	31.858	21.6	842	220.92
110	2004	330	1730	3.669	349.9	31.581	24.68	842	188.14
110	2004	330	1740	3.36	1.164	31.032	25.48	842	153.37
110	2004	330	1750	3.296	6.838	31.123	25.03	842	117.48
110	2004	330	1800	3.076	358.9	30.928	26.42	842	81.623
110	2004	330	1810	3.888	7.73	30.301	27.91	843	52.983
110	2004	330	1820	3.193	15.28	30.05	28.68	843	24.612
110	2004	330	1830	2.823	16.99	29.597	29.98	843	5.996

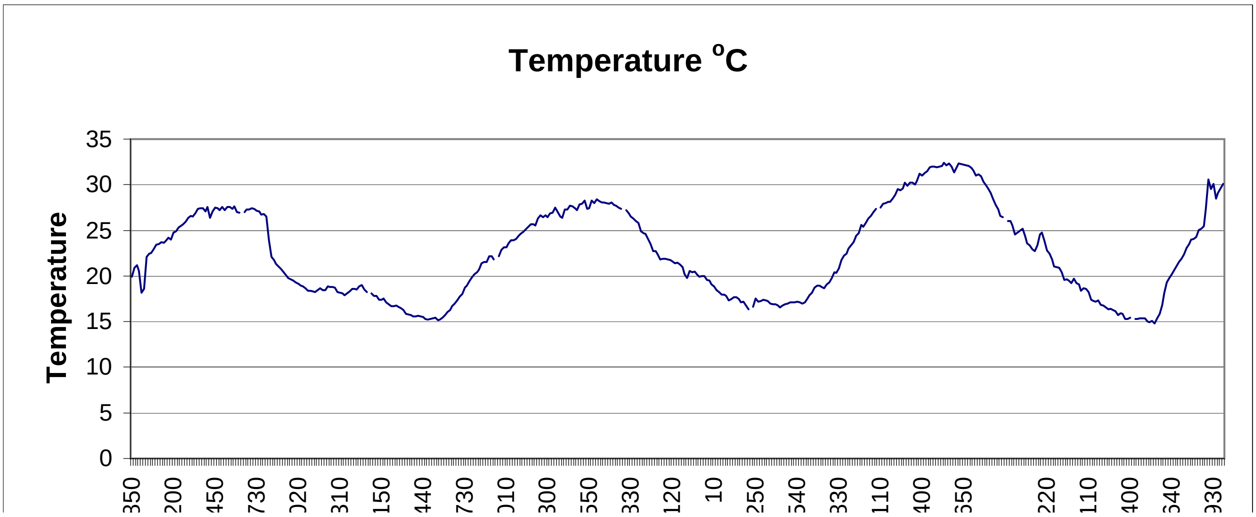
110	2004	330	1840	3.227	358	29.101	29.3	843	-2.5496
110	2004	330	1850	3.049	352.1	28.387	30.94	843	-6.8805
110	2004	330	1900	2.74	353.9	27.751	31.84	843	-7.8156
110	2004	330	1910	2.083	349.6	27.303	33.66	843	-8.6005
110	2004	330	1920	1.734	344.7	26.592	34.72	843	-8.1069
110	2004	330	1930	1.469	337.1	26.449	35.68	843	-8.3662
110	2004	330	1940	1.198	355.4	26.038	35.75	843	-7.3442
110	2004	330	1950	0.826	47.99	26.051	38.16	843	-6.807
110	2004	330	2000	1.381	150.6	25.55	44.95	844	-7.2392
110	2004	330	2010	1.116	175.3	24.576	45.27	844	-6.3456
110	2004	330	2020	0.312	178.3	24.79	44.09	844	-7.2647
110	2004	330	2030	0.71	53.62	24.972	43.56	844	-5.311
110	2004	330	2040	0.708	65.76	25.176	49.85	844	-6.802
110	2004	330	2050	0.437	66.73	24.335	55.14	844	-7.4553
110	2004	330	2100	0	0	23.581	51.49	844	-6.4521
110	2004	330	2110	0	0	23.374	50.72	844	-6.5902
110	2004	330	2120	0.644	198.8	22.958	49.47	845	-5.5746
110	2004	330	2130	1.753	222.3	22.73	47.13	845	-3.1517
110	2004	330	2140	2.592	233.7	23.329	41.77	845	-1.5977
110	2004	330	2150	1.974	255.6	24.529	37.23	845	-3.1736
110	2004	330	2200	1.492	302.7	24.747	37.39	845	-3.8458
110	2004	330	2210	1.213	307.1	23.845	39.63	845	-5.3466
110	2004	330	2220	0.403	313	22.764	45.38	845	-7.8509
110	2004	330	2230	0.21	305.5	22.41	47.65	845	-7.9322
110	2004	330	2240	0.901	341.4	21.823	53.68	845	-7.4632
110	2004	330	2250	1.1	318.9	21.056	54.39	845	-7.0723
110	2004	330	2300	0.518	316.2	20.973	53.52	845	-6.1004
110	2004	330	2310	0.152	206.5	20.876	53.55	845	-6.9517
110	2004	330	2320	0.572	31.83	20.431	55.13	845	-7.3867
110	2004	330	2330	1.315	325.2	19.588	57.26	845	-6.3548
110	2004	330	2340	1.008	328.7	19.631	63.97	845	-4.9412
110	2004	330	2350	1.596	327.3	19.473	62.71	845	-4.2594
110	2004	330	2400	1.136	341.9	19.239	62.91	844	-4.3657
110	2004	331	10	1.045	351.8	19.716	66.8	844	-5.0975
110	2004	331	20	0.911	320.9	19.231	69.37	844	-6.4015
110	2004	331	30	0.388	324.5	19.05	66.34	844	-7.5116
110	2004	331	40	0.989	339.1	18.41	64.88	844	-4.7096
110	2004	331	50	0.866	334.4	18.658	61.11	844	-4.3
110	2004	331	100	0.133	334.9	18.618	61.97	844	-5.7236
110	2004	331	110	0.01	334.9	18.205	64.64	844	-6.969
110	2004	331	120	0.16	325.4	17.415	67.1	844	-6.916
110	2004	331	130	0.085	292.8	17.258	63.15	844	-4.4481
110	2004	331	140	1.562	38.08	17.205	68.71	844	-3.2813
110	2004	331	150	0.21	84.4	17.296	72.6	844	-5.6242
110	2004	331	200	0	0	16.857	73.2	844	-5.2926
110	2004	331	210	0.541	341.3	16.759	74.7	844	-4.9798
110	2004	331	220	0.266	85.1	16.584	75.4	844	-4.62
110	2004	331	230	0.28	12.21	16.37	76	844	-4.1821
110	2004	331	240	0.043	34.17	16.44	77.3	844	-3.8974
110	2004	331	250	0.623	139.1	16.28	79.1	844	-2.4617

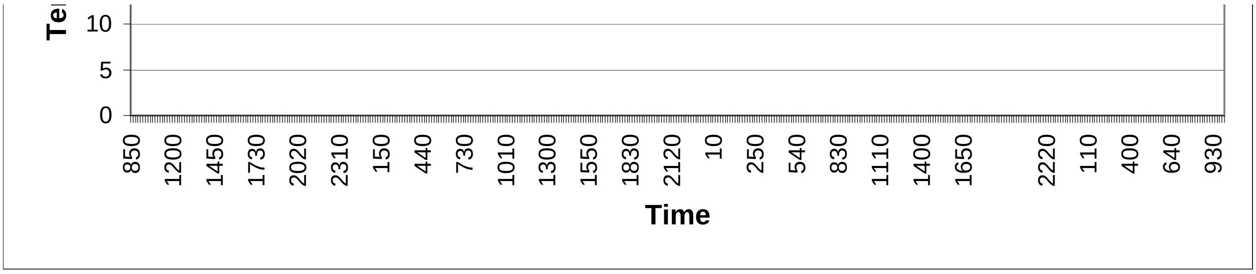
110	2004	331	300	1.609	179	16.13	80.2	844	-2.9371
110	2004	331	310	1.829	213	15.679	78.1	844	-3.1122
110	2004	331	320	1.042	200.1	15.91	75	844	-3.1936
110	2004	331	330	1.504	205.2	15.82	75.7	844	-3.81
110	2004	331	340	0.692	209.4	15.283	76.2	844	-4.9648
110	2004	331	350	0.285	191	15.271	75.5	844	-3.77
110	2004	331	400	0.86	187.9	15.44	75.8	844	-3.72
110	2004	331	410	0.608	169.6	15.274	75.9	844	-3.1819
110	2004	331	420	0.434	180.9	15.323	75.3	844	-3.1819
110	2004	331	430	0.501	168.7	15.364	72.4	845	-2.8972
110	2004	331	440	0.833	168.7	15.384	71.1	845	-2.4905
110	2004	331	450	0.448	123.1	15.383	70.6	845	-3.5542
110	2004	331	500	0.333	287.4	15.01	73.5	845	-1.2984
110	2004	331	510	0.116	195.3	14.972	71.6	845	2.1431
110	2004	331	520	0	0	15.049	72.1	845	10.666
110	2004	331	530	0.135	76	14.804	77.3	845	31.784
110	2004	331	540	0	0	15.362	77.9	845	60.023
110	2004	331	550	0	0	15.864	77	845	93.276
110	2004	331	600	0.893	57.34	16.855	77.8	846	128.76
110	2004	331	610	0.439	66.84	18.07	70.9	846	161.41
110	2004	331	620	0.298	37.92	19.295	65.25	846	198.87
110	2004	331	630	0.472	359.6	19.774	62.93	846	236.31
110	2004	331	640	0.939	23.29	20.17	62.45	846	274.42
110	2004	331	650	2.305	49.98	20.695	64.09	846	314.94
110	2004	331	700	2.988	48.53	21.046	64.31	846	357.03
110	2004	331	710	3.712	38.92	21.567	64.31	846	399.86
110	2004	331	720	3.916	35.51	21.908	63.49	846	435.59
110	2004	331	730	4.949	35.75	22.34	62.69	847	474.54
110	2004	331	740	5.128	37.32	23.087	62.21	847	510.15
110	2004	331	750	4.961	25.25	23.473	61.22	847	547.71
110	2004	331	800	4.845	35.49	24.004	60.46	847	586.44
110	2004	331	810	5.352	32.4	24.03	59.4	847	623.01
110	2004	331	820	4.82	26.77	24.284	58.31	847	651.7
110	2004	331	830	5.114	14.76	25.007	57.02	847	683.76
110	2004	331	840	4.705	11.97	25.212	55.87	847	715.83
110	2004	331	850	4.629	10	25.482	54.77	847	740.14
110	2004	331	900	1.158	88.4	27.324	48.73	847	
110	2004	331	910	0.059	69.88	30.593	41.66	847	
110	2004	331	920	0.282	10.19	29.512	43.94	847	
110	2004	331	930	0.361	2.79	30.082	43.49	845	
110	2004	331	940	0.358	1.299	28.51	42.21	842	
110	2004	331	950	0.703	0.153	29.12	41.49	843	
110	2004	331	1000	1.158	0.114	29.63	40.95	850	
110	2004	331	1010	0.109	7.29	30.07	40.49	851	

Graph 1: Wind speed vs Time

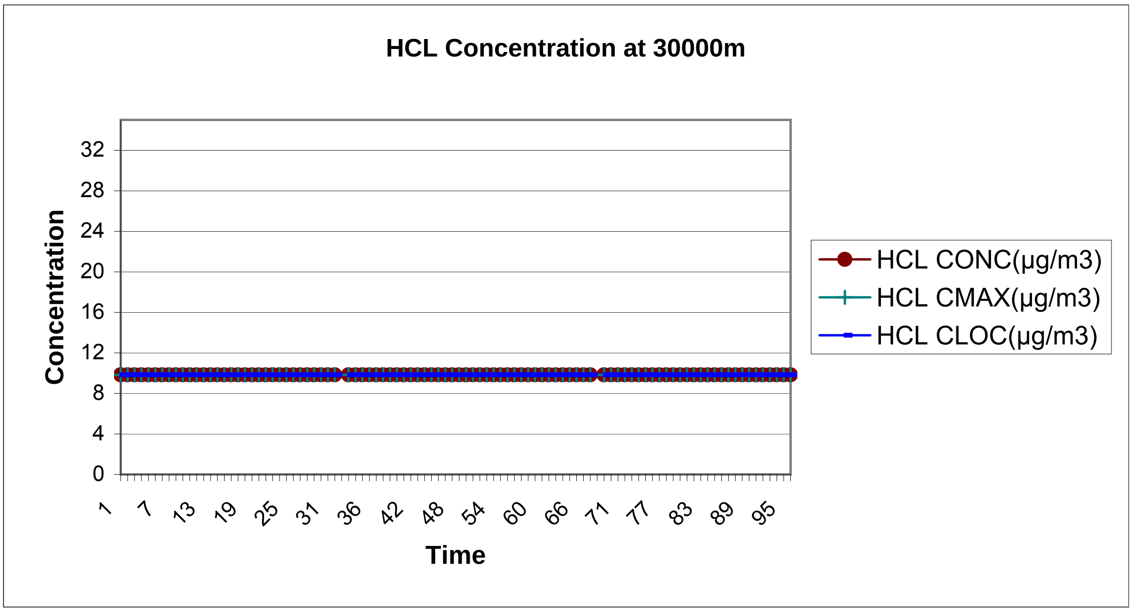


Graph 2: Temperature vs Time

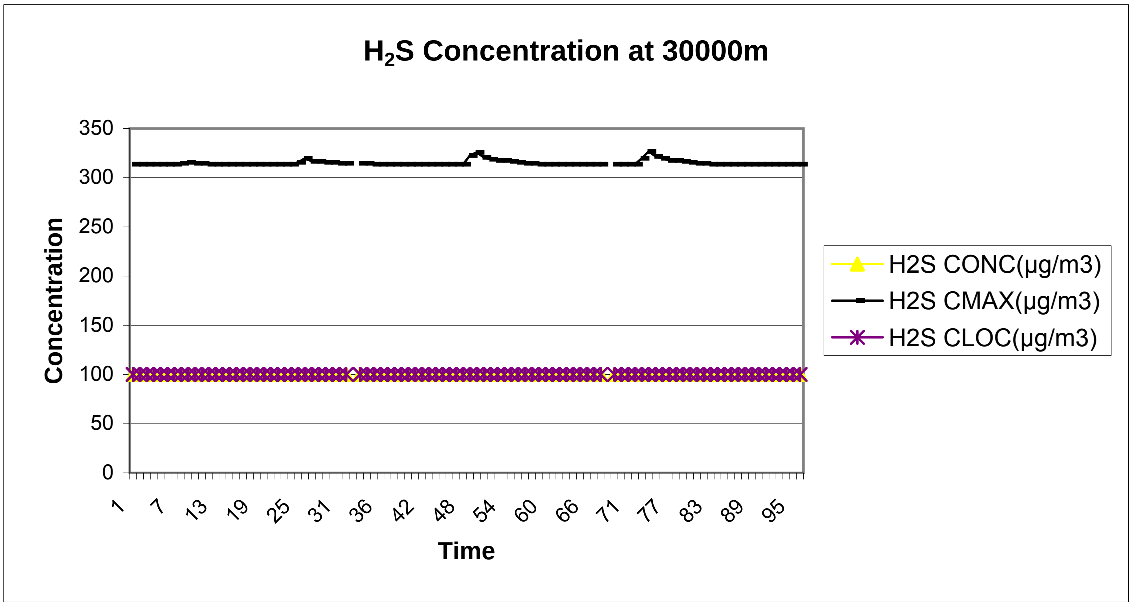



Te
10
5
0
850
1200
1450
1730
2020
2310
150
440
730
1010
1300
1550
1830
2120
10
250
540
830
1110
1400
1650
2220
110
400
640
930
Time

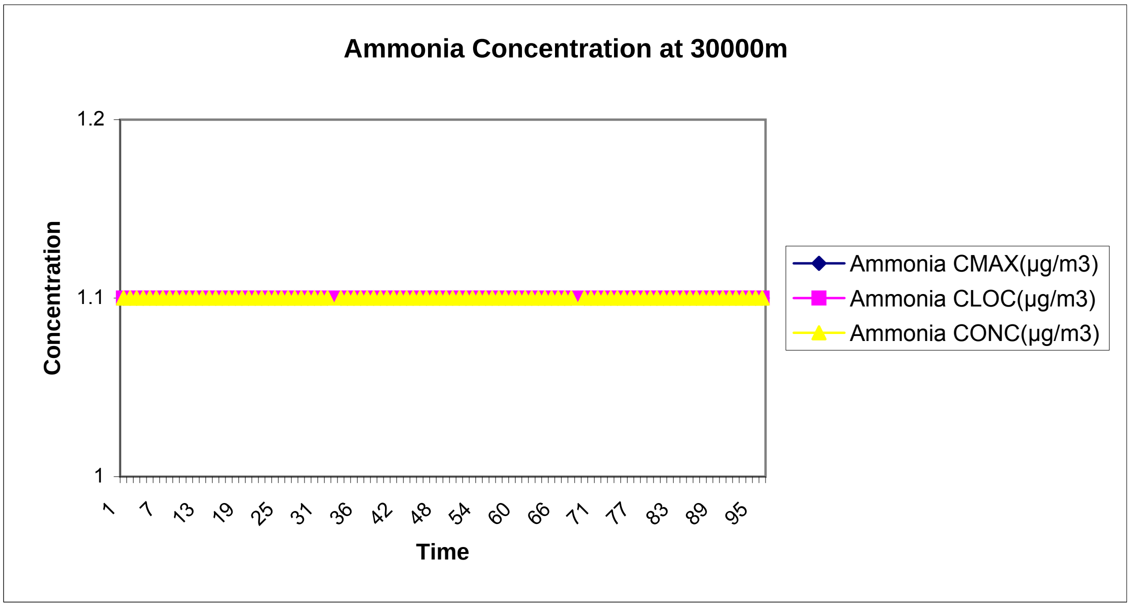
Graph 3: HCL concentration at 30000m



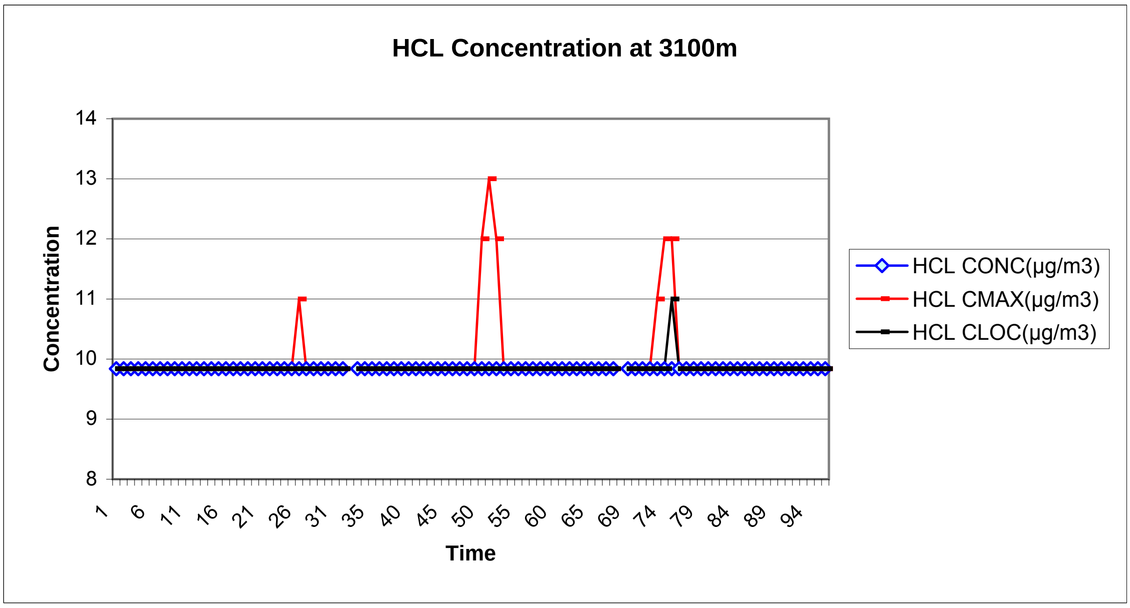
Graph 4: H_2S concentration at 30000m



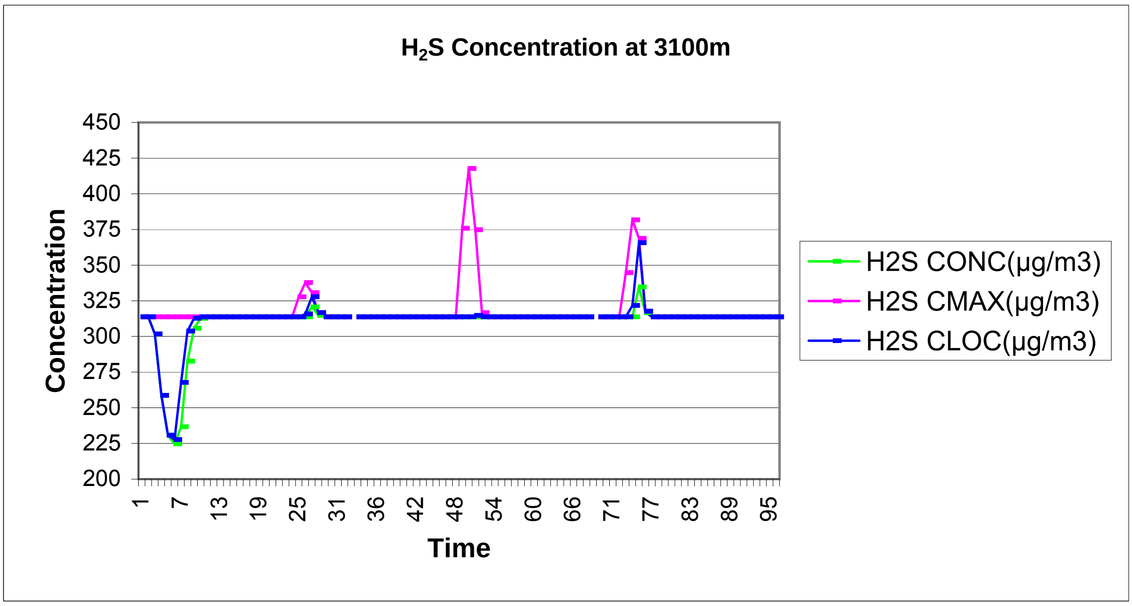
Graph 5: Ammonia concentration at 30000m



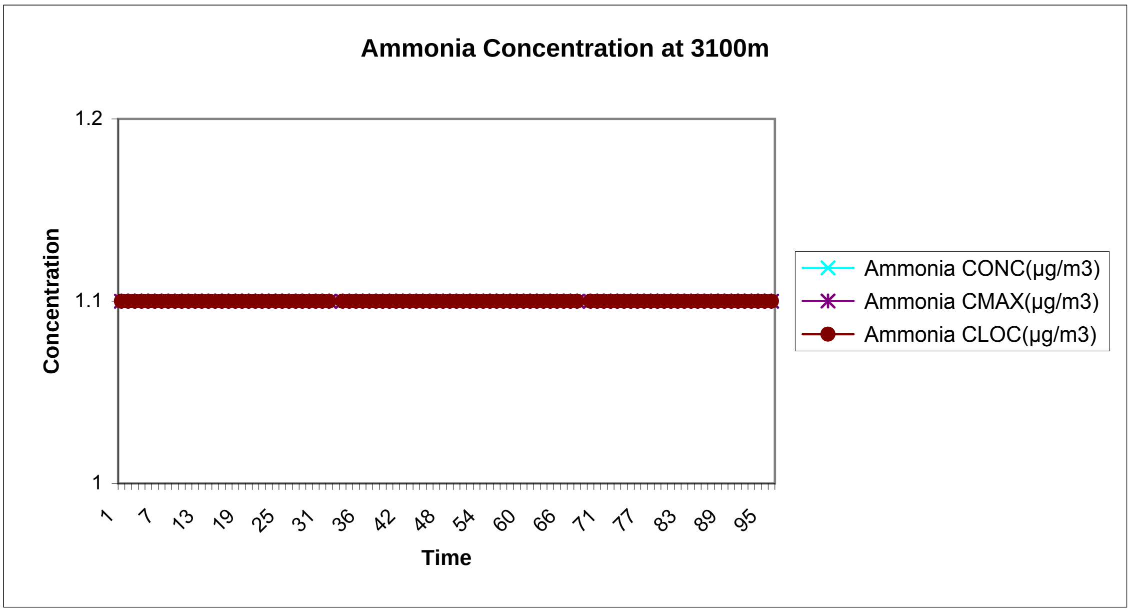
Graph 6: HCL concentration at 3100m



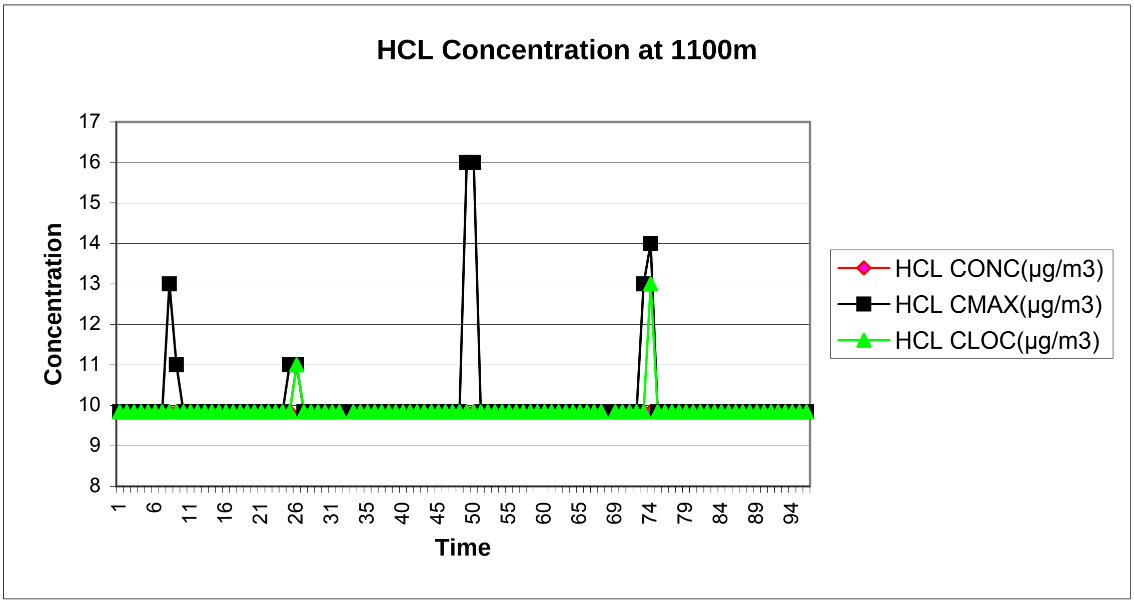
Graph 7: H_2S concentration at 3100m



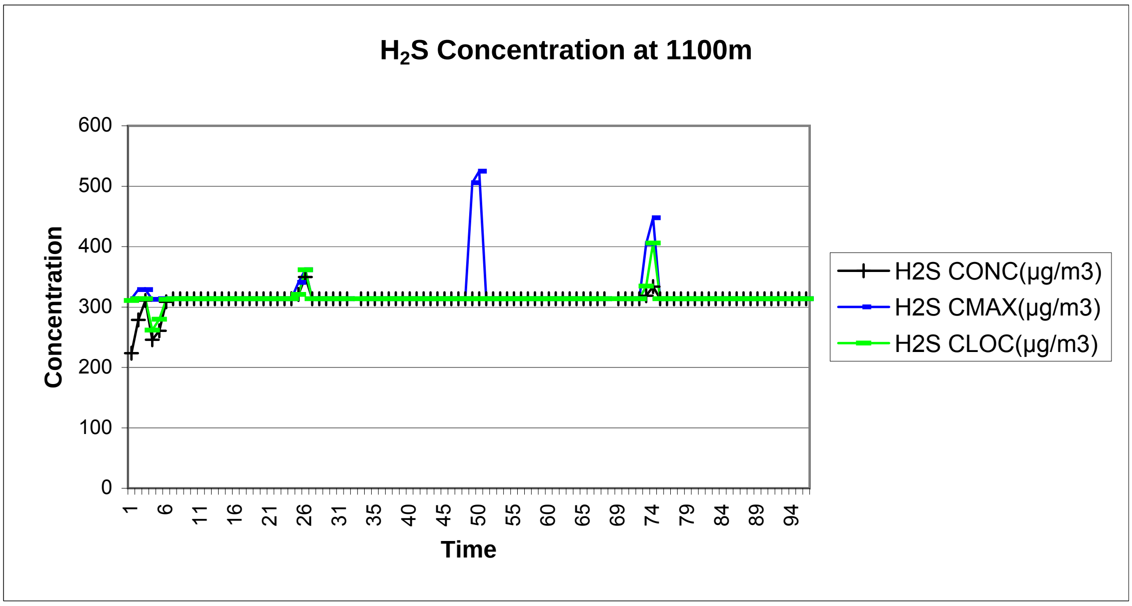
Graph 8: Ammonia concentration at 3100m



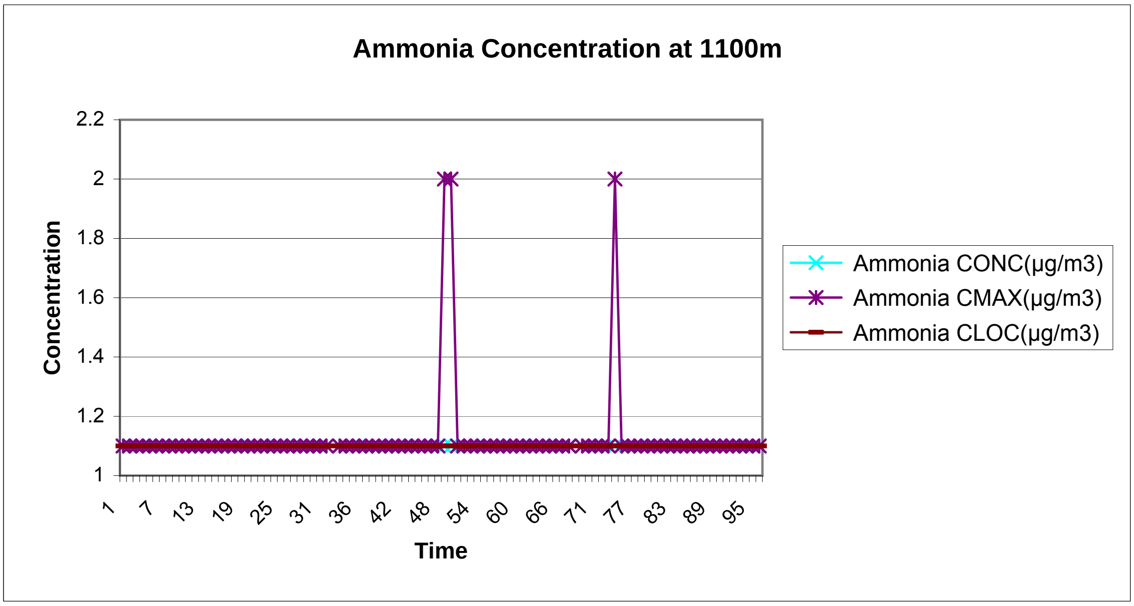
Graph 9: HCL concentration at 1100m



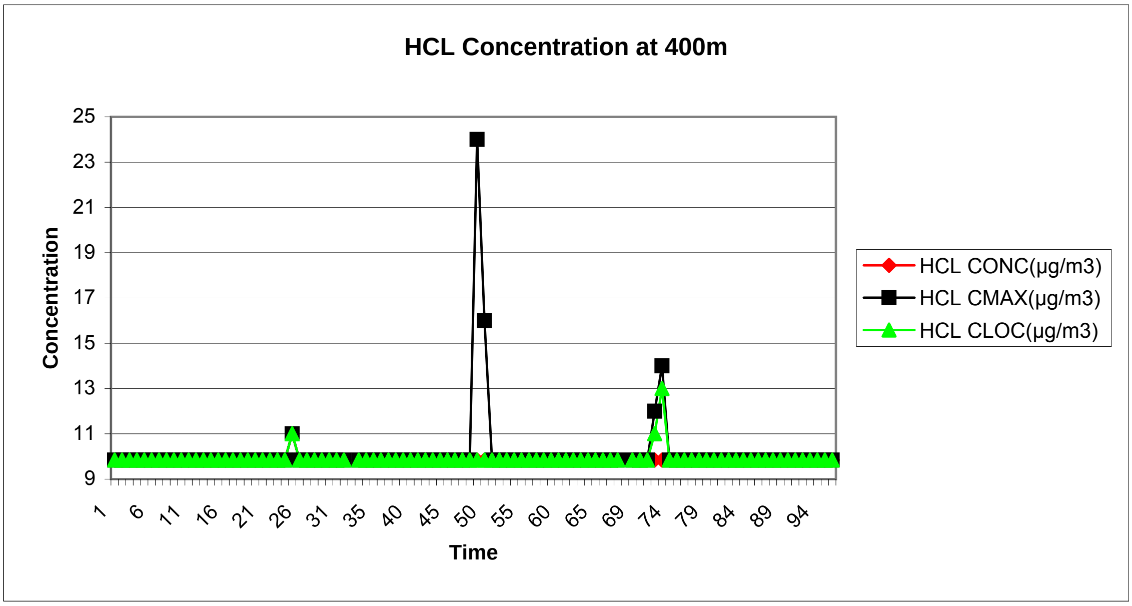
Graph 10: H_2S concentration at 1100m



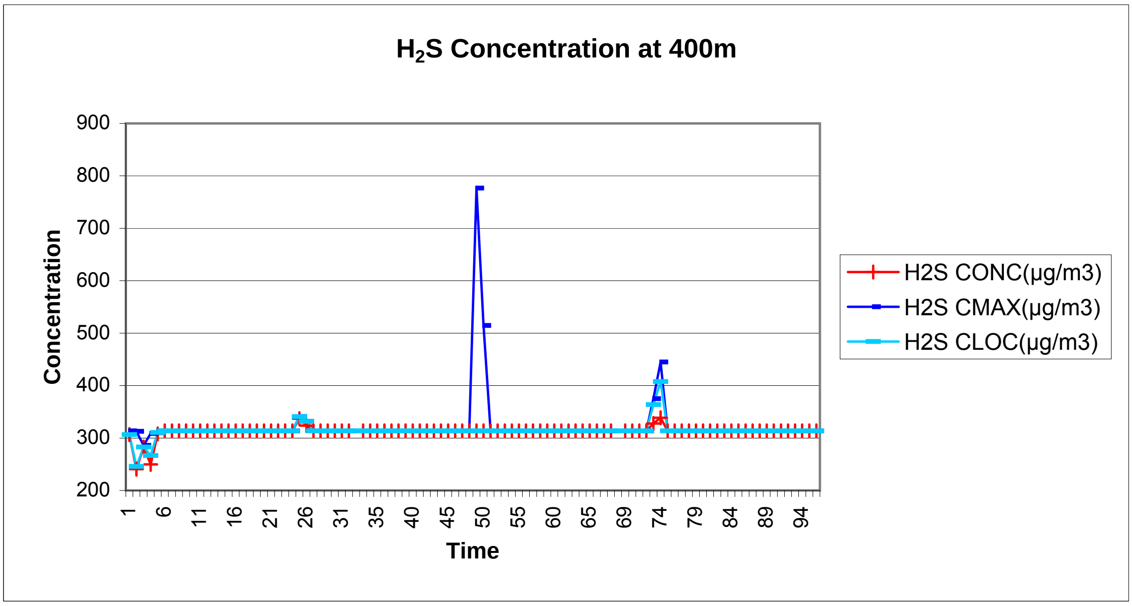
Graph 11: Ammonia concentration at 1100m



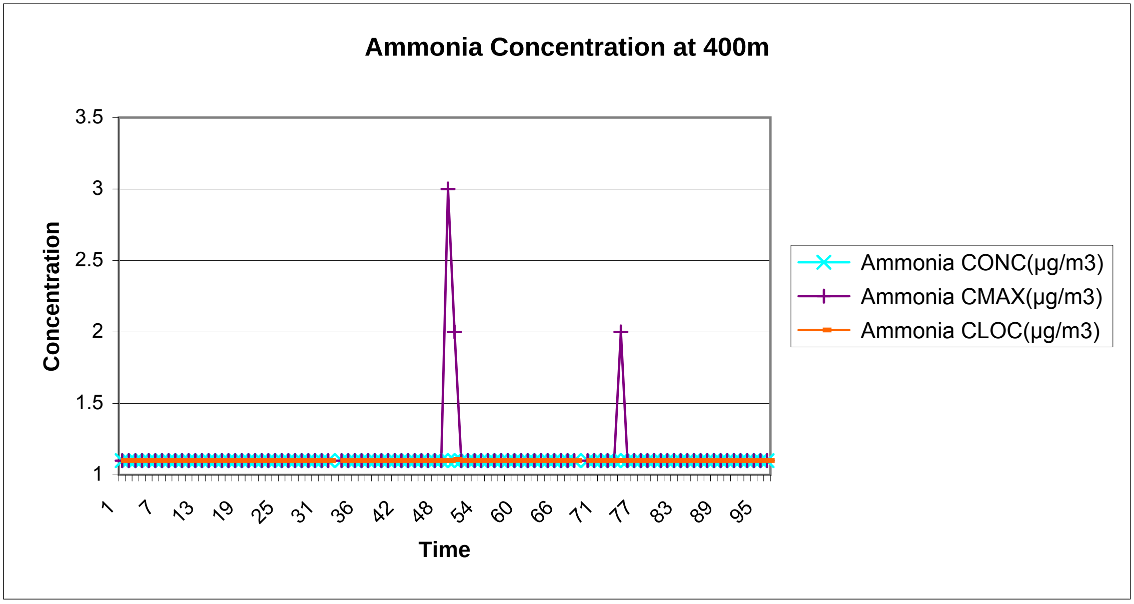
Graph 12: HCL concentration at 400m



Graph 13:H_2S concentration at 400m



Graph 14: Ammonia concentration at 400m



ANNEXURE 2

(Water quality analysis)

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Ref No : **05/2664L A**
Issued at : **Johannesburg**
Date : **2005.01.25**
MP/lm

Page 1 of 2
COMPANY NAME : Company X
SUBJECT : Analysis of 18 samples of LIQUID
MARKED : As below
INSTRUCTED BY : Johan Kok
ORDER NO. : T59601
RECEIVED ON : 2004.12.02
LAB NO(S) : E24520 – E24537
--

Analysis on as received basis:

SAMPLE MARKS	NO. 1 POND SAMPLE NO. 1	NO. 1 POND SAMPLE NO. 2	NO. 1 POND SAMPLE NO. 3	NO. 1 POND SAMPLE NO. 4
pH Value @ 21°C *	10.2	10.3	10.3	10.3
Conductivity mS/m @ 25°C *	6200	9445	9450	9340
Sodium, Na	61750	66950	60650	67650
Chloride, Cl	77700	72630	76665	77700
Sulphate, SO_4	33335	74755	74300	33975
Free and Saline Ammonia as NH_4	18.2	26	42	39

SAMPLE MARKS	NO. 2 POND SAMPLE NO. 1	NO. 2 POND SAMPLE NO. 2	NO. 2 POND SAMPLE NO. 3	NO. 2 POND SAMPLE NO. 4
pH Value @ 21°C *	10.5	10.6	10.5	10.5
Conductivity mS/m @ 25°C *	9180	9180	9200	5000
Sodium, Na	62350	60050	61350	62250
Chloride, Cl	70450	70450	70450	71485
Sulphate, SO_4	31885	31970	31880	31515
Free and Saline Ammonia as NH_4	18.9	18.4	16.7	17.3

The results are expressed in mg/ℓ where applicable.

* Accredited to ISO/IEC 17025 : 1999 (E)
SANAS ACCREDITED LABORATORY NO. T0040

2/…………………..

Ref No : 05/2664L A

Page 2 of 2

Analysis on as received basis:

SAMPLE MARKS	NO. 3 POND SAMPLE NO. 1	NO. 3 POND SAMPLE NO. 2	NO. 3 POND SAMPLE NO. 3	NO. 3 POND SAMPLE NO. 4
pH Value @ 21°C *	10.2	10.2	9.4	10.2
Conductivity mS/m @ 25°C *	7820	7760	7350	7520
Sodium, Na	37750	40850	32750	36450
Chloride, Cl	46620	46620	41440	41440
Sulphate, SO_4	20705	61815	19765	19960
Free and Saline Ammonia as NH_4	397	419	1140	18.0

SAMPLE MARKS	NO. 4 POND SAMPLE NO. 1	NO. 4 POND SAMPLE NO. 2	NO. 4 POND SAMPLE NO. 3	NO. 4 POND SAMPLE NO. 4
pH Value @ 21°C *	10.4	10.4	10.4	10.4
Conductivity mS/m @ 25°C *	9150	9140	9130	9120
Sodium, Na	61750	62250	58450	62050
Chloride, Cl	70450	134680	69410	69410
Sulphate, SO_4	30740	31085	31390	31200
Free and Saline Ammonia as NH_4	18.0	20	20	18.0

SAMPLE MARKS	ALKALINE SOLUTION	BYPASS ACID SOLUTION
pH Value @ 21°C *	10.4	1.2
Conductivity mS/m @ 25°C *	8650	7600
Sodium, Na	36750	1725
Chloride, Cl	45585	12430
Sulphate, SO_4	21340	10835
Free and Saline Ammonia as NH_4	1290	6445

The results are expressed in mg/ℓ where applicable.
A list of test methods is appended.

* Accredited to ISO/IEC 17025 : 1999 (E)
SANAS ACCREDITED LABORATORY NO. T0040

ANNEXURE 3

(NIOSH Methodologies)

Hydrogen Chloride in Workplace Atmospheres

Method no.:	ID-174SG
Control no.:	T-ID174SG-PV-01-0202-M
Matrix:	Air
Collection Procedure:	A known volume of air is drawn through a silica gel tube. Particulates are collected on the glass fiber plug while HCl is collected on the silica gel sorbent.
Recommended Air Volume:	7.5 liters
Recommended sampling rate:	0.5 liters per minute
Analytical Procedure:	The silica gel tube is desorbed with standard eluent and is analyzed by Ion Chromatography (IC).
Detection Limit:	See section 2.3
Precision and Accuracy:	(CV_A) = 0.225 for HCl
Method Classification:	P
Date:	February 1986

Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Salt Lake City, Utah 84115-1802

1. Introduction

This method describes the collection and analysis of airborne hydrogen chloride using Ion Chromatography. Other acids which can be collected and analyzed simultaneously are HBr, H_3PO_4, HNO_3, and H_2SO_4.

1.1 History (9.1, 9.2)

Prior to the use of this method, HCl was collected using 0.1 *N* NaOH in an impinger and analyzed by specific ion electrode, or by adding $AgNO_3$ and measuring the turbidity of the AgCl formed.

1.2 Uses (9.3)

Hydrogen chloride is used in the manufacture of pharmaceutical hydrochlorides, making vinyl chloride from acetylene, alkyl chlorides from olefins, and arsenious chloride from arsenious oxide. Hydrogen chloride is also used in the chlorination of rubber and in organic reactions involving isomerization, polymerization, and alkylation. HCl is also used to make chlorine, when it is economical.

1.3 Physical and Chemical Properties (9.4, 9.5)

Specific Gravity: 1.268
Melting Point: -114.8°C
Boiling Point: -84.9°C
Molecular Weight: 36.46

2. Working Range and Detection Limit

2.1 The working range for a 7.5-liter air sample is 0.01 to 1.0 ppm for Cl^- for a 10-mL sample volume. This corresponds to 0.10 to 10.0 µg of chloride. The upper range can be extended by sample dilution.

2.2 The qualitative detection limits for Cl^- were calculated using the Student's T-Test. The detection limit for Cl^- is 0.10 µg at a confidence level of 95%. This detection limit was calculated based on a sample volume of 10 mL and an injection volume of 100 µL. The detection limit may be improved by using a larger injection volume (for auto sampler only), or by using a smaller volume than 10 mL to desorb the sample.

3. Stability, Collection Efficiency, and Coefficient of Variation.

3.1 The storage stability of HCl on silica gel tubes was found to be acceptable. Aqueous HCl was spiked onto 9 silica gel tubes at a level corresponding to 1.0 × PEL. Air with 80% humidity and 25°C was pumped through the tubes at 0.5 Lpm for 15 minutes. Three tubes were analyzed on that day (Day 0). Three tubes each were analyzed 7 and 14 days later. There were no significant losses of HCl.

SAMPLE	**DAY**	**PPM**	**AVE**	**STD. DEV.**
1STA	0	6.12		
2STA	0	7.31	6.60	0.511
3STA	0	6.38		
4STA	7	6.06		
5STA	7	6.40	6.13	0.192
6STA	7	5.94		
7STA	14	5.46		
8STA	14	6.10	6.07	0.482

9STA	14	6.64

All samples were re-analyzed on day 14, and it was found that there were no losses. This suggests that once the tubes were desorbed the HCl is not lost for at least 2 weeks.

3.2 Aqueous HCl was spiked onto 9 silica gel tubes at a level corresponding to 1.0 × PEL. Air with 80% humidity and 25°C was pumped through the tubes at 0.5 Lpm for 15 minutes. Part B of the sample were analyzed and no breakthrough was found. This is in accordance with a NIOSH study (9.6) which found that the collection efficiency of silica gel tubes in generated HCl test atmospheres was 100%.

3.3 The coefficient of variation (CV_A) for the analytical method in the range of 35 to 114 µg Cl^- was 0.225 (9.7).

4. Interferences

Large quantities of fluoride will cause some masking of the chloride peak.

5. Advantage and Disadvantages

5.1 The method can be automated and is quick and accurate.

5.2 Thin procedure uses silica gel tubes instead of impingers which are used in other sampling methods for HCl. This eliminates the inherent problems of using impingers.

5.3 Unlike previous methods, particulates are not an interference in this method, since they can be captured on the glass fiber filter in the tube and analyzed separately, if necessary.

6. Sampling Procedure

6.1 Apparatus - Silica gel sorbent tubes, SUPELCO, Inc. ORBO-53 (or equivalent silica gel tubes which have been demonstrated to show low levels of the anions of interest), personal sampling pump with calibrated flow in line with a silica gel tube to an accuracy of ±10% at the 95% confidence limit at the recommended flow rate.

6.2 The silica gel tube is attached to a calibrated personal sampling pump and the sampling tube is placed in the sampling area or worker's breathing zone. At a flow rate of 0.5 liters per minute, 7.5 liters of air are drawn through the sampling tube.

6.3 After sampling, the silica gel tube is removed from the tubing, sealed and identified with OSHA Form 21, and shipped to the Laboratory for analysis.

6.4 With each batch of up to 20 samples, a blank tube which has had no air drawn through it is submitted for analysis. The blank tube should be from the same lot of tubes used for sampling.

6.5 It is very important to list as interferences any particulate acids or salts known to be present In the workplace atmosphere.

7. Analytical Procedure

7.1 Apparatus - Ion exchange chromatograph, equipped with electrical conductivity detector and recorder, or integrator, 10 mL pipette, 1 mL plastic syringe with male Luer fitting, Anion Separator Column 3 × 250 mm with Concentrator Column, Anion Suppressor Column 10 × 100 mm, and appropriate volumetric glassware for dilutions and standard preparation.

7.2 Reagents - All reagents used should be ACS analyzed reagent grade or better.

7.2.1 Deionized water with a specific conductance of 10 µmho/cm or less for preparation of eluents and other solutions which will be used in the analysis.

7.2.2 Chloride Stock Standard (1000 µg/mL Cl^-) -- Dissolve 1.648 g NaCl and dilute to 1 liter with deionized water. Chloride working standards are made by diluting the stock solution with standard eluent.

7.2.3 Standard Eluent (0.003 M $CO_3^=$/0.0024 M HCO_3^-) Dissolve 5 g Na_2HCO_3 and 5 g $NaHCO_3$ in 20-liter carboy with deionized water.

7.2.4 Regenerant Solution (1 N H_2S0_4). Carefully add 111 mL of concentrated H_2SO_4 to 2 liters of deionized water and dilute to 4 liters.

7.3 Safety Precautions

7.3.1 When using the Ion Chromatograph, the column door should be kept closed during the analysis in case the columns burst. To avoid this danger the pressure should be checked at the beginning of the analysis and periodically during the analysis. The pressure should not exceed 500 psi.

7.3.2 Care should be used when handling reagents, especially the regenerant solution (1 N H_2SO_4), to avoid chemical burns.

7.3.3 Care should be exercised when using laboratory glassware. Chipped pipettes, volumetric flasks, beakers, or any glassware with sharp edges exposed should not be used in order to avoid the possibility of cuts, abrasions, and lost samples.

7.3.4 Pipetting should never be done by mouth -- a bulb should *always* be used.

7.4 Standard Preparation

7.4.1 Working standards are prepared in the analytical range of 0.2 µg/mL to 50 µg/mL from dilutions of the 1000 µg/mL stock solution. These standard solutions should be prepared fresh weekly.

7.4.2 If an auto sampler capable of variable volume injections is used, a 3 µg/mL Cl^- standard is used. This intermediate working standard should be prepared fresh monthly.

7.5 Sample Preparation

7.5.1 The sample tube used with this analysis can be separated into 3 parts. The first part is the glass fiber filter plug which collects any particulate. The second part is a silica gel backup section (section A) which collects the acid mists. The third part is a silica gel section (section B) which collects any acid mists not collected by section A. The second and third parts are separated by a foam plug, which is discarded.

7.5.2 Score the sample tube with a file in front of the primary sorbent section (section A) and break the tube at the score line. Transfer the glass fiber filter plug and section A to a clean 20 mL vial. If the analysis is to be done only for HCl, the glass fiber filter plug can be discarded. If sulfuric and/or phosphoric acids are requested, the glass fiber filter plug must be analyzed separately.

7.5.3 Place silica gel section B in a separate clean 20 mL vial.

7.5.4 If the air volume is greater than or equal to 1liter, pipette about 5 mL of eluent (0.003 M $CO_3^=$/0.0024 M HCO_3^-) into each sample vial and cap tightly. If the air volume is less than 1 liter, a smaller volume of eluent is used.

7.5.5 Place the vial in a large beaker with DI water and boil for 10 minutes. Let cool and dilute to 10.0 mL with eluent in a volumetric flask (if the air volume is less than 1 liter, dilute to 5 mL in a volumetric flask). When particulate acids are listed as interferences, the glass fiber plug should be discarded. Sample solutions which are not clear should be filtered before analysis.

7.5.6 If using an auto sampler, transfer some of the sample into an appropriate sampling vial. The vial should be at least half full. Label each vial with the appropriate laboratory identification number.

7.5.7 For hand injection, use 1 mL of the eluent to flush the 0.1 mL injection loop thoroughly. When using automatic injection try to use about a 100 µL injection volume. The autosampler is less accurate below 100 µL.

7.6 Analysis

7.6.1 For general instrument set up refer to Section 7 of the Ion Chromatography Standard Operating Procedure (9.8)

7.6.2 The normal instrument parameters are:

Sensitivity: 30 µmho full scale
Eluent: 0.003 *M* Na_2CO_3 and 0.0024 *M* $NaHCO_3$
Flow Rate: 138 mL/hr, approximately 30% on vernier
Concentrator Column: 3-mm I.D. × 50-mm
Anion Separator Column: 3-mm I.D. × 250-mm
Suppressor Column:10-mm I.D. × 100-mm
Run Time: Approximately 20 minutes, depending upon analytical conditions.

7.6.3 With the instrument set up and stabilized, place the auto sampling vial into the sampling tray using tray positions one through five for standards.

7.6.4 Enter the proper parameters into the auto sampler. See Section 4 of the Ion Chromatography Standard Operating Procedure (9.8)

7.6.5 Start the auto sampler and observe the first few chromatograms to ensure proper operation. Periodically check the zero offset between samples to correct any baseline drift and to ensure proper sensitivity and retention time of the analytes.

7.6.6 Use the timer to stop the run if the auto sampler is to be left unattended.

7.6.7 For hand injection, a 1-mL aliquot is taken up in a syringe from the 20-mL vial and injected into the injection port with the toggle switch in the load position. After the sample is loaded, switch the toggle to the inject position and start the integrator or push the PIP button if a strip chart recorder is being used.

7.6.8 For both hand and auto sample injections, record the sample number onto the chromatogram. A record of the sample identity and instrument conditions should be kept.

7.6.9 As the analysis proceeds, check the retention times of standards vs. samples to ensure uniformity.

7.6.10 If interfering substances are present, establish positive identity of the peaks by spiking known amounts of standard solution, or try to obtain better separation by changing the eluent concentration or by reducing the flow rate.

7.7 Calculations

7.7.1 Peak areas or heights of the standards are used to construct a standard curve using the OSHA Auto Colorimetric Program. The samples results are obtained from a plot of peak height or peak area vs. concentration. The blank corrected sample values are then calculated using the Auto Colorimetric Program.

7.7.2 When using the OSHA Auto Colorimetric Program, sample numbers and volumes are entered into the calculator in the following manner:

Sample Number, Peak Area or Height, L Air Volume, mL Solution Volume, mL Aliquot Volume.

7.7.3 Air Concentration values are calculated by the following equation:

$$mg/m^3 = \frac{(\mu g\ \text{calculated})(mL\ \text{sample vol})(GF^*)(\text{dilution factor})}{(\text{liters of air})(mL\ \text{aliquot})}$$

GF* = Gravimetric Factor = 1.03 for HCl

7.7.4 HCl is reported in ppm rather than in mg/m^3. To convert the mg/m^3 values to ppm, the mg/m^3 value must be multiplied by the conversion factor 0.671.

8. Reporting Results for Compounds Determined by Ion Chromatography

8.1 Results are reported on the OSHA Form 91 in ppm for HCl, using two significant figures.

8.2 The estimated detection limit calculated by the Auto Colorimetric Program is reported on the OSHA Form 91 when no analyte is detected.

8.3 The presence of significant unidentifiable peaks is noted on the OSHA Form 91.

8.4 All data processor printouts and chart recorded chromatograms are filed in a central file according to laboratory sample identification.

8.5 Calculations are checked by a fellow chemist before the completed OSHA Form 91's are given to the supervisor.

HYDROGEN SULFIDE

6013

H_2S MW: 34.08 CAS: 7783-06-4 RTECS: MX1225000

METHOD: 6013, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA :	C 20 ppm; P 50 ppm/10 min	**PROPERTIES:**	gas; d (liq) 1.54 g/mL @ 0 °C;
NIOSH:	C 10 ppm/10 min		BP - 60 °C; VP 20 atm @ 25 °C;
ACGIH:	10 ppm; STEL 15 ppm		vapor density (air=1) 1.19;
	(1 ppm = 1.39 mg/m^3 @ NTP)		explosive range 4.3 to 46% v/v in air

SYNONYMS: sulfuretted hydrogen; hydrosulfuric acid; hepatic gas; stink damp

SAMPLING

SAMPLER:	FILTER + SOLID SORBENT TUBE (Zefluor, 0.5 µm; coconut shell charcoal, 400 mg/200 mg)
FLOW RATE-RANGE:	0.1 to 1.5 L/min
-RECOMMENDED:	0.2 L/min
VOL-MIN:	1.2 L @ 10 ppm
-MAX:	40 L
SHIPMENT:	routine
SAMPLE STABILITY:	at least 30 days @ 25 °C [1]
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	1.4 to 22.0 mg/m^3 [1] (20-L samples)
BIAS:	- 0.23% [1]
OVERALL PRECISION ($\bar{S}_{rT}$):	0.059 [1]
ACCURACY:	± 11.8%

MEASUREMENT

TECHNIQUE:	ION CHROMATOGRAPHY, CONDUCTIVITY
ANALYTE:	sulfate ion
DESORPTION:	2 mL 0.2 M NH_4OH + 5 mL 30% H_2O_2
INJECTION VOLUME:	50 µL
ELUENT:	40 mM NaOH, 1.5 mL/min
COLUMN:	Ion-Pac AS4A separator, AG4A guard
CALIBRATION:	SO_4^{2-} in deionized water
RANGE:	17 to 200 µg per sample
ESTIMATED LOD:	11 µg per sample
PRECISION ($\bar{S}_r$):	0.031 [1]

APPLICABILITY: The working range is 0.6 to 14 ppm (0.9 to 20 mg/m^3) for a 20-L air sample [1]. The method is applicable to 15-min samples taken at 1 L/min and 10-min samples taken at 1.5 L/min. The upper limit of loading depends on the concentrations of hydrogen sulfide and other substances in the air, including water vapor. High relative humidity (80%) increases the capacity of the sampler four-fold, relative to dry air. Some lots of charcoal have excessively high sulfur backgrounds and/or poor desorption efficiencies; therefore, screening of each lot should be done before field use.

INTERFERENCES: SO_2 is a positive interference, equivalent to H_2S by approximately twice the SO_2 concentration by weight. Methyl and ethyl mercaptans do not interfere [1].

OTHER METHODS: Alternate methods are S4 [2] which uses impinger collection, and P&CAM 296 [3] which uses a molecular sieve sampler but has poor stability.

REAGENTS:

1. Ammonium hydroxide solution, 25%.
2. Hydrogen peroxide, 30%.*
3. Sodium hydroxide, 50% (w/v).*
4. Extraction soln: 0.2 M NH_4OH.
5. Eluent: 40 mM NaOH. Dilute 4.16 mL of 50% NaOH to 2 L with deionized water (degassed).
6. Suppressor regenerant: 0.025 N H_2SO_4. Dilute 1.4 mL concentrated H_2SO_4 to 2 L with deionized water.*
7. Calibration Stock solution: 1 mg/mL (as anion). Dissolve 0.1814 g K_2SO_4 in 100 mL deionized water.
8. H_2S, calibration gas mixture, or permeation device.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing 20/40 mesh activated (600 °C) coconut shell charcoal (front = 400 mg, back = 200 mg) separated by a 6-mm urethane foam plug. A silanized glass wool plug precedes the front section and a 6-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available. Zefluor PTFE prefilter, 0.45-µm, 25-mm, with porous plastic support pad in 25-mm cassette.
   NOTE: Some lots of charcoal have excessively high sulfur backgrounds, and/or desorption efficiencies. Screen each lot before field use.
2. Personal sampling pump, 0.1 to 1.5 L/min, with flexible connecting tubing.
3. Ion chromatograph, conductivity detector, integrator and columns (page 6013-1).
4. Centrifuge tubes, 15-mL, plastic with screw caps.
5. Syringes, 10-mL, polyethylene with luer tip.
6. Syringe filters, 13-mm, 0.45-µm pore size.
7. Vials, autosampler, 4-mL, PTFE-lined caps.
8. Micropipettes, disposable tips.
9. Pipettes, 2-, 3-, 5-mL.
10. Volumetric flasks, 10-, 25-mL.
11. Vortex mixer (optional).

SPECIAL PRECAUTIONS: Hydrogen peroxide is a strong oxidizer causing burns to skin and mucous membranes. Sulfuric acid and sodium hydroxide are extremely corrosive to all body tissue. Wear protective clothing and eye protection. All work should be performed in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler and attach prefilter with a small piece of flexible tubing immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.1 and 1.5 L/min for a total sample size of 15 to 40 L.
4. Cap the sorbent tubes with plastic caps and plug prefilter cassettes. Pack securely for shipment.
   NOTE: The prefilters may be discarded or analyzed for particulate sulfates by, e.g., Method 6004.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate screw-top centrifuge tubes. Discard the glass wool and foam plugs.
6. Add 2.0 mL of 0.2 M NH_4OH and 5.0 mL H_2O_2 to each centrifuge tube. Attach screw cap and loosen 1/4 turn.
7. Allow to react at least 10 min. Tighten cap and shake for 30 s or vortex 10 s.

8. Dilute to 10 mL with 3 mL of deionized water. Cap and shake vigorously.
9. Transfer sample to 10-mL plastic syringe fitted with in-line filter.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range 0.1 to 20 µg sulfate ion per mL of sample (1 to 200 µg per 10 mL).
    a. Add known amounts of calibration stock solution to deionized water in 10- or 25-mL volumetric flasks and dilute to the mark. Prepare fresh working standards biweekly.
    b. Analyze together with samples and blanks (steps 14 and 15).
    c. Prepare calibration graph (peak height vs. µg SO_4^{2-} per sample).
11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 10). Prepare four tubes at each of three levels plus three media blanks.
    a. Generate concentrations of H_2S from a calibration gas mixture or a permeation device. Mix with dilution air as necessary.
    b. Collect samples at a flow rate of 1 L/min for 30 min.
    c. Cap the tubes and allow to stand overnight.
    d. Desorb (steps 5 through 9) and analyze together with working standards (steps 14 and 15).
    e. Prepare a graph of DE vs. µg sulfate recovered.
12. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph is in control.

MEASUREMENT:

13. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 6013-1.
14. Inject a 50-µL sample aliquot manually or with autosampler.
15. Measure peak height.
    NOTE: If peak height is above the linear range of the working standards, dilute with deionized water, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

16. Determine the mass, µg (corrected for DE) of sulfate ion found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
17. Calculate concentration, C, of hydrogen sulfide in the air volume sampled, V (L), applying the factor 0.3548 (MW H_2S/MW SO_4^{2-}) for the conversion of SO_4^{2-} to H_2S:

$$C = \frac{0.3548\ (W_f + W_b - B_f - B_b)}{V},\ \mathrm{mg/m^3}.$$

EVALUATION OF METHOD:

The method was evaluated by sampling generated test atmospheres of H_2S in air [1]. Time-weighted average samples were taken at four concentration levels over a range of 1.4 to 22 mg/m^3 (1 to 16 ppm). For ceiling concentrations or short-term exposure limits, 15-L samples were collected at 1 L/min. Breakthrough was determined for coconut charcoal from a generated atmosphere at a concentration of 20 ppm (2 x PEL) and at both low (~20%) and high (~80%) relative humidity (RH). Breakthrough volumes for low and high RH were 21 L and 84 L, respectively, corresponding to capacities of 588 µg of H_2S (low RH) and 2352 µg of H_2S (high RH). At 1 x PEL, the equivalent breakthrough volume is 42 L (low RH) and 164 L (high RH). Large coconut charcoal tubes have sufficient capacity to collect a 4-h sample at the PEL of 10 ppm, as well as STEL samples (15 ppm for 15 min). H_2S samples are stable for at least

30 days. Recoveries, based on mass of H_2S found on samples analyzed on day 1, were 97.2% for ambient storage and 98.9% for refrigerated storage. The overall method for H_2S has a limit of detection of 11 µg per sample and a limit of quantitation of 17 µg per sample. A mean bias of -0.17% was determined from the recoveries of six samples generated at each of four concentration levels (0.1, 0.5, 1 and 2 x PEL) with a precision ($\bar{S}_r$) of 0.031. The method had a total precision including pump error ($\bar{S}_{rT}$) of 0.059, and an estimate of overall error of ±11.6%.

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[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 6, P&CAM 296, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

METHOD WRITTEN BY:

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AMMONIA by IC 6016

NH_3 MW: 17.03 CAS: 7664-41-7 RTECS: BO0875000

METHOD: 6016, Issue 1 **EVALUATION: FULL** **Issue 1: 15 May 1996**

OSHA :	50 ppm	**PROPERTIES:**	gas; MP -77.7 °C; BP -33.4 °C; VP 888 kPa (8.76 atm) @ 21.1 °C; vapor density 0.6 (air = 1); explosive range 16 to 25% v/v in air
NIOSH:	25 ppm; STEL 35 ppm; Group III Pesticide		
ACGIH:	25 ppm; STEL 35 ppm (1 ppm = 0.697 mg/m^3 @ NTP)		

SYNONYMS: none

SAMPLING

SAMPLER:	SOLID SORBENT TUBE (sulfuric acid-treated silica gel) a 0.8-µm MCE prefilter may be used to remove particulate interferences.
FLOW RATE:	0.1 to 0.5 L/min
VOL-MIN:	0.1 L @ 50 ppm
-MAX:	96 L @ 50 ppm [1]
SHIPMENT:	routine
SAMPLE STABILITY:	at least 35 days @ 5 °C [2]
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	17 to 68 mg/m^3 [1] (30-L samples)
BIAS:	− 2.4% [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.071 [1]
ACCURACY:	± 14.5%

MEASUREMENT

TECHNIQUE:	ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION
ANALYTE:	ammonium ion (NH_4^+)
EXTRACTION:	10 mL deionized water
INJECTION VOLUME:	50 µL
ELUENT:	48 m<u>M</u> HCl/4 m<u>M</u> DAP-HCl/4 m<u>M</u> L-histidine-HCl; 1 mL/min alternate: 12 m<u>M</u> HCl/0.25 m<u>M</u> DAP-HCl/ 0.25 m<u>M</u> L-histidine-HCl; 1 mL/min
COLUMNS:	HPIC-CS3 cation separator; HPIC-CG3 cation guard; CMMS-1 cation micromembrane suppressor
CONDUCTIVITY SETTING:	30 µS full scale
CALIBRATION:	standard solutions of NH_4^+ in deionized water
RANGE:	4 to 100 µg per sample [3]
ESTIMATED LOD:	2 µg per sample [3]
PRECISION ($\bar{S}_r$):	0.038 [2]

APPLICABILITY: The working range is 24 to 98 ppm (17 to 68 mg/m^3) for a 30-L sample. This method is applicable to STEL measurements when sampled at ≥0.2 L/min.

INTERFERENCES: Ethanolamines (monoethanolamine, isopropanolamine, and propanolamine) have retention times similar to NH_4^+. The use of the alternate (weak) eluent will aid in separating these peaks.

OTHER METHODS: This method combines the sampling procedure of methods S347 [4] and 6015 with an ion chromatographic analytical procedure similar to Method 6701 [5] and OSHA Method ID-188 [3].

REAGENTS:

1. Water, deionized, filtered.
2. Sulfuric acid (H_2SO_4), 0.01 N:*
   Add 0.28 mL conc. H_2SO_4 to 500 mL deionized water in 1-L volumetric flask. Dilute to 1 L with deionized water.
3. Hydrochloric acid (HCl), 1 N:*
   Add 82.5 mL conc. HCl to 500 mL deionized water in 1-L volumetric flask. Dilute to 1 L with deionized water.
4. 2,3-diaminopropionic acid monohydrochloride (DAP-HCl)
5. L-histidine monohydrochloride monohydrate (L-histidine-HCl)
6. Eluent (48 mM HCl/4 mM DAP-HCl/4 mM L-histidine-HCl): Place 0.560 g DAP-HCl and 0.840 g L-histidine-HCl in a 1-L volumetric flask. Add 48 mL of 1 N HCl, dilute to volume with deionized water. Prepare monthly.
7. Alternate eluent (12 mM HCl/0.25 mM DAP-HCl/0.25 mM L-histidine-HCl): Dilute 252 mL strong eluent and 36 mL 1 N HCl to 4 L with deionized water. Prepare fresh for each use.
8. Tetramethylammonium hydroxide (TMAOH), 25%, (Aldrich Chemical Co. Milwaukee, WI).
9. Regenerant solution: Dilute 57.4 mL of 25% TMAOH to 4 L with deionized water.
10. Ammonia stock solution, 1000 µg/mL as NH_3 (1059 µg/mL as NH_4^+): Dissolve 3.1409 g ammonium chloride in deionized water. Dilute to 1 L.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
   a. Prefilter: 37-mm mixed cellulose ester membrane filter, 0.8-µm pore size, stainless steel or porous plastic screen in two piece cassette filter holder.
   b. Sulfuric acid-treated silica gel, glass tube, unsealed and fire-polished, 6.0 cm long, 6-mm OD, 4-mm ID, containing two sections of 20/40 mesh sulfuric acid-treated silica gel (200 mg front/100 mg back) separated and held in place with plugs of silylated glass wool, and capped with plastic caps. Tubes are commercially available.
2. Personal sampling pump, 0.1 to 0.5 L/min, with flexible tubing.
3. Ion Chromatograph with conductivity detector, cation column and guard, and cation micromembrane suppressor (see p 6016-1).
4. Syringes, 10-mL, polyethylene, Luer tip.
5. Centrifuge tubes, 15-mL, graduated, plastic with screw caps.
6. Volumetric flasks, 10-, 50-, 100-mL, and 1-L.
7. Syringe filters, 13-mm, 0.8-µm, membrane filter.
8. Micropipets, disposable tips.
9. Analytical balance (sensitivity to 0.01 mg).

SPECIAL PRECAUTIONS: Concentrated acids are corrosive to skin. Handle acid in a fume hood. Wear protective gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.1 and 0.5 L/min for a total sample size of 0.1 to 96 L.
3. Cap the sampling tubes with plastic (not rubber) caps immediately after sampling.
4. Pack securely for shipment.

SAMPLE PREPARATION:

5. Remove caps from sampling tubes. Transfer the front and back sections of sulfuric acid-treated silica gel to separate 15-mL graduated centrifuge tubes.
   NOTE: Firm tapping of the tube may be necessary to effect complete transfer of the sulfuric acid-treated silica gel.
6. Add 10 mL of deionized water to each centrifuge tube. Cap and shake vigorously. Allow to stand 45 minutes with occasional shaking. (Desorption is complete in 45 minutes.)

NOTE: Analyses should be completed within one day after the ammonia is desorbed.

7. Transfer samples to 10-mL syringes fitted with inline syringe filters for manual injection or transfer to autosampler vials.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 1 to 110 µg NH_3 per sample (about 0.11 to 12 µg/mL NH_4^+).
   a. Add known aliquots of ammonia stock solution to 0.01 N H_2SO_4 in 10-mL volumetric flasks.
      NOTE: Prepare standards just before use.
   b. Analyze working standards together with samples and blanks (steps 9 through 11).
   c. Prepare calibration graph (peak height vs. µg NH_3).

MEASUREMENT:

9. Set ion chromatograph to conditions given on page 6016-1, according to manufacturer's instructions.
10. Inject 50-µL sample aliquot manually or with autosampler. For manual operation, inject 2 to 3 mL of sample from filter/syringe to ensure complete rinse of sample loop.
11. Measure peak height.
    NOTE: If peak height exceeds linear calibration range, dilute with 0.01 N H_2SO_4, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

12. Determine the mass, µg, of ammonia found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
13. Calculate concentration, C, of NH_3 in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \ \mathrm{mg/m^3}$$

EVALUATION OF METHOD:

This method combines the sampling procedure of NIOSH Methods S347 [4] and 6015 with the ion chromatographic analytical procedure of NIOSH Method 6701 [5] and OSHA Method ID-188 [3]. This method will serve as an alternate analytical procedure to the automated spectrophotometric procedure of method 6015. Although the methods from which this method is derived are fully evaluated methods, the combination of the sulfuric acid-treated silica gel sampler and IC analysis has not received a full evaluation as such. During the development of the passive monitor method for ammonia (6701), sulfuric acid-treated silica gel tubes were used as one of the reference methods [5]. The silica gel samples with IC analysis showed good agreement with the other reference methods, bubbler collection with colorimetric analysis using Nessler's Reagent, and bubbler collection with IC analysis.

A storage stability study compared the sulfuric acid-treated silica gel tube and sulfuric acid-treated carbon beads used in OSHA Method ID-188. When stored at room temperature for five days and then refrigerated for 21 days, silica gel samples had a mean recovery of 102 ± 3.8% (n = 8), while carbon beads had a mean recovery of 95 ± 1.6% (n = 8). The samples stored on carbon beads for 35 days showed significantly lower (although still acceptable) recovery compared to samples stored for 14 days: 103 ± 3.8% for silica gel (n = 12), and 108 ± 7.0% for carbon beads (n = 12) [2].

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